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Natta, Giulio

Selected 2 of 3 candidates

NATTA G (325 references)

NATTA GIULIO (410 references)

Refine by Document Type started

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239 references were found when refined by Document Type "Patent"

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Bibliographic Information

Process for producing elastomers and intermediates for synthetic rubbers. Natta, Giulio; Mazzanti, Giorgio; Boschi, Giorgio. (Montedison S.p.A., Italy). U.S. (1976), 16 pp. CODEN: USXXAM US 3957743 19760518 Patent written in English. Application: US 74-446920 19740228. Priority: . CAN 85:64458 AN 1976:464458 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (u-96)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3957743	A	19760518	US 1974-446920	19740228
<u>Priority Application</u>				
US 1956-629085	A2	19561218		
US 1961-147970	A2	19611026		
US 1965-514764	A2	19651108		
US 1967-626367	A1	19670322		
US 1971-161281	A1	19710709		

Abstract

Ethylene (I)-propene (II) monomer mixt. is polymd. in the presence of the halogen-contg. catalyst essentially free of microcryst. precipitates (prepd. by mixing an alkyl Al compd. with a hydrocarbon-soluble V compd.), while maintaining a II/I ratio >4 in the liq. phase and at least 1:1 in the gas phase to give a substantially amorphous, linear rubber. Thus, 0.025 mole trihexyl aluminum, 300 cm³ heptane, 96.5 g propane, 88.5 g propene, and 12 g ethylene is heated with stirring to 45° and 0.8 mole VOCl₃ in 50 mm heptane is added. After a spontaneous temp. increase to 65°, 150 cm³ MeOH is added to stop the reaction. The polymn. mixt. is purified and coagulated to give 43 g product contg. 66.4% amorphous EPR (85% propene).

Bibliographic Information

Bonding ethylene copolymers to fibers. Natta, Giulio; Severini, Febo; Portolani, Augusto; Tavazzani, Carlo. (Montedison S.p.A., Italy). U.S. (1975), 10 pp. CODEN: USXXAM US 3860442 19750114 Patent written in English. Application: US 72-245289 19720418. Priority: . CAN 82:172371 AN 1975:172371 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 489 + U 544).

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3860442	A	19750114	US 1972-245289	19720418

Priority Application

US 1969-876184	A1	19691128
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Abstract

Resorcinol-HCHO copolymer (I) adhesives contg. EPDM or ethylene-propene rubber grafted with a water-sol. vinyl or vinylidene acid, e.g. acrylic acid (II) or methacrylic acid, improve the bonding strength between fibers and EPDM or ethylene-propene rubbers. Thus, an emulsion contg. ethylene-propene rubber 100, PhMe 900, Phenopon Co 436 (III) 12, and H₂O 900 g was concd. to 37% solids, stirred (170 g) with Bz₂O₂ 1.35, III 1.3, and II 12.1 g for 6 hr to give 209 g homogenous latex contg. 10.6% bound II. Rayon fabric was dipped in an aged mixt. of 83 g of the latex and 129 g of aq. I soln., dried, and vulcanized between 2 layers of a typical ethylene-propene rubber compn. to give a laminate with bonding strength 6.3 kg/cm at 20°, compared with 0.8 kg/cm at 23° for an adhesive contg. unmodified ethylene-propene rubber.

Bibliographic Information

Polymeric composition comprising poly(vinyl chloride). Natta, Giulio; Beati, Enrico; Severini, Febo; Toffano, Silvio. (Montecatini Edison S.p.A.). U.S. (1974), 6 pp. CODEN: USXXAM US 3812204 19740521 Patent written in English. Application: US 72-248592 19720428. Priority: . CAN 81:170461 AN 1974:570461 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 460)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3812204	A	19740521	US 1972-248592	19720428

Priority Application

US 1964-375663	A2	19640616
US 1970-12462	A1	19700219

Abstract

Vinyl chloride graft polymn mixts. giving impact-resistant moldings consisted of 4-20% graft polymer, 0.5-5% ungrafted backbone polymer, such as EPR, 1-butene-ethylene copolymer [25087-34-7], and cyclooctadiene-ethylene-propylene copolymer [52892-55-4], and 75-95.5% PVC [9002-86-2], the total backbone polymer content (grafted and nongrafted) in the compn. being 2-25%. For example, 30 g EPR (45% ethylene), 200 cm³ water, 4 g poly(vinyl alc.), and 350 cm³ liq. vinyl chloride were stirred for 18 hr, heated at 70.deg. for 2 hr, treated with 600 cm³ water and 1.2 g Bz₂O₂, and stirred at 70.deg. for 14 hr, and the polymer mixt. was stabilized with 1% di-Bu laurate and 3% dibasic Pb stearate, calendered at 150-60.deg., and molded at 160.deg. to give a molding with Izod impact strength 12.4 kg-cm/cm notch at 0.deg. and Rockwell R hardness 100, compared with 4.8 at 23.deg. and 100, resp., for PVC.

Bibliographic Information

High-molecular-weight, crystalline, head-tail connected, linear poly(α -methacrylonitrile). Natta, Giulio; Mazzanti, Giorgio; Dall'Asta, Gino. (Montecatini Edison S.p.A.). Ger. (1974), 7 pp. Division of Ger. 1,520,242 (See Belg. 611,491, CA 57:10048a). CODEN: GWXXAW DE 1795630 19740124 Patent written in German. Application: DE 61-1795630 19611212. Priority: . CAN 81:92248 AN 1974:492248 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 347)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1795630	B2	19740124	DE 1967-1795630	19611212
DE 1795630	C3	19740822		

Priority Application

IT 1960-21506	A	19601214		
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Abstract

The title poly(methacrylonitrile) (I) [25067-61-2], m. 200-60.deg., is prepd. by polymn. in hydrocarbons at 0-100.deg. with Be or Mg (halo)alkyl catalysts. Thus, addn. over 30 min of 10 g methacrylonitrile to 410 mg diethylmagnesium [557-18-6] in 100 ml PhMe stirred at 70.deg. and stirring 6 hr at 70.deg. give 9.5 g I, m. 220-50.deg., insol. in most org. solvents but swollen by PhCN, AcPH, PhNO₂, and DMF (which remove a small amt. of amorphous I), highly resistant to acids but sapond. by 50% KOH, which can be molded at 240-60.deg..

Bibliographic Information

Terpolymers of ethylene, propylene, and 1,3-butadiene. Natta, Giulio; Rebaudo, Giovanni; Beati, Enrico. (Politecnico de Milano; Montecatini Edison S.p.A.). Ital. (1970), 11 pp. CODEN: ITXXAX IT 879026 19701102 Patent written in Italian. Application: IT 19691211. CAN 81:79116 AN 1974:479116 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 1223)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 879026		19701102	IT	19691211

Abstract

A catalyst system contg. Et₃Al [97-93-8], VOCl₃ [7727-18-6] or VCl₄ [7632-51-1], and trichloroacetic acid [76-03-9] was used in the manuf. of S-vulcanizable ethylene-propylene-1,3-butadiene copolymer (I) [25189-22-4] with a predominantly trans-1,4-configuration and mol. wt. >20,000. Thus, butadiene 21, C₃H₆ 86, and C₂H₄ 17 g were mixed in 150 ml heptane at 60.deg.. Et₃Al (1 g) and 0.36 g VOCl₃ were mixed 5 min in 50 ml heptane and 1.25 g Cl₃CCO₂H was added. The catalyst mixt. was added to the monomer mixt. and polymn. was carried out in 30

min. The terpolymer obtained was compounded with vulcanizing additives and vulcanized in 60 min at 150.deg. to give a rubber which was 91% insol. in boiling heptane after 96 hr.

Bibliographic Information

Cyclopentene homopolymers. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). Fr. Addn. (1972), 7 pp. Addn. to Fr. 1,394,380 (CA 68:3656h). CODEN: FAXXA3 FR 95917 19720310 Patent written in French. Priority: IT 65-23518 19651020. CAN 79:32401 AN 1973:432401 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (L 465/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 95917		19720310		

Priority Application

IT 1965-23518	19651020
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Abstract

Mainly trans polypentenamer [ring-opened poly(cyclopentene)] [25587-79-5] was prepd. by polymg. 300-3000:1 moles monomer/mole tungsten dichloride [13470-12-7] at -30.deg. or -20.deg. in the presence of 4:3 molar ratio aluminum trichloride [7446-70-0]-WCl₂ mixt., 0.1-5 moles/mole WCl₂ benzoyl peroxide [94-36-0], and EtnAlX₃-n (X = Cl or Br, n = 1, 1.5, 2). Thus, the polymer was prepd. using 10 cm³ cyclopentene, 600:1 molar ratio monomer/WCl₂, 0.082 g WCl₂-4/3 AlCl₃ mixt., 0.188 mmole ethylaluminum dichloride [563-43-9], and 0.094 mmole Bz₂O₂ at -20.deg.. The polymer contained 27:63% cis-trans double bonds.

Bibliographic Information

Filament-forming regular linear head-to-tail polymers of unsaturated hydrocarbons. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U.S. (1973), 8 pp. CODEN: USXXAM US 3715344 19730206 Patent written in English. Application: US 55-514099 19550608. Priority: . CAN 78:148866 AN 1973:148866 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (L 59+L 63)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3715344	A	19730206	US 1955-514099	19550608
DE 1794361	B1	19730719	DE 1967-1794361	19550604
DE 1794361	C2	19740228		
SE 316903	B	19691103	SE 1967-6302	19550608
SE 317192	B	19691110	SE 1966-12870	19550608
SE 322052	B	19700323	SE 1967-9251	19550608
US 4125698	A	19781114	US 1958-770484	19581029
US 6365687	B1	20020402	US 1992-883912	19920512

Priority Application

IT 1954-24227	A	19540608
IT 1954-25109	A	19540727
DE 1954-24348	A	19540803
US 1955-514097	B3	19550605
US 1958-710840	B1	19580124
US 1983-498699	B1	19830527
US 1986-906600	B1	19860910
US 1990-607215	B1	19901029
US 1991-719666	B1	19910624

Abstract

Mixts. of amorphous and linear, head-to-tail polypropylene (I) [9003-07-0] were prepd. that could be sepd. by fractional dissoln. to obtain semisolid to solid amorphous I, solid partially cryst. I having high mol. wt., and highly cryst., fiber forming I having very high mol. wt. Thus, propylene was polymd. at 55-60.deg. in the presence of $TiCl_4$ and Et_3Al in gasoline to form a mixt. of amorphous and cryst. C_3H_6 polymers, which could be molded at 130.deg.. The mixt. was successively extd. with boiling acetone, ether, and heptane to obtain an oil., low-mol.-wt. fraction 2.8, an amorphous compd. 39, and a partially cryst. solid (m. 150.deg.) 19%, resp. The insol. residue [d. 0.92 and intrinsic viscosity 3.333 (100 ml/g, tetrahydronaphthalene) was molded at 140-50.deg. to cryst. sheets having diam. 0.3 mm, breaking load 32 kg/cm², and elongation 40%.

Bibliographic Information

Molded structures from propylene or 1-butene polymers. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). Ger. (1972), 6 pp. Division of Ger. 1,094,985. CODEN: GWXXAW DE 1494168 19721026 Patent written in German. Application: DE 55-37302 19550604. Priority: IT 54-24227 19540608. CAN 78:17510 AN 1973:17510 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u59+ u63)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1494168	B	19721026	DE 1958-M37302	19550604
DE 1494168	C3	19730530		
DE 1794361	B1	19730719	DE 1967-1794361	19550604
DE 1794361	C2	19740228		
SE 316903	B	19691103	SE 1967-6302	19550608
SE 317192	B	19691110	SE 1966-12870	19550608
SE 322052	B	19700323	SE 1967-9251	19550608
US 4125698	A	19781114	US 1958-770484	19581029
US 6365687	B1	20020402	US 1992-883912	19920512

Priority Application

IT 1954-24227	A	19540608
IT 1954-25109	A	19540727
DE 1954-Z4348	A	19540803
US 1955-514097	B3	19550605
US 1958-710840	B1	19580124
US 1983-498699	B1	19830527
US 1986-906600	B1	19860910
US 1990-607215	B1	19901029
US 1991-719666	B1	19910624

Abstract

Linear, cryst., homotactic, head-to-tail propylene or 1-butene polymers were prepd. and spun into fibers with good appearance and mech. properties. Thus, polypropylene (I) [9003-07-0] prepd. using $Pr_3Al-TiCl_4$ catalyst was extd. successively with acetone, ether, and heptane, leaving a cryst. residue of 41.4% (based on original I) with m.p. 180.deg.. The residue was spun into fiber at 170-200.deg. and cold drawn 400%, giving a product with breaking load 30 kg/mm² initial cross-section and elongation at break 50%.

Bibliographic Information

High-molecular-weight ethylene-alkylene copolymers. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio; Pasquon, Italo; Valvassori, Alberto; Zambelli, Adolfo. (Montecatini Edison S.p.A.). Ger. Offen. (1972), 25

pp. Division of Ger. 1,520,249 (See Belg. 615,314, CA 58:596g). CODEN: GWXXBX DE 1795634 19721019
Patent written in German. Priority: IT 61-5222 19610321. CAN 78:16774 AN 1973:16774 CAPLUS
(Copyright (C) 2007 ACS on SciFinder (R)) . (u 378)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1795634		19721019	DE 1962-1795634	19620320

Priority Application

IT 1961-5222	19610321
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Abstract

Ethylene was copolymerized with cis- or trans-2-butene, 2-pentene, or 1-phenyl-2-butene to form high-molecular-weight copolymers. Thus, cis-2-butene-ethylene copolymer (I) [28602-57-5] containing 1-2 mole % 2-butene was prepared by copolymerizing cis-2-butene with ethylene at -30 degrees under nitrogen in the presence of Et_2AlCl and $\text{VOCl}(\text{OEt})_2$, the partial pressure of ethylene being 100 torr. I was a white powder. 22 Other similar copolymers were also prepared.

Bibliographic Information

Polymers and copolymers of certain unsaturated hydrocarbons. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U.S. (1972), 9 pp. CODEN: USXXAM US 3582987 19720601
Patent written in English. Application: US 55-514098 19550608. Priority: . CAN 77:75822 AN
1972:475822 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 59 + u 63)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3582987	A	19710601	US 1955-514098	19550608

Priority Application

IT 1954-749	A	19540727
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Abstract

Solvent-separable mixtures of amorphous and crystalline olefin polymers were obtained using catalysts prepared in the presence of monomer, which improved polymer speed of formation and molecular weight. The crystalline polymers were spinnable and the amorphous ones rubbery. Thus, to triethylaluminum [97-93-8] hydrocarbon solution and propylene at 60 degrees was added titanium tetrachloride [7550-45-0] in small amounts to give polypropylene [9003-07-0] of molecular weight 11,000-78,000. Also polymerized were 1- and 2-butene, 1-pentene, 1-hexene, and styrene. Used in place of Et_3Al were Et_2Zn , Et_2AlCl , and Pr_3Al ; in place of TiCl_4 were VCl_4 , ZrCl_4 , TiBr_4 , and TiI_4 .

Bibliographic Information

Linear high polymers of conjugated diolefins. Natta, Giulio; Porri, Lido; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U.S. (1970), 8 pp. CODEN: USXXAM US 3550158 19701222 Patent written in English.
Application: US 68-755481 19680703. Priority: . CAN 74:64600 AN 1971:64600 CAPLUS (Copyright (C)
2007 ACS on SciFinder (R)) . (u 78 + u 78/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3550158	A	19701222	US 1968-755481	19680703

Priority Application

US 1968-755481

A

19680703

Abstract

The title polymers with high crystallinity (>90% trans-1,4 units) were prepd. by the polymn. of butadiene (I), isoprene, or 1,3-pentadiene in the presence of a 2-component catalyst contg. 1:1-10 (mole ratios) TiCl₃, VCl₃, VOCl₃ or CrO₂Cl₂ and Et₃Al or Et₂Zn. Thus, a mixt. contg. 70 cm³ I and 6.3 g 1:5.3 (mole ratio) VCl₃-Et₃Al mixt. was stirred in a ball mill for 7.5 hr at room temp. to give 55 g product of which 17.2% was solid polybutadiene, sol. in CH₂Cl₂, contg. 99%trans-1,4 units, which (80 parts with 20 parts extender oil) was S-vulcanized 5-20 min at 150° to give materials with 75-300 kg/cm² tensile strength.

Bibliographic Information

Copolymers of ethylene, higher α -olefins, and monocyclomonoolefins or alkyl derivatives thereof.

Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio; Pasquon, Italo; Valvassori, Alberto; Zambelli, Adolfo. (Montecatini Edison S.p.A.). U.S. (1970), 5 pp. CODEN: USXXAM US 3505301 19700407 Patent written in English. Application: US 67-610037 19670118. Priority: . CAN 72:133863 AN 1970:133863 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 390/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3505301	A	19700407	US 1967-610037	19670118

Priority Application

US 1967-610037

A

19670118

Abstract

The title polymers are prepd. in the liq. phase at -80 to + 100° in the presence of catalysts contg. hydrocarbon-sol. V compds. and metal alkyls or metal alkyl halides (Al, Be, or Li). Thus, 1 millimole VOCl₃ and 2.5 millimoles trihexylaluminum were mixed in 10 ml C₇H₁₆ at -20° under N, added to 20 ml cyclopentene at -20° under N, and polymd. 8 min with addn. of a 1:2 molar C₂H₄-propylene gas mixt. at 200 l./hr. The reaction was quenched with MeOH and the product was washed and coagulated with acetone, giving 2 g of a product which was amorphous when examd. by x-ray diffraction. A mixt. of copolymer 100, tetramethylthiuram disulfide 1, and mercapto-benzothiazole 0.5 part was vulcanized in a press for 60 min at 150°, giving a vulcanizate with tensile strength 53 kg/cm², elongation 480%, and 300% m odulus 17 kg/cm². Other catalyst components used were VCl₄, V acetylacetonate, Et₂AlCl, and Et₃Al. Cycloheptene, cyclohexene, cyclooctene, and 4-methyl-1-cyclopentene were also used as cycloolefins. The use of VCl₃ as a catalyst component and of 1-butene as a monomer are also claimed. These polymers contain olefinic unsatn. derived from ring-opened cycloolefin groups. They are useful as vulcanizable elastomers.

Bibliographic Information

Crystalline isotactic copolymers of styrene derivatives prepared with ionic coordination catalysts.

Natta, Giulio; Sianesi, Dario; Corradini, Paolo. (Montecatini Edison S.p.A.). U.S. (1970), 5 pp. CODEN: USXXAM US 3489737 19700113 Patent written in English. Application: US 65-490641 19650927. Priority: . CAN 72:79942 AN 1970:79942 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 255)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3489737	A	19700113	US 1965-490641	19650927

Priority Application

US 1965-490641 A

19650927

Abstract

The title copolymers were prepd. by copolymg. styrene with a lower-alkyl- or halo-substituted styrene (I) in the presence of coordination catalysts prepd. from transition-metal halides, e.g. Ti chlorides, and Al alkyls. Thus, 0.23 g iso-Bu₃Al in 20 ml C₆H₆ was added to a mixt. of 35 g styrene and 17 g p-methylstyrene under N at 70°. A suspension of 0.20 g TiCl₃ in 20 ml C₆H₆ was then added. After 15 hr, MeOH was added to decomp. the catalyst and coagulate the copolymer. The copolymer product (31 g) had intrinsic viscosity 4.5 dl/g (1% soln. in tetrahydronaphthalene, 100°) and contained 34% p-methylstyrene units. X-ray anal. indicated that the copolymer crystd. in a hexagonal symmetric lattice characteristic of cryst. polystyrene, with the coil size along axis c remaining unvaried (6.65 .ANG.), but with a deformation of axes a and b (from 21.90 to 23.0 .ANG.). Ir showed that, even after prolonged thermal annealing, bands due to the statistical distribution of different monomeric units along the spiral chains were absent. The temp. of complete disappearance of crystn., detd. under a polarizing microscope, was 220-5°. Similar copolymers were prepd. from styrene and o-methylstyrene, o-fluorostyrene, p-fluorostyrene, p-chlorostyrene, o-chlorostyrene, or m-methylstyrene.

Bibliographic Information

Polymerization of cyclopentene to unsaturated high polymers. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U.S. (1969), 3 pp. CODEN: USXXAM US 3476728 19691104 Patent written in English. Application: US 66-587652 19661019. Priority: IT 65-10293 19651020. CAN 72:32460 AN 1970:32460 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4465/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3476728	A	19691104	US 1966-587652	19661019
BE 688500	A	19670419	BE 1966-688500	19661019

Priority Application

IT 1965-10293 A 19651020

Abstract

Stereoregular polypentenenes were prepd. by polymg. cyclopentene (I) at -50° to +70° in the presence of WCl₂, alkylaluminum halides, AlCl₃, and possibly org. peroxides. Polymn. at <1:1 alkylaluminum halide-WCl₂ mole ratios yielded cis-cyclopentene polymer units and polymn. at 1-5:1 mole ratios yielded trans units. Thus, 10 ml I under N at -30° was treated 1 hr with 0.082 g 4:3 AlCl₃-WCl₂ mixt., 0.023 g Bz₂O₂, and 0.188 millimole Et₂AlCl to yield 3.5 g polypentene, η 8 dl/g (PhMe at 30°). Ir bands at 10.35 and 7.1 μ indicated an 85:15 trans-cis ratio. Similarly prepd. were the following polypentenenes (polymn. temp., hr polymn. time, alkylaluminum halide, alkylaluminum halide-WCl₂ mole ratio, % yield, and trans-cis ratio given): -30°, 1, Et₃Al₂Cl₂, 1:1, 25, 80:20; -20°, 1, EtAlCl₂, 1:1, 14, 73:27; -20° 1, Et₂AlBr, 1:1, 25, 80:20; -30°, 1, Et₂AlCl, 0.25:1, 55, 9:91; -20°, 1, EtAlCl₂, 1:1, 39, 77:23.

Bibliographic Information

High-molecular-weight bicyclic hydrocarbon polymers. Natta, Giulio; Mazzanti, Giorgio; Dell'Asta, Gino; Sartori, Guido; Motroni, Giuseppe. (Montecatini Societa Generale per l'Industria Mineraria e Chimica). Ital. (1966), 10 pp. CODEN: ITXXAX IT 718796 19661102 Patent written in Italian. Application: IT 19640327. CAN 71:50679 AN 1969:450679 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4507)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 718796		19661102	IT	19640327

Abstract

Bicyclic unsatd. monomers are polymd. in the presence of a catalyst system contg. a V or Cr compd. with an organo-Al compd. to give high mol. wt. hydrocarbon polymers which are not crosslinked. Thus, 25 ml. PhMe contg. 2 millimoles VCl₄ was placed in a reactor under N and cooled to -20°. Et₃Al (5 millimoles) and 1 ml. bicyclo[3.2.0]hepta - 2,6-diene were added rapidly and the mixt. was stirred 15 hrs. The reaction was terminated by the addn. of 300 ml. MeOH contg. 5 ml. concd. HCl and 0.15 g. polymer, a 17% conversion, was recovered. The polymer, which was sol. in C₆H₆, PhMe, and PhCl, and insol. in MeOH, EtOH, Et₂O, and Me₂CO, had intrinsic viscosity 0.4 dl./g. in PhMe at 30° and its ir spectrum showed 1 units. Similar polymers were obtained in 10-87% conversions from bicyclo[4.2.0]oct-7-ene, and bicyclo[4.3.0]nona-3,-7-diene. Other catalyst systems used contained V acetylacetonate, Et₂AlCl, Cr acetylacetonate, and CrO₂Cl₂.

Bibliographic Information

Vulcanizable olefin-alkylidene norbornene copolymers. Natta, Giulio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazzareno. (Montecatini Edison S.p.A.). Fr. Addn. (1968), 7 pp. Addn. to Fr. 1428661. CODEN: FAXXA3 FR 92768 19681227 Patent written in French. Priority: IT 19660601. CAN 71:40034 AN 1969:440034 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 501/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 92768		19681227	FR	19670530
GB 1186776			GB	
IT 816508			IT	

Priority Application

IT 19660601

Abstract

Addn. to Fr. 1,428,661 (CA 65: 10779g). Linear, vulcanizable, unsatd., high-mol.-wt. ethylene-propylene-5-ethylidene-2-norbornene terpolymers are prepd. in the presence of a binary catalyst system. Thus, 2000 cc. anhyd. n-heptane, 1.5 cc. 5-ethylidene-2-norbornene, and 0.125 millimole Et₂Zn were mixed at -20°. A 3:1 mixt. of propylene and ethylene was introduced at 1200 l./hr. Then 3.7 millimoles Et₂AlCl in 15 cc. n-heptane and 0.5 milli-mole V tris(acetylacetonate) in 15 cc. anhyd. toluene were added. Seventeen min. after introducing the catalyst, the reaction was stopped by adding 10 cc. MeOH contg. 0.1 g. phenyl-β-naphthylamine. The product was worked up, yielding 41 g. terpolymer contg. 55% propylene with a Mooney viscosity [ML (1 + 4), 100°] of 96. A vulcanizate was prepd. by mixing the terpolymer 100, HAF carbon black 50, phenyl-β-naphthylamine 1, S 2, ZnO 5, (Me₂NCS)₂S₂ 1, and mercaptobenzothiazole 0.5 part in a press for 1 hr. at 150°. The resulting vulcanized sheet had a tensile strength of 205 kg./cm.² and an elongation at break of 440%. Similarly used was VOCl₃.

Bibliographic Information

Separation of polypropylenes of differing tacticities. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U.S. (1969), 8 pp. CODEN: USXXAM US 3438956 19690415 Patent written in English. Application: US 68-746767 19680723. Priority: . CAN 70:115698 AN 1969:115698 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 59 + u 63)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3438956	A	19690415	US 1968-746767	19680723
SE 316903	B	19691103	SE 1967-6302	19550608
SE 317192	B	19691110	SE 1966-12870	19550608
SE 322052	B	19700323	SE 1967-9251	19550608
US 4125698	A	19781114	US 1958-770484	19581029
US 6365687	B1	20020402	US 1992-883912	19920512

Priority Application

IT 1954-24227	A	19540608
IT 1954-7749	A	19540608
IT 1954-25109	A	19540727
DE 1954-Z4348	A	19540803
US 1955-514097	B3	19550605
US 1958-710840	B1	19580124
US 1983-498699	B1	19830527
US 1986-906600	B1	19860910
US 1990-607215	B1	19901029
US 1991-719666	B1	19910624

Abstract

Polypropylene (I) comprising 3 different linear, regular, head-to-tail polymers was extd. with boiling Et₂O to remove the atactic, amorphous I and leave a residue which consisted of partially cryst. (stereoblock) macromols. and the isotactic macromols. The partially cryst. I was removed with boiling n-heptane. Thus, 1.8 g. TiCl₄ dissolved in 50 ml. anhyd. gasoline was added dropwise at 5-10° to a soln. of 11.4 g. Et₃Al in 150 ml. gasoline. The soln. was dild. to 500 ml., thoroughly dried and evacuated, and 190 g. liq. propylene (II) was added. After the pressure had fallen from .apprx. 10 to 2 atm., an addnl. 160 g. II was added. After 20 hrs., 95 g. MeOH was added to decomp. the catalyst, and the reaction product formed was drenched with gasoline and MeOH and extd. The polymer was suspended in (iso-Pr)₂O, and the suspension was heated while stirring and bubbling with gaseous HCl. After 4 hrs., a small amt. of MeOH was added to ppt. the polymer, which was filtered off under suction. The white spongy polymer product had a transparent rubberlike appearance at 140° and was definitely melted at 155°. The solid polymer mixt. was extd. with boiling acetone, Et₂O, and n-heptane. The acetone ext. consisted of oily, low-mol.-wt. products and amounted to 2.8% of the solid polymer product. The ether ext., corresponding to 39% of the total polymer, was completely amorphous. The n-heptane ext., corresponding to 19% of the total polymer, had an intrinsic viscosity of 1.2-1.3 and was a partially cryst. solid at room temp. The residue insol. in acetone, ether, and n-heptane had a sp. gr. of 0.92 and an intrinsic viscosity, detd. in tetrahydronaphthalene soln. of 3.33 dl./g. Similar sepn. were carried out with I prepd. with various titanium halides and organoaluminum compds.

Bibliographic Information

Isotactic polystyrene and poly-1-pentene. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U.S. (1969), 5 pp. CODEN: USXXAM US 3435018 19690325 Patent written in English. Application: US 58-732810 19580505. Priority: . CAN 70:106996 AN 1969:106996 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (4 5 9 + 4 6 3)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3435018	A	19690325	US 1958-732810	19580505

Priority Application

US 1958-732810	A	19580505
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Abstract

Styrene is polymd. in C7H16 in the presence of Et3Al and TiCl4 to prep. a mixt. of amorphous and cryst., isotactic polystyrene macromols. The mixt. is treated with HCl to remove the inorg. impurities and then with acetone and HCl to ext. the amorphous polymer, giving cryst., isotactic polystyrene. An isotactic propylene-styrene copolymer is prepd. similarly, except that the extn. is carried out in turn with boiling acetone, Et2O, and C7H16. Also, a highly cryst. poly-1-pentene is prepd. similarly by extn. of the oily polymer with acetone and the amorphous polymer with EtOAc. Poly-1-hexane is prepd. similarly and extd. with MeOH, leaving a polymeric residue having marked viscoelastic properties. The polymers are useful as filaments, sheets, films, etc., and can be shaped prior to removal of the amorphous fraction, which serves as a plasticizer for the cryst. fraction and can be extd. later from the shaped article. Thus, 400 ml. C7H16 contg. 11.4 g. Et3Al and 250 g. styrene was heated to 68°, treated with 50 ml. heptane contg. TiCl4, kept at 68-70° for 3 hrs., and treated with 50 ml. C7H16 contg. 3.8 g. TiCl4. After 3 addnl. hrs., 100 ml. MeOH was added to give a suspension of fine powder in a viscous liq. The reaction mass was then treated with HCl to dissolve the inorg. products. A large amt. of MeOH was added and the coagulated polymer was sepd. by filtration and extd. with acetone contg. HCl. The residue was vacuum dried at 80° to give 30 g. highly cryst. polystyrene having a mol. wt. of 2,800,000, d. 1.08, and 1st-order transition temp. >210°. This polymer could be extruded at >230° or drawn at lower temps.

Bibliographic Information

Isotactic poly-1-butene. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U.S. (1969), 4 pp. CODEN: USXXAM US 3435017 19690325 Patent written in English. Application: US 58-741715 19580613. Priority: . CAN 70:106993 AN 1969:106993 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) · (u 59 + u 63)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3435017	A	19690325	US 1958-741715	19580613
SE 316903	B	19691103	SE 1967-6302	19550608
SE 317192	B	19691110	SE 1966-12870	19550608
SE 322052	B	19700323	SE 1967-9251	19550608
US 4125698	A	19781114	US 1958-770484	19581029
US 6365687	B1	20020402	US 1992-883912	19920512

Priority Application

IT 1954-10037	A	19540727
IT 1954-25109	A	19540727
IT 1954-24227	A	19540608
DE 1954-Z4348	A	19540803
US 1955-514097	B3	19550605
US 1958-710840	B1	19580124
US 1983-498699	B1	19830527
US 1986-906600	B1	19860910
US 1990-607215	B1	19901029
US 1991-719666	B1	19910624

Abstract

Isotactic poly-1-butene is prepd. by the polymn. of 1-butene or a 7:3 mixt. of 1-butene and 2-butene in gasoline in the presence of Et3Al and TiCl4, followed by successive solvent fractionation of the crude polymer with boiling acetone or Et2O to remove the sol., amorphous macromols. from the insol., cryst., isotactic macromols. The polymer, before or after extn. of the amorphous macromols. which exert a plasticizing action on the isotactic macromols., is useful for prepn. of shaped articles, sheets, and fibers. Thus, 160 ml. gasoline contg. 5.7 g. Et3Al and 85 g. 1-butene was heated to 81° in a 435-ml. autoclave, treated with 35 ml. gasoline contg. 1.8 g. TiCl4,

and, after 1 hr., treated with addnl. $TiCl_4$ in gasoline. The mixt. was agitated at $90-8^\circ$ for several hrs. The polymer was purified as described in U.S. 3,112,300 to give 10 g. of a white, cryst. polymer softening at 110° . The residue of the extrn. with ether comprised 46% of the total polymer and had an intrinsic viscosity of 1.44 ml./g. in tetrahydronaphthalene.

Bibliographic Information

Crystalline polyolefins. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Montecatini Edison S.p.A.). U. S. Reissue (1969), 6 pp. CODEN: UUXXA2 US 26517 19690114 Patent written in English. Application: US 67-647299 19670616. Priority: . CAN 70:97604 AN 1969:97604 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 73/E)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 26517	E	19690114	US 1967-647299	19670616

Priority Application

IT 1955-13629	A	19550926
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Abstract

Same disclosure. Four more claims added.

Bibliographic Information

Linear polynaphthofurans. Natta, Giulio; Bressan, G.; Farina, M. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1966), 15 pp. CODEN: ITXXAX IT 715633 19661001 Patent written in Italian. Application: IT 19640228. CAN 69:28100 AN 1968:428100 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (L 495)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 715633		19661001	IT	19640228

Abstract

Naphtho[2',1':2,2]furan (I), naphtho[1',2':2,3]furan (II), and naphtho[2',3':2,3]furan (III) are polymd. in the presence of Et_2AlCl , $AlCl_3$ -amino acid reaction products, $TiCl_3$ -amino acid reaction products, and bis(2-methylbutyl) dichlorotitanate (IV) to give the title polymers. (\pm)-Phenylalanine [(\pm)-V] and (\pm)-alanine (IV) are used. Thus, a soln. of 0.3 g. I in 10 ml. PhMe is added to a soln. of 0.02 ml. Et_2AlCl in PhMe at -60° , and the mixt. is kept 15 hrs. at between -50° and -60° to give 0.3 g. poly(naphthofuran). Similarly prepd. are the following poly(naphthofurans) (monomer and catalyst given): II, $TiCl_4$ -(\pm)-V, $[\eta]$ 1.65 dl./g. ($CHCl_3$, 30°); I, $AlCl_3$ -(\pm)-V; I, $AlCl_3$ -VI; III, IV; and the following optically active polymers [monomer, catalyst, and $[\alpha]_D$ given]: I, $AlCl_3$ -(-)-V, -20° ; I, $AlCl_3$ -(-)-V, -41° ; I $AlCl_3$ -(-)-V, -, $[\eta]$ 0.4 dl./g. ($CHCl_3$, 30°); I, $TiCl_4$ -(-)-V, -16° , $[\eta]$ 1.02 dl./g. ($CHCl_3$, 30°); II, $AlCl_3$ -(-)-V, -145° and (after heating to 350°) -110° ; II, $AlCl_3$ -(+)-V, 123° and (after 1 hr. at 290°) 110° , $[\eta]$ 0.26 dl./g. and (after 1 hr. at 290°) 0.15 dl./g.; III, (+)-IV, -.

Bibliographic Information

Poly(allyl cyanide). Natta, Giulio; Mazzanti, G.; Giannini, U.; Brukner, G. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1966), 6 pp. CODEN: ITXXAX IT 718894 19661102 Patent written in Italian. Application: IT 19640403. CAN 69:28098 AN 1968:428098 CAPLUS (Copyright (C)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 718894		19661102	IT	19640403

Abstract

Allyl cyanide (I) is polymd. at between -50° and -100° in the presence of mixts. of (1) n-octylsodium (II) and (2) linear alc., e.g. allyl alc., MeOH, and EtOH, II-alc. molar ratio 2:1-20:1, in n-heptane to give the title polymer. Thus, a mixt. of 8.3 g. I and 20 ml. n-heptane is cooled to -78° , 1 millimole allyl alc. is added, a mixt. of 2.95 millimoles II in 20 ml. n-heptane is slowly added, the mixt. is agitated 21 hrs. at -78° , and MeOH-contg. HCl is added to give 2.62 g. polymer. The polymer is extd. with boiling Me₂CO to give 30% cryst. residue.

Bibliographic Information

High-molecular-weight bicycloalkene and bicycloalkadiene homopolymers. Natta, Giulio; Mazzanti, G.; Dall'Asta, Gino; Motroni, G. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1966), 23 pp. CODEN: ITXXAX IT 718795 19661102 Patent written in Italian. Application: IT 19640327. CAN 69:28095 AN 1968:428095 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 500)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 718795		19661102	IT	19640327

Abstract

I compds., where n and m are 0 or 1 and R is CH₂CH₂ or CH:CH, are polymd. in the presence of mixts. of (1) transition metal compds. and (2) organometallic compds. to give polymers II, III, and IV. A mixt. of 5.0 ml. bicyclo[4.3.0]nona-3,7-diene and 0.2 millimole WCl₆ is cooled to -30° , 1.0 millimole Et₂AlCl is added, and the mixt. is agitated 3 hrs. under N at -30° and added to 300 ml. MeOH contg. 5 ml. concd. HCl to give product. A mixt. of the product and 10 ml. C₆H₆ contg. 0.01 g. 2-C₁₀H₇NHPh is agitated 24 hrs., the mixt. is filtered, and the filtrate is added to 500 ml. MeOH contg. 5 ml. concd. HCl to give 2.3 g. polymer II, $[\eta]$ 0.6 dl./g. (PhMe, 30°), contg. >90% trans double bond units and <10% cis double bond units. Similarly prepd. are [monomer, catalyst components, polymer, m.p., and $[\eta]$ (in dl./g.) given]: bicyclo[4.2.0]oct-7-ene, TiCl₄ and Et₃Al, III, $65-75^{\circ}$, 0.28; bicyclo[3.2.0]hepta-2,6-diene, TiCl₄ and Et₃Al, IV, -. Ir data are given.

Bibliographic Information

Catalysts for polymerization of alkyl β -vinylacrylates. Natta, Giulio; Farinq, Mario; Donati, Mario. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1966), 10 pp. CODEN: ITXXAX IT 712291 19660803 Patent written in Italian. Application: IT 19610417. CAN 68:96526 AN 1968:96526 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 322 / A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 712291		19660803	IT	19610417

Abstract

Compds. of the general formula $RCH:CHCH:CHCO_2R_1$, where R is H, Me, or Ph and R_1 is Me or Bu, polymd. in the presence of an organolithium- or organosodium-Lewis base [e.g. tetrahydrofuran (THF)] complex. A ketylithium compd. is prepd. from Li, Ph_2CO , and THF. Thus, 0.5 g. fluorene is treated under N with a soln. of 3 millimoles BuLi in PhMe to give fluorenyllithium (I), I is cooled to -50° , 3.9 g. Me sorbate is added, and MeOH is added after 16 hrs. to give 2.7 g. poly(Me sorbate) (II). Similarly prepd. are (catalyst given): poly(Bu sorbate) (III), $LiNEt_2$; II, Li- Ph_2CO -THF; III, octylsodium; poly(Me β -vinylacrylate), BuLi-THF; III, BuLi-THF; II, BuLi-anisole; II, BuLi-pyridine; II, BuLi-Bu $_3N$; poly(lauryl sorbate), BuLi-Bu $_3N$; II, BuLi- $PhNMe_2$; III, BuLi- Ph_3P ; poly(Bu β -styrylacrylate), BuLi-THF; III, a compd. prepd. from BuLi and Bu $_4N^+I^-$.

Bibliographic Information

Poly[2-(9H-carbazol-9-yl)ethyl methacrylate]. Natta, Giulio; Longi, Paolo; Pellino, Ennio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1966), 4 pp. CODEN: ITXXAX IT 708024 19660604 Patent written in Italian. Application: IT 19631105. CAN 68:13592 AN 1968:13592 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) .(4 473)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 708024		19660604	IT	19631105

Abstract

The title polymer (I) is prepd. in the presence of Et_2NMgBr , $PhMgBr$, and 9 lithio-9H-carbazole (II). A mixt. of $CH_2=CMeCO_2Me$ 450, 2-(9H-carbazol-9-yl)ethanol 231, $Ti(OBu)_4$ 14, and 2-C $_{10}H_7NHP$ 1 g. is refluxed to give 120 g. III, m. 79° . III (10 g.) and PhMe are introduced into a reactor under N at 30° , 0.3 g. Et_2NMgBr is added, and the mixt. is agitated 4-5 hrs. and treated with 500 ml. MeOH contg. 2-3 ml. concd. HCl to give I, m. 288° . Similarly prepd. are the following I (catalyst used and m.p. given): $PhMgBr$, -; II, 285° .

Bibliographic Information

Homopolymers from cyclopentene. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Fr. (1965), 14 pp. CODEN: FRXXAK FR 1394380 19650402 Patent written in French. Priority: IT 19630410. CAN 68:3656 AN 1968:3656 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (4 4 6 5)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1394380		19650402	FR 1964-969983	19640407
DE 1299868			DE	
DE 1770444			DE	
DE 1795738			DE	
GB 1010860			GB	
IT 701182			IT	
US 3458489		19690729	US 1964-339455	19640122
US 3549607		19701222	US 1968-787622	19681227

Priority Application

IT	19630410
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Abstract

Catalysts are specified for the polymn. of cyclopentene (I) by ring-opening to give high mol. wt. linear polypentenamers (II) composed of (CH₂)₃CH:CH or (CH₂)₂CH:CHCH₂ units. The double bonds can be >90% cis or >90% trans according to the catalyst used. The cis form is given by MoCl₅-Et₃Al and WCl₆-Et₂Be, and the trans form by WCl₆-Et₃Al, TiCl₄-Et₃Al, ZrCl₄-Et₃Al, and (PhO)₃MoCl₂-Et₂AlCl. For example, 9 millimoles (C₆H₁₃)₃Al was slowly added under dry N to a stirred soln. of 3.6 millimoles MoCl₅ in 30 cc. dry n-C₇H₁₆ at -30°. The mixt. was added to 7.7 g. I, stirred at -30° for 20 hrs., treated with 5 cc. BuOH and 20 mg. phenyl-β-naphthylamine (III), and poured into 200 cc. MeOH contg. 5 cc. 38% HCl. The pptd. II was dried in N, treated with 50 cc. MeOH contg. 2 cc. 38% HCl and 20 mg. III, sepd. by decantation, washed with MeOH, and dried in vacuo at room temp. to give 2.1 g. II contg. only cis double bonds (ir spectrum). II find use as elastomers, esp. after vulcanization, and as thermosetting resins.

Bibliographic Information

Optically active benzofuran polymers. Natta, Giulio; Farina, Mario; Donati, Mario; Bressan, Giancarlo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1965), 3 pp. Addn. to Ital. 641183. CODEN: ITXXAX IT 686875 19650318 Patent written in Italian. Application: IT 19610126. CAN 67:100591 AN 1967:500591 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 351/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 686875		19650318	IT	19610126

Abstract

Addn. to Ital. 641,183 (see Brit. 930,524, CA 59: 8896d). Benzofuran (I) is polymd. in the presence of reaction products, prepd. at -75°, of (a) EtAlCl₂ and (b) optically active compds., e.g. (-)-phenylalanine (II), camphorsulfonic acid (III), and (-)-brucine (IV), to give the title polymers. Thus, 0.15 ml. EtAlCl₂ was added to a mixt. of 0.47 g. I and 30 ml. PhMe, the mixt. kept 15 min., cooled to -75°, a soln. of 1.95 g. I in 5 ml. PhMe added, the mixt. kept 20 hrs., and MeOH added to give 0.77 g. optically active I polymer, α_D -2.65° (C₆H₆, 2.0%), [α]_D -33.1°, [M]_D -39.1°. Similarly prepd. are the following optically active I polymers [optically active catalyst component, α_D, [α]_D, and mol. rotation [M]_D given], III, -0.68° (CHCl₃, 4.7%), -3.6°, -4.3°; IV, +0.47° (C₆H₆) 4.2%), +2.8°, +3.3°.

Bibliographic Information

Syndiotactic polypropylene. Natta, Giulio; Zambelli, Adolfo; Pasquon, Italo. (Montecatini Edison S.p.A.). U.S. (1967), 2 pp. CODEN: USXXAM US 3335121 19670808 Patent written in English. Application: US 19630703. CAN 67:100577 AN 1967:500577 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 406)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3335121		19670808	US 1963-292773	19630703

Abstract

Polypropylene having crystallinity due exclusively to syndiotactic structure is prepd. by polymn. of propylene in contact with a homogeneous catalyst prepd. from V acetylacetonate (I) and organometallic Al halides. The I is mixed with an organometallic Al monohalide at 0° in an aromatic hydrocarbon solvent, and a reaction product sol. in the solvent which is a homogeneous catalyst for propylene polymn. is formed. Thus, at -78°, 100 cc. PhMe, 10⁻³ mole V acetylacetonate, 5 × 10⁻³ mole Et₂AlCl, and 80 g. propylene was kept for 24 hrs. The mixt.

was coagulated with MeOH to obtain 2 g. polypropylene of intrinsic viscosity 0.5 (in tetrahydronaphthalene at 135°) and its crystallinity index 80. The V acetylacetonate-Et₂AlCl ratio is preferably 1:5. At a ratio of 1:10, completely amorphous polypropylene is obtained. When 10-3 mole anisole is incorporated into the mixt., 0.35 g. polypropylene of intrinsic viscosity 0.19 and its index 236 are obtained.

Bibliographic Information

Polymerization of α -olefins. Natta, Giulio; Giachetti, Ettore; Pasquon, Italo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ger. (1967), 2 pp. CODEN: GWXXAW DE 1238667 19670413 Patent written in German. Priority: IT 19571107. CAN 67:54587 AN 1967:454587 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (4192)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1238667		19670413	DE 1958-M60666	19581106

Priority Application

IT	19571107
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Abstract

Isotactic polymers of α -olefins with a controlled, comparatively low av. mol. wt. are prepd. by polymn. in the presence of a catalyst system consisting of the reaction product of a Group IVB-VIB metal halide with an organometallic compd. of a Group I-III metal and the reaction product of a Zn, Cd, or Hg halide with the organometallic compd. Thus, an autoclave was charged with 0.5 g. TiCl₃, a soln. of 1 cc. Et₃Al in heptane, the reaction product of 0.5 g. anhyd. ZnCl₂ and 1 cc. Et₃Al, and 250 cc. heptane. Then, propylene was passed into the soln. at 2.3 atm. at 70°. After 2.5 hrs., the polymn. was discontinued and the polymer was washed with methanolic HCl and with MeOH. The polymer contained 13.8% Et₂O-extractable components, 14.2% C₇H₁₆-extractable components, and 72% residue with a viscosity in tetrahydronaphthalene of 0.64. If the polymer was prepd. without the reaction product of ZnCl₂ and Et₃Al, a polymer was obtained that contained 14.8% ether-extractable material, 5.4% C₇H₁₆-extractable material, and 79.8% residue with a viscosity of 3.24. Similar results were obtained with the reaction product of CdCl₂ and Et₃Al as catalyst.

Bibliographic Information

Polymerization of unsaturated hydrocarbons. Natta, Giulio; Valvassori, Alberto; Sartori, Guido; Turba, Vittorio. (Montecatini Edison S.p.A.). Ital. (1965), 21 pp. CODEN: ITXXAX IT 693475 19650820 Patent written in Italian. Application: IT 19621228. CAN 67:22705 AN 1967:422705 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (4454)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 693475		19650820	IT	19621228

Abstract

trans-1,2-Divinylcyclobutane (I) and 1,2,4-trivinylcyclohexane (II) are polymd. at -80° to +125° in n-heptane in the presence of a mixt. contg. (1) an org. Al compd., such as iso-Bu₃Al, Et₂AlCl, or trihexylaluminum, and (2) a Ti or V compd., such as TiCl₄, TiCl₃, or VCl₄, to give unsatd. polymers contg. units of the general formula III as well as [-CH₂CH:CHCH₂-]. A mixt. of 4 millimoles TiCl₄, 2 millimoles iso-Bu₃Al, and 20 ml. n-heptane is kept 15 min. at 0°, 5 ml. I is added, and 10 ml. MeOH contg. 0.1 g. 2-C₁₀H₇-NHPH is added after 5 hrs. to give I homopolymer (IV), its band at 10.35 μ . Similarly prepd. is a II homopolymer. IV is ozonized and the product

treated with MeOH to give di-Me succinate. The polymers may be vulcanized to form elastomers.

Bibliographic Information

Shock-resistant styrene polymer mixtures. Natta, Giulio; Beati, Enrico; Severini, Febo. (Montecatini Edison S.p.A.). Ital. (1965), 14 pp. CODEN: ITXXAX IT 696119 19651005 Patent written in Italian. Application: IT 19630515. CAN 67:22430 AN 1967:422430 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 461)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 696119		19651005	IT	19630515

Abstract

Styrene (I) and mixt. of I and CH₂:CHCO₂Me are graft copolymerized on amorphous ethylene (II)- α -olefin copolymers and amorphous II-propylene (III)-cyclooctadiene (IV) terpolymers to give graft copolymers; the graft copolymers are mixed with polystyrene (V) to give mixts., contg. 5-25 wt. % amorphous polymer, which can be used in the manuf. of shaped articles. The V mol. wt. is 100,000-500,000. Thus, a mixt. of 50 g. II-III 1:1 copolymer, 50 g. I, and 2 g. cumyl peroxide is heated 2 hrs. at 135° to give 100 g. graft copolymer; a mixt. of 20 g. prepd. graft copolymer and 8 g. V (mean mol. wt. 260,000) is calendered .apprx.5 min. at 170-80° to give a product (contg. 10% II-III copolymer), impact strength 3.5 kg. cm./cm. (23°), impact strength 2.1 kg. cm./cm. (0°), Rockwell hardness 67, which is kept 16 days at 70° to give 2.6, 1.5, and 72, resp. Also prepd. are II-1-butene copolymer-I graft copolymer, II-III-IV terpolymer-I graft copolymer contg. 5% IV, II-III copolymer-I-Me acrylate graft copolymer.

Bibliographic Information

Substantially linear, regularly head-to-tail polymers of deuterated and tritiated monomers. Natta, Giulio; Peraldo, Mario; Farina, Mario. (Montecatini Edison S.p.A.). U.S. (1967), 14 pp. CODEN: USXXAM US 3303177 19670207 Patent written in English. Priority: IT 19581212 - 19590321. CAN 66:116133 AN 1967:116133 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 227 + U 227/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3303177		19670207	US 1959-859041	19591211
DE 1420610			DE	

Priority Application

IT	19581212
IT	19590321

Abstract

Normally solid, cryst. poly(α -deuteriopropylenes), consisting predominantly of monomer units derived from the cis or trans form of α -deuteriopropylene, are provided. In these polymers, both the asym. C atoms of each successive monomer unit in the chain show isotactic stereoregularity, at least for long portions of the chain. For example, cis- α -deuterio- β -methylethylene (cis-propylene-1-d) was prepd. from cis-1-bromopropylene by reaction with finely divided Li in cold ether and decompn. of the propenyllithium thus formed with D₂O. The configuration of the product is detd. by the ir spectrum of the hydrocarbon (very intense absorption at 12.50 μ) and from the configuration of the Li derivs. cis-Propylene-1-d (52 cc.) is introduced in the absence of air and moisture into a glass vial contg. 0.225 g. Et₃Al, 0.065 g. TiCl₃, and 30 cc. n-heptane. After 36 hrs. at 20°, 0.087 g. polymer,

63% insol. in boiling heptane, is obtained. Cryst. polymers were also obtained from trans-propylene-1-d, propenyl Me ether, propenyl Et ether, propenyl Bu ether, propenyl iso-Bu ether, and 1-butenyl Me ether.

Bibliographic Information

Chromium carbonyl complexes with polystyrene. Natta, Giulio; Calderazzo, Fausto; Ercoli, Raffaele. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ger. (1967), 2 pp. CODEN: GWXXAW DE 1235595 19670302 Patent written in German. Priority: IT 19580321. CAN 66:95607 AN 1967:95607 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 204)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1235595		19670302	DE 1959-M40832	19590316

Priority Application

IT	19580321
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Abstract

The title compds. are prepd. from Cr(CO)₆ and polystyrene (I). Thus, 4 g. I and 6 g. Cr(CO)₆ were heated under pressure at 190° for 10 hrs. The solid product was taken up in PhMe, pptd. with EtOH, and heated at 10-2 mm. to remove any Cr(CO)₆. The yellow polymer contained bound Cr and softens at a temp. approx. that of unmodified I. The adduct can be used as a catalyst and a carrier for Cr when a soln. of Cr in an org. solvent is desired. This adduct gives a higher yield than the reaction product of Cr(CO)₆ and Ph₂Cr.

Bibliographic Information

Stereospecific polymerization of vinyl ethers. Natta, Giulio; Mazzanti, Giorgio; Dall'Asta, Gino. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). U.S. (1967), 3 pp. CODEN: USXXAM US 3297671 19670110 Patent written in English. Priority: IT 19600803. CAN 66:55986 AN 1967:55986 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 320)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3297671		19670110	US 1961-127860	19610731

Priority Application

IT	19600803
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Abstract

Vinyl ethers undergo stereospecific polymn. in the presence of a new cationic catalyst. Thus, 15 g. vinyl isobutyl ether is added with continuous agitation during 2 hrs. to 400 mg. TiCl₃ cocrystd. with AlCl₃ in 150 cc. toluene under N at -78°. The agitation is continued for 4 more hrs., the soln. viscosity increases remarkably, and some polymer ppts. in the form of a gel. The reaction is stopped by addn. of 30 cc. BuOH. The soln. is dild. to completely dissolve the polymer and is then filtered and poured slowly, while agitating, into a 5-fold vol. of MeOH. The pptd. polymer is collected, washed thoroughly with MeOH, and dried at .apprx.75° under reduced pressure to give 12.3 g. nontacky white solid poly(vinyl isobutyl ether) (I), intrinsic viscosity 2.67 at 30°. I is sol. in org. solvents, such as hydrocarbons, halogenated hydrocarbons, esters, and ethers. I is insol. in MeOH, EtOH, and acetone. It can be extruded into filaments that can be oriented by stretching, or it can be molded at 110-40° into very transparent laminates or films. The catalyst soln. may be extd. for 18 hrs. in a Soxhlet extractor prior to use; the I obtained has somewhat better characteristics.

Bibliographic Information

Trioxane copolymers. Natta, Giulio; Pregaglia, Gianfranco; Mazzanti, Giorgio; Binaghi, Marco. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ger. (1966), 3 pp. CODEN: GWXXAW DE 1229298 19661124 Patent written in German. Priority: IT 19621213. CAN 66:38362 AN 1967:38362 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)), (U 453)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1229298		19661124	DE 1963-M59198	19631210

Priority Application

IT	19621213
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Abstract

The prepn. of trioxane (I) copolymers, $[-CH_2OCH_2O_2CMe_2CH_2OCH_2O-]_n$ (II), from I and an unsatd. monomer e.g. Me₂C:CO (III) or CH₂:CHCOMe (IV), in the presence of a Lewis acid is described. Thus, to a 60° soln. of 10 cc. benzene and 0.1 cc. BF₃.Et₂O under N, was added dropwise over 1 hr. a 30-cc. benzene soln. contg. 10 g. I and 0.9 cc. III. After stirring for 5 hrs., the polymer sepd. was washed with Na₂CO₃ soln. and water and dried at 60° to yield 4.2 g. II. It had an intrinsic viscosity of 0.12 in. HCONMe₂ and a II content of 6.5 wt. %. Other copolymers were similarly prepd. from the following components: 5 cc. benzene, 0.3 cc. 10% soln. of BF₃.Et₂O in heptane (V), and a mixt. of 20 cc. benzene, 10 g. I, and 0.7 cc. III (product 6.8 g. II); 5 cc. benzene, 0.5 cc. of a 10% BF₃.Et₂O soln. in V, and a mixt. of 20 cc. benzene, V 10 g. I, and 0.7 cc. IV (product 2 g. copolymer).

Bibliographic Information

Optically active copolymers. Natta, Giulio; Farina, Mario; Donati, Mario. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1965), 12 pp. Addn. to Ital. 642096. CODEN: ITXXAX IT 691991 19650716 Patent written in Italian. Application: IT 19601230. CAN 66:29426 AN 1967:29426 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) .(U 357/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 691991		19650716	IT	19601230

Abstract

Addn. to Ital. 642,096. A method for synthesizing optically active copolymers is described. Thus, 1.9 g. Bu sorbate and 1.9 g. PhCH:CHCH:CHCO₂Bu in 20 ml. anhyd. toluene were copolymerized at -40° for 3 hrs. by 3 millimoles iso-amyllithium (obtained from (S)(+)-2-methyl-1-chlorobutane, $[\alpha]_{20}^D = 1.65$, and Li in petroleum ether) resulting in 1.4 g. amorphous copolymer $[\alpha]_{20}^D = +0.60$.

Bibliographic Information

Trioxane-indene copolymers. Natta, Giulio; Pregaglia, Gianfranco; Mazzanti, Giorgio; Binaghi, Marco; Roffia, Paolo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1965), 7 pp. CODEN: ITXXAX IT 689046 19650405 Patent written in Italian. Application: IT 19630304. CAN 66:29414 AN 1967:29414 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 463)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 689046		19650405	IT	19630304

Abstract

Mixts. of trioxane and indene are copolymerized at 25-70° in the presence of BF₃ etherate (I) to give materials contg. CH₂O units and units of the general formula II. The copolymers have <0.3%/min. wt. loss (225° ± 5°). Thus, to 0.1 ml. I in 10 ml. C₆H₆ under N, 5 g. trioxane and 0.5 ml. indene in 10 ml. C₆H₆ is introduced in .apprx.15 min. at room temp. and the mixt. agitated 6 hrs. and treated with MeOH to give 0.8 g. polymer, wt. loss (225° ± 5°) 0.06%/min.

Bibliographic Information

Linear ethylene- α -olefin copolymers. Natta, Giulio; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1965), 11 pp. Addn. to Ital. 638656. CODEN: ITXXAX IT 691945 19650716 Patent written in Italian. Application: IT 19601125. CAN 66:29397 AN 1967:29397 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 334/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 691945		19650716	IT	19601125

Abstract

Mixts. of ethylene and propylene are copolymerized at 20-80° in the presence of mixts. contg. vanadyl bis(acetylacetonate) or vanadyl tris(acetylacetonate) (I), Et₂AlCl, and Ph₂NMe, Ph₃N, or Ph₃P. Thus, a 4:1 molar propylene-ethylene mixt. is introduced into 350 ml. n-heptane at 200 l./hr. at 25°, 7 millimoles Et₂AlCl and 1.4 millimoles Ph₂Nme in 20 ml. C₆H₆ at 25° are mixed with a soln. of 1.4 millimoles I in 20 ml. C₆H₆ and the catalyst mixt. is added, the monomer introduction continued 18 min. at 250 l./hr., and 50 ml. MeOH added to give 4.9 g. ethylene-propylene copolymer (II) as compared with 2.2 g. for the control (absence of Ph₂NMe). II contains 47 mole % ethylene. The Me₂CO ext. contains 1% product; the ether ext. contains 35% product (the extd. material contains 45.5 mole % ethylene); and the hexane ext. contains 64% product (the extd. material contains 51 mole % ethylene).

Bibliographic Information

Olefinic copolymers. Natta, Giulio; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Ital. (1965), 8 pp. Addn. to Ital. 638375. CODEN: ITXXAX IT 691975 19650716 Patent written in Italian. Application: IT 19601223. CAN 66:29359 AN 1967:29359 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 340/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 691975		19650716	IT	19601223

Abstract

Addn. to Ital. 638,375. An improved method for making copolymers of ethylene and higher α -olefins, by using a

mixt. of alkylaluminum dihalide and organovanadium compds. as a catalyst at -10° to -50° , is described. Thus, 350 ml. anhyd. n-heptane was satd. at -20° from 4:1 ethylene-propylene. The catalyst (prepd. at -20° from 14 millimoles EtAlCl_2 and 2.8 millimoles V triacetylacetonate in 40 ml. anhyd. toluene) was then added, and the monomers were added (300 l./hr.) for an addnl. 10 min. The product (6.5 g.) was an amorphous copolymer, contg. 50 mole % ethylene.

Bibliographic Information

Hydrocarbon polymers of divinylcyclooctene and at least one alpha-olefin. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). U.S. (1966), 4 pp. CODEN: USXXAM US 3281398 19661025 Patent written in English. Priority: IT 19620302 - 19630805. CAN 66:19562 AN 1967:19562 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 410/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3281398		19661025	US 1964-386746	19640731
IT 795057			IT	

Priority Application

IT	19620302
IT	19630805

Abstract

Vulcanizable high mol. wt., linear, amorphous polymers are prepd. from 1,2-divinylcyclooct-5-ene (I) and C2-8 α -olefins. A monomer mixt. is polymerized in the liquid phase in contact with the catalyst obtained by mixing a vanadium compd. from the group contg. vanadium halides, vanadium oxyhalides, and org. salts of vanadium, and an organometallic compd. of Al or Be. Thus, 200 cc. anhyd. n-heptane and 5 cc. I are introduced to a reactor under N, and a gaseous 2:1 propylene-ethylene mixt. is added at 200 l./hr. A catalyst formed at -20° in N from 2 millimoles VCl_4 and 10 millimoles Et_2AlCl and 3 ml. anhyd. n-heptane is added to the mixt., the propylene-ethylene gas mixt. was increased to 400 l./hr., and after 10 min., 10 ml. MeOH contg. 0.1 g. N-phenyl- α -naphthylamine (II) is added. The polymer is treated with aq. HCl and water and dried in vacuo to obtain 7 g. solid product which is amorphous, is a nonvulcanized elastomer, and is completely sol. in boiling n-heptane. The terpolymer (100 parts) is mixed with 1, S 2, ZnO 5, tetramethylthiuram disulfide 1, and mercaptobenzothiazole 0.5 part, and is vulcanized 60 min. at 150° , to give a vulcanized polymer of tensile strength 28 kg./cm.², elongation at break 530%, and 300% modulus 12 kg./cm.² A monomer also used is butene. Other catalysts used are vanadium triacetate, vanadium tribenzoate, vanadium tristearate, vanadium triacetylacetonate, methylaluminum sesquichloride, vanadium oxytrichloride, diisobutyl aluminum chloride.

Bibliographic Information

Vulcanizable olefin copolymers. Natta, Giulio; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Fr. (1966), 7 pp. CODEN: FRXXAK FR 1430560 19660304 Patent written in French. Priority: IT 19640317. CAN 66:19557 AN 1967:19557 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 499)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1430560		19660304	FR 1965-9218	19650315
GB 1062543			GB	
IT 717266			IT	

Priority Application

Abstract

By using catalysts prepd. from V compds. and organometallic compds. or the hydrides of Al, Li and Al, or Be, linear, amorphous, unsatd. copolymers of ≥ 1 dienes or cyclic polyenes having an unsatd. bridge with C₂H₄ and ≥ 1 α -olefins are obtained. Suitable dienes and cyclic polyenes include 8-methylbicyclo [3.2.2] nona-2,6-diene (I), bicyclo[2.2.2]octa-2,5,7-triene, 7-methylenebicyclo-[2.2.1]hept-2-ene, and 7-isopropylidenebicyclo[2.2.1]hept-2-ene. The preferred α -olefins used with C₂H₄ are propylene and 1-butene. The catalyst are well dispersed, amorphous, and colloidally dispersed or even completely sol. in the hydrocarbons used as the copolymerization solvent, such as aliphatic, cyclo-aliphatic, and aromatic hydrocarbons or their mixts. The co-polymerizations are effected at -80 to 125°. When the catalysts are prepd. from halogenated alkylaluminums and V triacetylacetonate, V trialkylates, or halogenated vanadyl alcoholates at 0-125°, a complexing agent chosen from the ethers, thio ethers, tertiary amines and trisubstituted phosphines should be used. For example, 350 cc. anhyd. n-C₇H₁₆ and 2 cc. I were introduced into a reactor maintained at -20°. A 1:2 molar mixt. of C₂H₄ and propylene is introduced at 300 l./hr. The catalyst is previously prepd. by reaction at -20° in a N atm. and in 30 cc. of anhyd. n-C₇H₁₆ of 1 millimole VCl₄ and 5 millimoles Et₂AlCl. The catalyst is fed into the reactor under N pressure. After 8 min., the reaction is stopped by addn. of 10 cc. MeOH contg. 0.1 g. phenyl- α -naphthylamine. After washing and drying, 6 g. of a solid amorphous product is obtained having the characteristics of an unvulcanized elastomer. In a laboratory roll mill, 100 parts by wt. of the terpolymer is mixed with phenyl- α -naphthylamine 1, S 2, ZnO 5, tetramethylthiuram disulfide 1, and mercaptobenzothiazole 0.5 part. The mixt. is vulcanized in press at 150° for 60 min.

A vulcanized product is obtained with a tensile strength of 37 kg/cm.², an ultimate elongation of 510%, and a modulus at 300% elongation of 13 kg./cm.²

Bibliographic Information

Catalyst for stereospecific polymerization of α -olefins to highly crystalline polymers having isotactic structures. Natta, G.; Pasquon, I.; Zambelli, A. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 3 pp. IT 686950 19650920 Patent language unavailable. Application: IT 19610303. CAN 65:73945 AN 1966:473945 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 302/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 686950		19650920	IT	19610303

Abstract

A catalyst compn. is obtained from a mixt. of EtAlCl₂, TiCl₃ violet crystals, and an aliphatic or aromatic primary or secondary amine with an amine/EtAlCl₂ ratio of $0.5 \pm 0.1/1$. A 500-cc. stainless-steel reactor is fitted with an agitator and the temp. controlled at 70°. To this reactor is added 1 cc. PhMe, 0.5 g. TiCl₃ violet crystals of the modification contg. 4.6% Al as AlCl₃ in solid soln. [G. Natta, Chim. Ind. (Milan) 42, 1207-24(1960)], and an 0.5 molar ratio of Et₂NH to EtAlCl₂. The soln. is satd. with C₃H₆ until the pressure reaches 5 atm. After 3 hrs., 19 g. of polymer is obtained having an intrinsic viscosity of 4.1 (in Tetralin at 135°). This polymer is 93% isotactic polypropylene (insol. in boiling n-C₇H₁₆, 2% sol. in boiling Et₂O, and 5% sol. in boiling n-C₇H₁₆).

Bibliographic Information

High-melting poly-1-pentene. Natta, G.; Danusso, F.; Gianotti, G. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 9 pp. IT 688289 19650329 Patent language unavailable. Application: IT 19630223. CAN 65:65919 AN 1966:465919 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 456)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 688289		19650329	IT	19630223

Abstract

Isotactic poly-1-pentene(I) is heated to 80° to prep. a stable polymorphous form of I (II), having a higher m.p. (80-130°), a different d. and x-ray pattern than normally prepd. I, and suitable for manuf. of plastics and in the prepn. of fibers and membranes. The process can be completed with or without pressure and a temp. of 60° can be used to convert the I if it is in the metastable form. II has an x-ray spectrum having Cu-K α radiation that represents reflection for max. crystallinity at angles of 2 θ of 8.4, 11.5, 16.3, 17.7, 18.7-20, and 21.0°. Thus, a sample of I was subjected to a pressure of 2000 atm. at 130° for 1 hr. to prep. a high-grade cryst. form of II.

Bibliographic Information

Vulcanizable copolymers of olefins. Natta, Giulio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazareno. (Montecatini Societa Generale per l'Industria Mineraria e Chimica). (1966), 10 pp. FR 1428661 19660218 Patent language unavailable. Priority: IT 19640225. CAN 65:57652 AN 1966:457652 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 501)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1428661		19660218	FR 1965-5930	19650217

Priority Application

IT 19640225

Abstract

A new class of amorphous unsatd. copolymers is prepd. by the use of catalysts acting by a coordinated anionic mechanism. The catalysts are prepd. from V compds. and organometallic compds. or the hydrides of Al, Be, or LiAl. The monomers are chosen from α -alkenyl derivs. of norbornene in which the double bond of the alkenyl group is of the vinylidene type and are copolymerized with C₂H₄ and one or more aliphatic α -olefins. Thus, to a suitable reactor are added 200 c.c. heptane and 1 c.c. 2-methyl-5-norbornene at -20°. A mixt. of 1 mole C₂H₄ and 2 moles propylene is fed in at a rate of 300 l./hr. The catalyst is prepd. in a 100 cc. flask, at -20° under N by reacting 1 millimole VOCl₃ with 5 millimoles Et₂AlCl in 30 cc. anhyd. heptane. The catalyst is fed into the reactor under N pressure. After 5 min. the reaction is stopped by the addn. of 20 cc. MeOH contg. 0.1 g. phenyl- β -naphthylamine. After washing and drying, 10.5 g. of a solid product is obtained which is amorphous by x-ray examn. and is similar to a nonvulcanized elastomer. On a lab. roll mill, 100 parts terpolymer is mixed with 1 part phenyl- β -naphthylamine, 2 parts S, 5 parts O, 50 parts C black, 1 part tetramethylthiuram disulfide and 0.5 part mercaptobenzothiazole. The mixt. is vulcanized in a press 60 min. at 150°. A vulcanized sheet is obtained which has a tensile strength of 153 kg./cm.², ultimate elongation of 340% and a modulus at 300% elongation of 136 kg./cm.²

Bibliographic Information

Unsaturated hydrocarbon homopolymers. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1966), 10 pp. FR 1425601 19660121 Patent language unavailable. Priority: IT 19640117. CAN 65:57228 AN 1966:457228 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 494)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1425601		19660121	FR	
GB 1035282			GB	

Priority Application

IT 19640117

Abstract

Linear, head-to-tail, high mol. wt. polymers are prepd. which are useful as elastomers, rubbers, foamed materials, thermosetting resins and plastics. Thus, 10 ml. of chromatographically pure cycloheptene is placed in a flask equipped with a stirrer under an atm. of dry N and cooled to -30° and there is added, with stirring 2 millimoles WCl_6 , followed by 10 millimoles $AlEt_2Cl$. The molar ratio of monomer/W is 42:1, and the molar ratio of Al/W is 5:1. The polymer begins to form very rapidly, as shown by an increase in the viscosity of the mixt. After 3 hrs. the flask is allowed to come up to ambient temp. and is kept there for an addnl. 17 hrs., when the mixt. has the consistency of a gel. The polymerization is stopped by the addn. of 5 ml. BuOH contg. 20 mg. phenyl- β -naphthylamine. The contents of the flask are poured into 10 ml. MeOH contg. 5 ml. 38% HCl. The pptd. polymer is dried in a N atm. and is redissolved in 20 ml. MeOH. The soln. is filtered and poured into 50 ml. MeOH contg. 2 ml. 38% HCl. The supernatant liquid is decanted and the polymer suspended in fresh MeOH. The suspension is filtered and the polymer washed with MeOH contg. 0.1% by wt. of phenyl- β -naphthylamine and dried in vacuo at ambient temp. to give 0.7 g. (9% conversion) of a fibrous rubbery but non-tacky polymer with an intrinsic viscosity in PhMe at 30° of 0.8. The ir spectrum indicates the presence of 95% trans unsatn. and also shows a regularity of structure indicative of crystn. A fiber sample which has been oriented and annealed shows an identity period along the axis of the fiber of 17.0 ± 0.3 A.

Bibliographic Information

Polymerization of aldehydes with catalysts containing metal-nitrogen bonds. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo. (Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1966), 3 pp. US 3252937 19660524 Patent language unavailable. Priority: IT 19600219. CAN 65:48197 AN 1966:448197 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 280)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3252937		19660524	US 1961-89378	19610215

Priority Application

IT 19600219

Abstract

Aldehydes of very high mol. wt. and thermal stability can be polymerized at -60 to -80° in the presence of catalysts having the general formula $Mep_1Me_{11}[N(R_1R_2)]_mX_n[OR_1R_2]_q$, in which R_1 and R_2 are the same or different alkyl, cycloalkyl, aryl, alkylaryl groups sep. bonded or forming a heterocyclic nucleus with an N atom; R_1 and R_2 are alkyl, aryl or alkylarene groups; Me_1 is an alkali metal, preferably Li; Me_{11} is a Group I, II, or III metal, preferably Be, Mg, or Al, or may be Li if p is 0; X is H or a halogen; p is 0 or a whole no.; m is a whole no.; n is 0 or a whole no.; $m + n$ is the sum of the valences of Me_1 and Me_{11} ; and q is 0 or 1. For example, 10 cc. freshly rectified n -PrCHO is poured, while in a N atm., into a test tube. The test tube is cooled to -80° and 0.005 g. $Al(NPh_2)_3$ in 1 cc. C_6H_6 is added. A gelatinous ppt. is formed; in a few min., the mass becomes solid. After 1 hr., 10 cc. BuOH is added under N, the mixt. is agitated, and 20 cc. MeOH is added. The white solid thus obtained is filtered, washed with MeOH, and dried at 40° under reduced pressure. The 7.2 g. of polymer (88%

conversion) is partially cryst. Of the polymer, 9.2% is extractable with boiling acetone; 23.6% is extractable with boiling diisopropyl. The extrn. residue consists of a highly cryst. isotactic polymer.

Bibliographic Information

Olefin copolymers. Natta, G.; Valvassori, A.; Sartori, G. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 24 pp. IT 686040 19650315 Patent language unavailable. Application: IT 19620404. CAN 65:48193 AN 1966:448193 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 425)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 686040		19650315	IT	19620404

Abstract

Linear amorphous vulcanizable copolymers were prepd. from C₂H₄ or higher α -olefins with dienes or polyenes contg. an atom different from C in the mol., with coordination catalysts. Thus, 350 cc. anhyd. n-heptane and 20 cc. Me₂Si(CH:CH₂)₂ was introduced into a reactor under N, a gaseous mixt. of 2:1 C₃H₆-C₂H₄ circulated at 200 l./hr., and a preformed catalyst consisting of the product of 30 cc. anhyd. n-heptane, 1 millimole TiCl₄, and 5 millimoles Et₂AlCl siphoned into the reactor to give an C₂H₄-MeCH:CH₂-Me₂Si(CH:CH₂)₂ terpolymer, which was vulcanized.

Bibliographic Information

Polymerizing unsaturated hydrocarbons with catalysts based on beryllium alkyls. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1966), 4 pp. US 3259613 19660705 Patent language unavailable. Priority: IT 19570716. CAN 65:48168 AN 1966:448168 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 175 + u 176/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3259613		19660705	US 1961-127851	19610731

Priority Application

IT	19570716
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Abstract

Be alkyl catalysts that contain protective agents against O and H₂O and are useful for prepg. isotactic polymers of propylene and 1-butene are prepd. These catalysts are composed of 3 compds.: R₂Be or RBeX (I), where R is a C₂-4 alkyl group and X is a halogen; a complex (II) of R'₃Al or R''₂AlX with an ether or org. base, where R' and R'' are alkyl groups and X is a halogen atom; and MCl_x (III), where M is Ti, V, Zr, or Cr, and x is the valence of M. The I:II:III mole ratio varies from 0.05:0.25:1 to 0.05:5.0:1.0. Thus, 1.8 g. TiCl₃, suspended in a C₇H₁₆ soln. contg. 0.9 g. Et₃AlOEt₂, and 0.07 g. 85% pure Et₂Be in 200 cc. anhyd. C₇H₁₆ were agitated at 75° for 5 min. and treated with propylene to bring the pressure to 3.4 atm. After 28 h., the mixt. was treated with 100 mL MeOH to yield 153 g. of a violet polymer (IV) in a yield of 2550 g. /g. Et₂Be. Fractionation of I by solvent extrn. with Me₂CO, Et₂O, and C₇H₁₆ left 90.2% cryst. isotactic residue with an intrinsic viscosity of 2.6.

Bibliographic Information

Olefin-acetylene terpolymers. Natta, Giulio; Mazzanti, Giorgio; Boschi, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1966), 7 pp. US 3256235 19660614 Patent language

unavailable. Priority: IT 19560627. CAN 65:39618 AN 1966:439618 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 114)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3256235		19660614	US 1957-668291	19570627

Priority Application

IT	19560627
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Abstract

New, substantially linear, high-mol.-wt. terpolymers of a 2-8 acetylenic hydrocarbon with C₂H₄ and ≥ 1 C₃-16 α -olefin are described. The new products, of mol. wt. 1000-100,000, are substantially free of homopolymers. They can be vulcanized by conventional methods. The resulting products are rubbers with low unsatn. and with an impact resilience higher than that of butyl rubber. Thus, a mixt. (l) of C₂H₄ 19, C₃H₆ 76.5, and C₂H₂ 4.5% is added to 0.03 mole trihexylaluminum in 250 ml. n-heptane under N at 5 atm. and 25° until the soln. is satd. Then, 0.01 mole VOCl₃ in 50 ml. n-heptane is added. I is added continuously for 2 hrs. at 60 l./hr. The product, a sirupy soln., is purified by treatment with aq. HCl. The product is then coagulated, filtered, and dried under vacuum. A black-violet solid (21 g.), which has elastic properties when subjected to rapid stresses, is obtained. The CCl₄ ext., 81% of the total product with an intrinsic viscosity of 1.4, is vulcanized by mixing with S 2, ZnO 5, and Vulcafor MBT 1.5%, and heating to 150° in a press for 60 min. This product has an elongation at break of 400% and an ultimate strength of 0.45 kg./mm.²

Bibliographic Information

Formaldehyde copolymers with alkyl vinyl ethers. "Montecatini" Societa Generale per l'Industria Mineraria e Chimica. Natta, Giulio; Pregaglia, Gianfranco; Mazzanti, Giorgio; Binaghi, Mario. (1964), 3 pp. IT 678555 19641211 Patent language unavailable. Application: IT 19620808. Priority: IT 19620808. CAN 65:12729 AN 1966:412729 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 442)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 678555		19641211	IT	19620808

Priority Application

IT	19620808
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Abstract

Random copolymers contg. CH₂O and CH₂CH(OR) units, where R = C₁-8 alkyl, are more stable than HCHO homopolymer. The copolymers are prepd. by polymerizing trioxane with 0.1-30 mole % CH₂:CHOR at 0-100° in anhyd. solvent using 0.001-1 mole % standard trioxane polymerization catalysts. The copolymer compn. ranges from 6:1 to 1000:1 CH₂O/CH₂CH(OR) mole ratio; the wt. loss is $\leq 0.3\%$ /min. at 225 \pm 5°. For example, 120 cc. PhNO₂ and 0.12 cc. BF₃-Et₂O were added to 25 g. trioxane at 20-25°. The mixt. became turbid after 50 sec., whereupon 1.5 cc. iso-BuOCH:CH₂ dissolved in 15 cc. PhNO₂, was added. After 6 hrs., the polymer was pptd. with MeOH, washed with hot 5% aq. Na₂CO₃, hot H₂O, and Et₂O, and dried overnight at 50°; yield: 6 g. Polymer wt. loss at 225 \pm 5° is 0.11%/min.

Bibliographic Information

Diolefin polymerization catalysts. Natta, Giulio; Carbonaro, Antonio; Bonfardeci, Augusto; Porri, Lido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 4 pp. IT 679828 19650105

Patent language unavailable. Application: IT 19621212. Priority: IT 19621212. CAN 64:94433 AN 1966:94433 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) , (U 434)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 679828		19650105	IT	19621212

Priority Application

IT	19621212
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Abstract

Comps. contg. (a) a $Vn+$ salt ($n > 2$, which is sol. in arom. solvents, (b) $AlCl_3$, or $AlBr_3$, (c) thiophene, and (d) an arom. solvent, (b): (a) mole ratio 5-50:1, (c): (b) ratio 1:3:1, are prepd, and can be used at -30° to $+30^\circ$. The catalysts can be used to prep. polybutadiene high in the 1,4-trans form. Thus, a mixt. of 60 mL C_6H_6 , 0.2 mL thiophene, 15 mL. piperylene (68% trans-pentadiene + 75% cis-pentadiene + 5% cyclopenta- diene), 0.010 g. V triacetylacetonate, and a soln. of 0.3 g. $AlBr_3$ in 5 mL. C_6H_6 , is kept 50 min. at 0° , treated with MeOH, and filtered to give 7.5 g. polymer, intrinsic viscosity (PhMe, 30°) 1.82. A mixt. of polypentadiene 100, 2-C₁₀H₇NHPh 1, lauric acid 2, ZnO 5, cyclohexylbenzothiazylsulfonamide 1, and morpholine disulfide 1 part is vulcanized for 40 min. at 150° to give a strength of 25 kg./cm.², an elongation at break of 1100%, and a modulus (300°) of 6 kg./cm.²

Bibliographic Information

Oxidation of olefinic unsaturated copolymers to α - ω dicarboxylic compounds. Natta, Giulio; Pasquon, Italo; Sartori, Guido; Valvassori, Alberto; Zambelli, Adolfo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 5 pp. IT 678556 19641211 Patent language unavailable. Application: IT 19620809. Priority: IT 19620809. CAN 64:68848 AN 1966:68848 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) , (U 441)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 678556		19641211	IT	19620809

Priority Application

IT	19620809
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Abstract

By proper control of the length and temp. of the oxidn. process, the double bonds present in the main chain of olefinic copolymers can be oxidized with the formation of CO groups. The temp. must be kept between -50° and 10° ; the time of the reaction must be controlled in order to conduct only a partial oxidn. of the double bonds. In this way, reactions leading to cross-linked structures or to the formation of hydroperoxides can be avoided. As oxidizing agents, mixts. of O_2 and O_3 or O_2 generating compds. are used and the reaction can even be conducted in 2 stages: e.g., a 1st oxidn. with O_3 is followed by a 2nd oxidn. with H_2O_2 . For example, a $CHCl_3$ soln. of 2 g. of an Et₂O ext. of an C₂H₄-propylene-butadiene terpolymer is oxidized at 0° for 90 sec. by a mixt. of O_2 and O_3 ; the flow rate of the gaseous mixt. is 30 l./hr. Then, the reaction mixt. is dild. with $CHCl_3$ and 10 ml. of 12-vol. H_2O_2 is added; after refluxing under stirring for 6 hrs., the soln. is poured in MeOH and Me₂CO. The ppt., after vacuum drying, weighs 1.8 g. The mol. wt. of the new compd. is approx. 103. The presence of the CO groups and disappearance of double bonds is confirmed by ir spectra.

Bibliographic Information

Poly(vinyl chloride)-based polymers. Natta, Giulio; Beati, Enrico; Severini, Febo; Toffano, Silvio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 19 pp. BE 649328 19641216 Patent language unavailable. Priority: IT 19630617. CAN 64:44835 AN 1966:44835 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 4 60)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 649328		19641216	BE	
FR 1401601			FR	

Priority Application

IT	19630617
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Abstract

Vinyl chloride (I) is polymerized by grafting on 5-25% cross-linked polymers or copolymers of α -olefins, their copolymers with C₂H₄, or terpolymers with a diene hydrocarbon. The polymerization is carried out at 50-150° in emulsion or in soln. with Bz₂O₂, tert-Bu₂O₂, K₂S₂O₈, dicumyl peroxide, or azodiisobutyronitrile. Thus, 350 cc. I was added to 30 g. of an ethylene-propylene copolymer (intrinsic viscosity 2.12 at 30° in PhMe) and 200 g. boiled H₂O contg. 4 g. poly(vinyl chloride) (III) in an autoclave under N. After 18 hrs. to allow partial soln. of the polymer, the mixt. was stirred at 70° for 2 hrs., 600 cc. H₂O and 1.2 g. II were injected, and stirring was continued for 14 hrs. at 70°. Cooling, washing, and drying gave 250 g. of a product contg. 12% copolymer. Extn. with C₇H₁₆ showed that 37.5% of the original copolymer had not been grafted. Calendering at 150-60° with addn. of 1% Bu₂Zn laurate and 3% Pb stearate produced a sheet that had an Izod impact strength of 12.4 kg.-cm./cm. notch at 0°, did not break in this test at 23° and had a Rockwell hardness of R 100, L 49. After 17 hrs. at 70°, a mixt. of 10 g. emulsified ethylenepropylene-cyclooctadiene terpolymer, 400 cc. H₂O, 120 g. I, and 0.5 g. II gave 60 g. graft copolymer that was mixed with 25 g. III to give 11.8% terpolymer. The stabilized, calendered sheet from this mixt. gave an Izod test of 11 at 0°, and 19.5 at 23°. These strong products are esp. useful as food wrappers in tropical climates.

Bibliographic Information

Crystalline isocyanate polymers. Natta, Giulio; Pietro, Joseph Di; Pregaglia, Gianfranco. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 6 pp. IT 678634 19641212 Patent language unavailable. Application: IT 19620622. CAN 64:44361 AN 1966:44361 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 4 31)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 678634		19641212	IT	19620622

Abstract

Compsds. of the general formula RNCO, where R is a C₁₋₇ alkyl group or a Ph group, in an inert solvent are contacted at between -78° and -30° with a compd. of the general formula MX_nR_m (I), where M is a Group I or II metal, X is a halogen, and R is an alkoxy, aryl, or C₁₋₇ alkyl group, I:RNCO molar ratio 1:100-2:100, to give high-mol.-wt. products which can be used in the prepn. of fibers. Thus, a mixt. of 50 ml. PhMe and 10 ml. BuNCO is cooled to -78°, EtLi (1 mole/100 moles BuNCO) is added, the mixt. is kept 24 hrs. at -78°, and 500 ml. MeOH is added to give a polymer, 43% conversion, $[\eta]$ (C₆H₆, 30°) 11.6, 20.8 wt. % is extd. by Me₂CO, 5.7 wt. % is extd. by ether, 3.2 wt. % is extd. by pentane, 22.0 wt. % is extd. by n-heptane, and 48.3 wt. % is extrn. residue.

Bibliographic Information

Poly- α -olefin compositions having improved dye affinity. Giustiniani, Piero; Natta, Giulio; Mazzanti, Giorgio; Crespi, Giovanni. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 3 pp. US 3153680 19641020 Patent written in English. Priority: IT 19590803. CAN 64:11997 AN 1966:11997 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 259/I)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3153680		19641020	US 1960-46344	19600801

Priority Application

IT	19590803
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Abstract

The compn. consists of (1) a linear crystallizable polypropylene, poly(4-methyl-1-pentene), or polystyrene, and (2) a linear poly(tert-Bu acrylate), poly(iso-Pr acrylate), poly(tert-Bu methacrylate), poly(iso-Pr methacrylate), or a polymer of R1OCH:CHR2, where R1 and R2 are Me or iso-Bu. Thus, a polymeric compn. contg. 10 wt. % isotactic poly(iso-Pr acrylate) and 90 wt. % polypropylene (90% isotactic) was spun at 220° under a pressure of 10-15 kg./cm.2 The resulting fiber was dyeable with dispersed acetate dyes, e.g., Cibacet Scarlet BR (C.I. Disperse Red 18) and Setile Direct Violet B (C.I. 62030). When the fiber was saponif. for several hrs. with boiling 20% alc. KOH, it was found to be dyeable with basic dyes, e.g., basic Fuchsin (C.I. 42510B) and Astrazon Blue G (C.I. 42025).

Bibliographic Information

Aqueous emulsions of hydrocarbon terpolymers. Natta, Giulio; Beati, Enrico; Severini, Febo; Toffano, Silvio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 4 pp. FR 1398305 19650507 Patent language unavailable. Priority: IT 19630612. CAN 63:99390 AN 1965:499390 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 476)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1398305		19650507	FR 1964-977541	19640609
BE 649132			BE	
GB 1031209			GB	

Priority Application

IT	19630612
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Abstract

Terpolymers of C2H4, propylene, and cyclooctadiene or dieyclopentadiene, manufd. in anhyd. media by Friedel-Craft or anionic coordinate catalysis, are converted to exceptionally heat-stable aq. emulsions with high solids content. The terpolymers are made into a paste with PhMe or C7H16 and 2-20% of a mixt. of nonionic and anionic surfactants is added while mech. homogenizing the paste. H2O is then added and the homogenization continued for 10 min. PhMe is distd, as the azeotrope at atm. or reduced pressure and the emulsion concd. by distn. to 32.5-44.5% solids. A low percentage of the polymer coagulates and is filtered off (0-5 g. from 75 g. of polymer).

Bibliographic Information

Isotactic polymers of α -olefins. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 17 pp. US 3197452 19650727 Patent language unavailable. Application: US 19580807. CAN 63:89449 AN 1965:489449 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 73 + u 73/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3197452		19650727	US 1958-753625	19580807

Abstract

The ratio of isotactic to atactic polymer in polyolefins (I) is detd. by the phys. and chem. properties of a polymerization catalyst formed by the reaction of a Group IVB-VIB heavy metal compd. (II) with a Group II or III metal alkyl (III). For max. crystallinity in I the metal atom of II should have a valence below the theoretical max. Amorphous I is favored by an amorphous II-III catalyst that is easily dispersed in the reaction medium; isotactic I is favored by a catalyst with cryst. character. Catalyst particles $>5-15 \mu$ give predom inantly cryst. I; those of smaller size yield amorphous I. Thus, a glass vial contg. 7.2 g. $TiCl_2$, a soln. of 11.4 g. Et_3Al in 500 ml. n-heptane and 2 steel balls was heated under N to 82° , 140 g. propylene was added and the mixt. stirred, for 10 hrs. at $80-5^\circ$, MeOH was added to give 115 g. (82%) polypropylene (IV). IV was extd. with hot Me_2CO , hot Et_2O , and hot n-heptane to sep. cryst. from amorphous IV. IV was at least 80% cryst. 1-Butene was also polymerized.

Bibliographic Information

Linear unsaturated copolymers of olefins. Natta, Giulio; Dall'asta, Gino; Mazzanti, Giorgio; Pasqon, Italo; Valvassori, Alberto; Zambelli, Adolfo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 7 pp. FR 1392142 19650312 Patent language unavailable. Priority: IT 19630410. CAN 63:73056 AN 1965:473056 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 390/C)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1392142		19650312	FR 1964-970133	19640408
GB 1006153			GB	

Priority Application

IT	19630410
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Abstract

An α -olefin, such as C_2H_4 , propylene, or 1-butene, and a cycloolefin having the formula I in which R is H or a C1-6 alkyl group and the no. of such alkyl groups bonded to the ring is 0-2, are co-polymerized at -80 to 125° in the presence of a Ti halide and an organometallic compd. or Groups IA, II, or III metal hydride to yield a high-mol.-wt., linear copolymer in which part of the copolymerized I has entered the chain by ring-opening, which preserves the double bond. The preferred catalyst is a trialkyl-aluminum-Ti halide combination (mole ratio 1:1-5:1). Thus, a cylindrical reaction vessel is evacuated and charged with N, 10 g. cyclopentene (II), and a freshly prepd. mixt. of 5.0 millimoles $(C_6H_{13})_3Al$ and a soln. of 3.6 millimoles $TiCl_4$ in 37 cc. dry heptane. The vessel is agitated in a bath at -30° and radio-active C_2H_4 is introduced so that its partial pressure is 50 mm. Hg, while the combined partial pressures of the N, solvent, and II is 750 mm. Hg. The reaction is run for 7 hrs. The mixt. is then poured into MeOH contg. HCl to ppt. the copolymer, which is filtered, washed with MeOH, and dried under reduced pressure at 100° . The product is 1.65 g. of a granular solid having an intrinsic viscosity of 3.5 (in Tetralin at 135°). The concn. of C_2H_4 in the copolymer (by radiochem. analysis) is 62.8% (corresponding to

80.2 mole %). As detd. by ir examn., polyethylene-type crystallinity is present along with trans-double bonds and ring structures giving evidence that II has reacted both by double bond opening and ring opening. The title products can be vulcanized in the same manner as natural rubber or butyl rubber to give elastomers having excellent mech. properties.

Bibliographic Information

Copolymerization of butadiene. Natta, Giulio; Porri, Lido; Carbonaro, Antonio; Pasquon, Italo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1965), 6 pp. DE 1190192 19650401 Patent language unavailable. Priority: IT 19610120. CAN 63:24948 AN 1965:424948 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4 3 6 3 + 3 6 3 / A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1190192		19650401	DE 1962-M51491	19620118

Priority Application

IT	19610120
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Abstract

Copolymerization of butadiene and diolefins to vulcanizable compds. in the presence of Al and V catalysts can be carried out in soln. if V or Al compds. sol. in org. hydrocarbons are used. For example, 1,3-butadiene 25, 1,3-pentadiene (98% trans) 5.2, Et₂AlCl 0.5, and V triacetylacetonate 0.02 are dissolved in C₆H₆ 150 parts. After 5 hrs. at 0°, the polymer is coagulated with MeOH. An amorphous polymer is obtained in a yield of 20%. The polymer can be vulcanized by morpholine sulfide in the presence of the usual accelerators, antioxidants, etc.

Bibliographic Information

Improved polypropylene fibers. Natta, Giulio; Longi, Paolo; Pellino, Ennio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 3 pp. FR 1381772 19641211 Patent language unavailable. Priority: IT 19630205. CAN 62:91622 AN 1965:91622 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4 4 5 5)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1381772		19641211	FR	
GB 1031852			GB	
NL 302845			NL	

Priority Application

IT	19630205
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Abstract

Mixts. of polypropylene (I) and 5-20 wt. % poly(aminoalkyl methacrylate) are drawn to give fibers with good dyeing properties. Thus, a mixt. of 90 parts I and 10 parts poly(diisopropylaminoethyl methacrylate) is extruded at .apprx.200° at 5 kg./cm.² to give fibers, the fibers are placed in a bath at 1: 100, 1 wt. % (of fibers) H₂SO₄ is added, 5 wt. % (of fibers) dye, such as C.I. Acid Red 115, C.I. Acid Yellow 11, C.I. Acid Blue 45, or Alizarin Blue BV, is added, and the bath is heated 1 hr. at 90-5° to give colors with good wash fastness.

Bibliographic Information

Copolymers of olefins. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio; Pasquon, Italo; Valvassori, Alberto; Zambelli, Adolfo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 6 pp. FR 1357379 19640403 Patent language unavailable. Priority: IT 19630523. CAN 62:67282 AN 1965:67282 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) , (U 390/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1357379		19640403	FR 1963-935316	19630518

Priority Application

IT	19630523
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Abstract

The amorphous copolymers are prepd. from C₂H₄ (I), a C₄-8 cycloolefin having a C₁-8 alkyl substituent, and olefins CH₂:CHR where R is a C₁-4 alkyl group, such as propylene (II). Polymerization is carried out at -50° to 50° with catalysts prepd. from a V compd., esp. VCl₄ or V triacetylacetonate, and an org. compd. of a metal from Groups Ia, II, or IIIa of the periodic table, esp. a dialkyl Al halide. Thus, 50 cc. cyclopentene (III) labeled with ¹⁴C and 50 cc. n-heptane (IV) were mixed at -30° with a 1:2 molar mixt. of I and II at a rate of 100 l./hr. under N. The catalyst was prepd. under N at -30° by mixing a soln. of 9 mmoles (n-C₆H₁₃)₃Al in 20 cc. IV with a soln. of 3.6 mmoles VCl₄ in 20 cc. IV. The reaction was stopped 30 min. after adding the catalyst by addn. of 20 cc. MeOH. After washing with dil. aq. HCl, the product was completely coagulated by a mixt. of MeOH and Me₂CO. The rubberlike amorphous product, 4.5 g., contained 12.5 mole % III and about the same mole % of I and II. It was sol. in IV at the b.p. and had an intrinsic viscosity of 1.6 in tetrahydronaphthalene at 135°. Under similar conditions, at a rate of 150 l./hr. for the addn. of I and II, a vulcanizable terpolymer was sepd. after 8 min.

Bibliographic Information

Vulcanizable diolefin-alkene copolymers. Natta, G.; Valvassori, A.; Sartori, G.; Giannini, U. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 30 pp. IT 664769 19640612 Patent language unavailable. Application: IT 19611205. CAN 62:67280 AN 1965:67280 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 405)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 664769		19640612	IT	19611205

Abstract

Conjugated dienes are copolymd. at 80-125° with mixts. of C₂H₄ and a higher α -olefin in the presence of the reaction product of a hydrocarbon-sol. V compd. and an organoaluminum compd. to give linear, homogeneous products; the products are vulcanized to give elastomers. Thus, a 4:1 M C₃H₆-C₂H₄ mixt. (I) is added in an amt. of 100 l./h. at -20° to 350 mL. n-C₇H₁₆ (II). Butadiene (III) is simultaneously introduced at 100 l./h. A soln. of 0.004 mol VCl₄ and 0.0010 mol (Me₂CHCH₂)₂AlCH₂CHMeCH₂CH₂Al(CH₂CHMe)₂ in 30 mL. II is added. Introduction of I and III is continued at 100 and 10 l./h., resp., and 20 mL. MeOH contg. 0.4 g. 2-C₁₀H₇NHPh is added to give 10 g. of amorphous, white terpolymer. The terpolymer is vulcanized for 30 min. at 150° in a press to give a sheet of rupture strength 58 kg./cm.², elongation at rupture 900%, and modulus (300%) 10 kg./cm.².

Bibliographic Information

Catalytic polymerization of diolefins. Natta, Giulio; Carbonaro, Antonio; Porri, Lido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 5 pp. FR 1376351 19641023 Patent language

unavailable. Priority: IT 19621212. CAN 62:66945 AN 1965:66945 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 437)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1376351		19641023	FR 1963-956285	19631206
GB 1033530			GB	
IT 679829			IT	

Priority Application

IT 19621212

Abstract

Diolefins are catalytically polymerized to 1,4-cis polymers using a catalyst prepd. at -30 to 30° by reaction of a Co salt sol. in aromatic hydrocarbons, an Al halide (Al: Co mole ratio <30: 1), and a Lewis base concn. of ≥0.5 mole/mole of Al halide in a solvent consisting of an aromatic hydrocarbon or a mixt. of aromatic and aliphatic hydrocarbons contg. ≥40-50% aromatic hydrocarbons. Thus, 0.0011 g. Co trisacetylacetonate, 0.2 g. anhyd. distd. AlBr₃, and 0.04 cc. thiophene were added to 30 cc. C₆H₆ at ambient temp. 5.0 g. butadiene was added at 0° and, after polymerization for 2 hrs. at 0° MeOH was added, giving 2.1 g. of a polymer. The polybutadiene consisted of the following structural units: 1,4-cis, 97; 1,2,2; and 1,4-trans, 1%. Similarly, butadiene was polymerized by using catalysts contg. AlCl₃, Co bis(acetylacetonate), pyrrole, Ph₃N, Et₃P, or Co(NO)₂Cl as the Lewis base in toluene or heptane. Similarly, isoprene formed a polymer contg. 75% 1,4-cis units and 1,3-pentadiene a polymer contg. 65% 1,4-cis units.

Bibliographic Information

Unsaturated vulcanizable copolymers. Natta, Giulio; Mazzanti, Giorgio; Pregaglia, Gianfranco; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 9 pp. FR 1377626 19641106 Patent language unavailable. Priority: IT 19621017. CAN 62:59818 AN 1965:59818 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 443)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1377626		19641106	FR 1963-950646	19631015
GB 1020064			GB	
IT 676810			IT	

Priority Application

IT 19621017

Abstract

C₂H₄ or a C₃-8 1-alkene is copolymerized with a polycyclic hydrocarbon contg. ≥ 1 cycloheptatriene ring at -80° to 125° in the presence of a mixt. of an organoaluminum compd. and a V halide, and the copolymers obtained are vulcanized to give elastomeric materials. Thus, a 2:1 C₃H₆-C₂H₄ mixt. (I) is added at 200 l./hr. at -20° to a mixt. of 200 ml. n-heptane (II) and 25 ml. 1,3,5-cycloheptatriene; a catalyst, which is prepd. from 1 millimole VCl₄, 5 millimoles Et₂AlCl, and 30 ml. II, is added, I is introduced at 400 l./hr., and 20 ml. MeOH contg. 0.1 g. 2-C₁₀H₇NHPh is added after 6 min. to give a product with a C₂H₄:C₃H₆ molar ratio of 1:1; this product is vulcanized 60 min. at 150° to give a film, rupture 23.4 kg./cm.², elongation at rupture 320%, modulus (300% elongation) 21.6 kg./cm.², permanent elongation (after rupture) 4%.

Bibliographic Information

Vulcanizable olefin copolymers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazareno. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 28 pp. BE 637939 19640116 Patent language unavailable. Priority: IT 19620928. CAN 62:52507 AN 1965:52507 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 438)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 637939		19640116	BE	
GB 1021755			GB	
GB 1023709			GB	
IT 675794			IT	
NL 298438			NL	

Priority Application

IT 19620928

Abstract

1-Alkenes are copolymerized with ≥ 2 of the following: (1) an alkenylcycloalkene, (2) an ω -alkenylpolycycloalkene, (3) a fused-ring polycyclic polyene, and (4) a diolefin contg. an endomethylene bridge, in the presence of a mixt. of an organoaluminum compd. and a V compd. to give products of mol. wt. $>20,000$; ether, thioether, tertiary amine, and triorganophosphine complexing agents can be used with catalysts prepd. from V acetylacetonate and V alkoxides. Thus, 1 Millimole VCl_4 is treated with 5 millimoles Et_2AlCl at -20° in 30 ml. n-heptane (I) to give a catalyst. A reactor is charged at -20° with 700 ml. I and 1.5 ml. cyclopentadiene (II)-2-vinylbicyclo[2.2.1]hept-5-ene (II) addn. product fraction (II-I vol. ratio 1:2.7), a $C_3H_6-C_2H_4$ mixt. (mole ratio 2:1) (IV) is introduced at 200 l./hr., the catalyst is added, the reactor is evacuated, IV is introduced at 400 l./hr., and 20 ml. MeOH contg. 0.1 g. 2-C₁₀H₇NHPh is added after 6 min. to give 38 g. l-sol. product. A compn. contg. 100 parts prepd. product is vulcanized 60 min. at 150° in a press to give a film of tensile strength 25.5 kg./cm.², elongation at rupture 520%, modulus (300% elongation) 14.5 kg./cm.², permanent elongation (at rupture) 16%.

Bibliographic Information

Linear olefin copolymers. Natta, Giulio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazareno. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1964), 11 pp. FR 1370902 19640828 Patent language unavailable. Priority: IT 19620809. CAN 62:52501 AN 1965:52501 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 423)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1370902		19640828	FR 1963-943750	19630805
GB 1018778			GB	
IT 678557			IT	

Priority Application

IT 19620809

Abstract

Olefins of the general formula $RCH:CH_2$, where R is H or a C₁-6 alkyl group, are polymerized with a diene or an ω -alkenyl-polycycloalkene, such as 2-vinylbicyclo[2.2.1]hept-5-ene (I), at between -50° and -10° in the presence of a mixt. of (1) an alkylberyllium or alkylaluminum compd., such as $MeBeCl$ or Et_2AlCl , and (2) a hydrocarbon-sol. V compd., such as $VOCl_3$ or V triacetylacetonate (II), to give unsatd., vulcanizable copolymers. The

products are vulcanized to give elastomers which have good mech. properties and can be used in the prepn. of various articles. Thus, a reactor contg. N is charged with 200 ml. n-heptane and 1 ml. I, a C₃H₆-C₂H₄ mixt. (2:1 molar ratio) is introduced at 200 l./hr., a catalyst (-20°, 1.4 millimoles II and 7 millimoles Et₂AlCl in 30 ml. PhMe) is added, the C₃H₆-C₂H₄ mixt. is introduced at 400 l./hr., and 20 ml. MeOH contg. 0.1 g. 2-C₁₀H₇NHPh is added after 35 min. The mixt. is treated with dil. HCl, treated with H₂O, and coagulated with Me₂CO to give 15.5 g. product, intrinsic viscosity (PhMe, 30°) 2.5. A mixt. of 100 parts product, 1 part 2-C₁₀H₇NHPh, 2 parts S, 5 parts ZnO, 1 part tetramethylthiuram disulfide, and 0.5 part mercaptobenzothiazole is vulcanized for 60 min. at 150° to give a film of tensile strength 30 kg./cm.², elongation at rupture 380%, and modulus (300% elongation) 15.5 kg./cm.².

Bibliographic Information

Ethylene-butadiene copolymers. Natta, Giulio; Zambelli, Aldo; Pasquon, Italo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 6 pp. FR 1361801 19640522 Patent language unavailable. Priority: IT 19620712. CAN 62:37627 AN 1965:37627 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 417)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1361801		19640522	FR 1963-940691	19630708
GB 1010790			GB	
IT 678656			IT	

Priority Application

IT	19620712
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Abstract

A copolymer which differs from conventional C₂H₄-butadiene copolymers is obtained with a catalyst, prepd. by mixing (a) VCl₄, (b) R₃Al, (c) R₂AlCl (in both of which R is C₁-10 alkyl), and (d) a weak Lewis base, such as Et₂O, iso-Pr₂O, iso-Bu₂O, Ph₂O, Ph₂S, Ph₂CO, PhNEt₂, or anisole; the a:b:d ratio is 1:2:2. The catalyst is prepd. at -100 to -50°, and the polymerization is carried out between -50 and -10° in an aliphatic, cycloaliphatic, or aromatic hydrocarbon solvent. X-ray diffraction spectra of the resulting copolymer show max. at angles 2θ = 20.5 and 23.2°, which are absent in conventional copolymers. The crystallinity disappears on heating to 50-60°, but the characteristic max. reappear on cooling; they are probably due to blocks of trans-1,4-polybutadiene units alternating with CH₂CH₂ units. In the ir spectrum, there are lines at 8.27, 9.25 and 11.20 μ which are absent in conventional copolymers, in addn. to weaker lines at 8.10, 9.50 and 12.95 μ which are characteristic for trans-1,4-polybutadiene. The copolymers can be vulcanized with the usual curing ingredients, and the vulcanizates have good mech. properties. In an example, a glass reactor, fitted with a stirrer, was cooled to -78° and 2 millimoles VCl₄, 4 millimoles each of anisole, iso-Bu₃Al and iso-Bu₂AlCl, and 200 ml. toluene and 80 g. butadiene were added. The temp. was raised to -25° and C₂H₄ was introduced. After 1 hr., 27 g. crude polymer was obtained. The catalyst was sepd., and the butadiene homopolymer was extd. with boiling Et₂O to give 24 g. partly cryst. polymer.

Bibliographic Information

Olefin copolymers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido; Turba, Vittorio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 16 pp.; Addn. to Belg. 631,165 (CA 60, 16087d). BE 638491 19640203 Patent language unavailable. Priority: IT 19621011. CAN 62:37626 AN 1965:37626 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 412/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 638491		19640203	BE	

FR AD84657
GB 1023285
NL 299010

FR
GB
NL

Priority Application

IT 19621011

Abstract

α -Olefins are copolymerized with a polyalkenyl-cycloalkane in the presence of a mixt. of (1) a V compd. and (2) a Group I, II, or III metal hydride or a Group I or III metal hydride complex, such as Et_2AlH (I), to give linear, amorphous copolymers. Thus, 1 millimole VCl_4 is treated with 5 millimoles I in 30 ml. anhyd. n-heptane (II) at -20° to give a catalyst. A 2:1 C_3H_6 - C_2H_4 mixt. is added to a mixt. of 200 ml. II and 7 ml. 1,2-divinylcyclobutane, the catalyst is added under N pressure, the mixt. is agitated 15 min., and 20 ml. MeOH contg. 0.1 g. 2- $\text{C}_{10}\text{H}_7\text{NHP}$ is added to give 5 g. product having a C_2H_4 - C_2H_6 molar ratio .aprx.1:1..

Bibliographic Information

Olefin copolymer elastomers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 13 pp.; Addn. to Belg. 623,698 (CA 59, 1821f). BE 638490 19640203 Patent language unavailable. Priority: IT 19621011. CAN 62:37625 AN 1965:37625 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (404/E)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 638490		19640203	BE	

Priority Application

IT 19621011

Abstract

C_2H_4 is copolymerized with α -olefins and monocyclic, nonconjugated polyenes in the presence of mixts. contg. a V compd. and a Group I, II, or III metal hydride or a Group I or III metal hydride complex, such as LiAlH_4 . Thus, 1 mmol VCl_4 is treated with 5 mmol Et_2AlH and 300 mL. n-heptane (I) at -20° under N to give a catalyst, and 20 mL. 1,5-cyclooctadiene in 200 mL. I is treated with a 2:1 M propylene- C_2H_4 mixt. at -20° to give a copolymer. The copolymer is compounded and the mixt. is vulcanized for 31 min. at 150° to give a product of tensile strength 25 kg./cm.², elongation at rupture 460%, and modulus (300%) 10 kg./cm.²

Bibliographic Information

Stereoregular polymers of 1-cyano-1,3-butadiene. Natta, Giulio; Giannini, Umberto; Cassata, Antonio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 4 pp. FR 1369261 19640807 Patent language unavailable. Priority: IT 19620920. CAN 62:37266 AN 1965:37266 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 430)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1369261		19640807	FR 1963-947609	19630916
DE 1186214			DE	
GB 1008604			GB	
IT 675261			IT	
US 3257365		19660621	US 1963-309963	19630919

Priority Application

IT

19620920

Abstract

Both cis- and trans-1-cyano-1,3-butadiene can be polymerized in hydrocarbon media with catalysts having the general formula MR_aX_b (M = an alkali or alk. earth metal, R = alkyl or aryl, a = 1 or 2, b = 0 or 1 (b = 0 when M = alkali metal), and a + b = the valence of M). Alkali metal derivs. are the best catalysts. The reaction is carried out at temps. preferably from -80 to -20°. The monomer:catalyst ratio is from 20:1 to 100:1. Both isomers give polymers of high (>90%) trans-1,4-content, but the cis isomer gives cryst. while the trans isomer amorphous products. By polymerizing mixts. of the isomers, products of varying crystallinity can be obtained. Thus, a mixt. of 15 cc. toluene and 0.86 g. cis-1-cyano-1,3-butadiene is cooled in a N atm. to -78°, and 0.83 millimole BuLi in 5 cc. toluene is added dropwise. After 5 hrs. at -78°, the polymer is pptd. with MeOH. The mixt. is filtered, washed with MeOH, and dried in vacuo to give 0.8 g. white cryst. solid.

Bibliographic Information

Vulcanizable olefin-silane copolymers. Natta, Giulio; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 8 pp. FR 1359995 19640430 Patent language unavailable. Priority: IT 19620420. CAN 62:23162 AN 1965:23162 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) · (U 4 2 5)

Patent Family Information

<u>Patent No.</u>	<u>Kind</u>	<u>Date</u>	<u>Application No.</u>	<u>Date</u>
FR 1359995		19640430	FR 1963-932063	19630419
GB 1001838			GB	

Priority Application

IT

19620420

Abstract

Unsatd. copolymers are produced from a mixt. of 1 mol olefin $RCH:CH_2$ (R = H or a C1-6 alkyl) with ≤ 0.2 mol polyene $SiR_1R_2R_3R_4$ in which the R's may be the same or different C2-8 alkylenes and also R3 and R4 may be H or alkyl, cycloalkyl, or aryl groups. Examples are $SiMe_2(CH:CH_2)_2$, $SiMe_2(CH_2CH:CH_2)_2$ (I), $Si(CH:CH_2)_4$, $Si(CH_2CH:CH_2)_4$, $SiEt_2(CH_2CH:CH_2)_2$, $Si-Ph_2(CH_2CH:CH_2)_2$, $Si(iso-Pr)_2(CH_2CH:CH_2)_2$, and $Si(sec-Bu)_2(CH_2CH:CH_2)_2$. Catalysts consist of: (1) compds. of V and an alkyl Al halide (II) at -10 to -50°; (2) II and V tris(acetylacetonate) (III), trialkoxides, or halogen-alkoxides prepd. at 0-125° in the presence of 0.05-1 mol/mol of II of a complexing agent, e.g. an ether, thioether, tertiary amine, or phosphine contg. ≥ 1 arom. or branched chain alkyl group; (3) 1-2 mol trialkyl Al and 1 mol V or vanadyl halide; or (4) 4-10 mol Et_2AlCl and 1 mol III. In general, the catalysts are formed from V or vanadyl compds. and org. compds. of Al, Be, or Li. The polymn. is carried out without solvent or with C_4H_{10} , C_5H_{12} , n-C7H16, PhMe, xylene, $CHCl_3$, $CHCl:CCl_2$, $CCl_2:CCl_2$, or PhCl. The catalyst is added periodically or continuously to the liq. system contg. 1 mol C_2H_4 per ≤ 4 mol $MeCH:CH_2$ (IV) or per ≤ 20 mol 1-butene. Thus, to 350 cc. n-C7H16 and 20 cc. I at -20° under N in a 750-cc. glass cylinder, a mixt. of 1 mol C_2H_4 with 2 mol $MeCH:CH_2$ was added and circulated at 200 l./h. A mixt. of 1 mmol VCl_4 and 5 mmol Et_2AlCl in 30 cc. n-C7H16 was prepd. at -20° and added by N pressure to the reagents. The gas mixt. circulated at 400 l./h. for 6 min.; then 20 cc. MeOH contg. 0.2 g. Ph β -naphthylamine was added. The polymer soln. was washed repeatedly under N with dil. aq. HCl and coagulated in Me_2CO to yield 11 g. of an elastomer which was sol. in hot IV and had a V:VI ratio of 1:1 as shown by the ir spectrum. The vulcanized product had a tensile strength of 35 kg./cm.2, elongation at rupture 420%, modulus at 300% 14 kg./cm.2, and deformation 8%. For the product vulcanized in a mixt. with 50 parts HAF carbon black, the resp. values were 280, 450, 115, and 10.

Bibliographic Information

High-molecular-weight polycarbonyl compounds. Natta, Giulio; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 16 pp. BE 634062 19631015 Patent language unavailable. Priority: IT 19620626. CAN 61:93280 AN 1964:493280 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 416)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 634062		19631015	BE	
FR 1361077			FR	
GB 993481			GB	
IT 678638			IT	

Priority Application

IT	19620626
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Abstract

Olefin copolymers with double bonds either in the side chains or in cyclic groups in the backbone can be oxidized by O₃ to give polycarbonyl compds. Thus, a soln. of 2 g. of a C₂H₄-diallyl copolymer (contg. 53 mole % C₂H₄ and 70% diallyl with respect to the total amt. polymerized in a 1.2 sequence) in 100 ml. CHCl₃ is cooled to 0° in a flask fitted with a gas inlet. A mixt. of O-O₃ (2 mole % O₃) obtained by passing pure O through an ozonizer is introduced into the soln. at a flow rate of 30 l./hr. The oxidn. is complete after 18 min. when 0.8 millimole O₃ has passed through the soln. The soln. contains 0.55 millimole of hexadiene polymerized in a 1.2 sequence. Infrared spectra reveal the presence of carbonyl groups (band at 5.75 μ). A band at 11 μ indicates that the initial amt. of vinyl groups has markedly decreased. The vulcanization is done by mixing 5 parts by wt. ZnO with 100 parts by wt. of oxidized compd. and heating the mixt. in a press for 20 min. at 150°. The vulcanized product has the following characteristics: resistance to traction 47 kg./cm.², max. stretch 380%, modulus at 300% extension 15 kg./cm.², residual extension at rupture practically zero.

Bibliographic Information

Poly(vinyl alkyl ethers). Natta, Giulio; Mazzanti, Giorgio; Dall'Asta, Gino. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 24 pp. BE 636435 19640221 Patent language unavailable. Priority: IT 19620822. CAN 61:92814 AN 1964:492814 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 444)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 636435		19640221	BE	
FR 1373210			FR	
NL 296754			NL	

Priority Application

IT	19620822
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Abstract

Vinyl alkyl ethers are polymd. in the presence of a compd. of the general formula [MX_nF_m]Y_p, where M is a Group IVb, Vb, VIb, or VIII metal, X is Cl or Br, m + n = valence of M, n is 0 or an integer of up to 1/2 valence of M, m is an integer, Y is an electron donor, such as pyridine, and p is 0 or an integer, to give highly cryst. polymers. Thus, a reactor is flushed with N and charged with a mixt. of 100 parts n-heptane, 15 parts CH₂Cl₂,

0.30 part TiF₃, and 10 parts vinyl iso-Bu ether, the mixt. is heated 24 h. at 60° and cooled. The mixt. is filtered to give 7.9 g. crude polymer, intrinsic viscosity (PhMe, 30°) 0.2, which is fractionated with solvents to give 3.3 parts of a product which is insol. in boiling Me₂CO, 4.6 parts of a product which is sol. in boiling Me₂CO, and 1.2 parts MeCOEt-insol. poly(vinyl iso-Bu ether), intrinsic viscosity (PhMe, 30°) 0.35, m. 140-5°, 42% crystallinity.

Bibliographic Information

Transition metal fluorides and fluoride-halides. Natta, Giulio; Mazzanti, Giorgio; Dall'Asta, Gino. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 14 pp. BE 636434 19640221 Patent language unavailable. Priority: IT 19620822. CAN 61:81915 AN 1964:481915 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 428)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 636434		19640221	BE	
DE 1210766			DE	
FR 1367205			FR	
GB 995186			GB	
IT 678565			IT	
NL 296753			NL	

Priority Application

IT 19620822

Abstract

Transition metal halides are treated with ethylidene fluoride (I) or BF₃ to give compds. of the general formula [MX_nF_m]Y_p, which can be used as polymerization catalysts, where M is Ti, Zr, V, Cr, Mo, W, Fe, Ni, or Co, m + n is the valence of M, X is Cl or Br, n is an integer between 0 and 1/2 or <1/2 (m + n), m is an integer, Y is an electron donor, and p is 0 or an integer. Thus, an autoclave is cooled to -78°, charged with a mixt. of 70 ml. EtCl, 11.0 g. γ-TiCl₃, and 4.7 g. I, closed, heated 15 hrs. at 90°, cooled, and the mixt. evapd. in vacuo to give 8.2 g. violet powder, Ti-Cl-F molar ratio 1:1.1:1.9. Similarly prepd. are the following (atoms and ratio given): V-Cl-F, 1:2:1.9; Ti-F, 1:3; V-F, 3:9; Fe-F, 1:3; Mo-F-Cl, 1:5.1:0.8. Also prepd. are CoF₂-pyridine complex and reaction product from 0.032 mole CrCl₃, 0.044 mole I, and 0.026 mole BF₃.

Bibliographic Information

Alkene-polycyclic polyene copolymers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazareno. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 46pp. BE 636255 19631216 Patent language unavailable. Priority: IT 19620817. CAN 61:77043 AN 1964:477043 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 440)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 636255		19631216	BE	
FR 1371435			FR	
GB 975724			GB	
IT 678563			IT	
NL 296467			NL	

Priority Application

IT 19620817

Abstract

Condensed polycyclic polyenes, such as 4,7,8,9-tetrahydroindene (I) and other bicycloalkadienes, are copolymerized with a C2-8 1-alkene in the presence of a catalyst prepd. from: (1) a Group V metal compd. and (2) a Group I, II, or III organometallic compd. or hydride or a complex hydride of a Group I or III metal. Amorphous, vulcanizable products are obtained. Thus, 2 millimoles VCl₄ is treated with 5 millimoles trihexylaluminum in 30 ml. n-C₇H₁₆ (II) to give a catalyst. The catalyst is introduced into a reactor contg. a mixt. of 120 ml. II and 10 ml. I and it is charged with a 1:8 mole ratio C₂H₄-C₃H₆ mixt. at 200 l./hr., 20 ml. MeOH contg. 0.1 g. 2-C₁₀H₇NHPh is added after 4 min., and the mixt. is filtered to give a C₂H₄-C₃H₆-I copolymer, infrared bands at 61.7, 7.25, and 13.313.8 μ . The amorphous copolymer (100 parts) is mixed with 2-C₁₀H₇NHPh 1, S 2, ZnO 5, tetramethylthiuram disulfide 1, and mercaptobenzothiazole 0.5 part and the mixt. obtained is vulcanized for 60 min. at 150° in a press to give a film of tensile strength 40 kg./cm.², elongation at rupture 670% modulus (300% elongation) 20 kg./cm.², and permanent elongation at rupture 10%.

Bibliographic Information

Vulcanizable ethylene copolymers. "Montecatini" Societa Generale per l'Industria Mineraria e Chimica. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido. (1964), 9 pp. FR 1353179 19640221 Patent language unavailable. Priority: IT 19620302. CAN 61:55461 AN 1964:455461 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) , (U 410)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1353179		19640221	FR 1963-926214	19630227
GB 988311			GB	
IT 665050			IT	

Priority Application

IT	19620302
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Abstract

Amorphous, vulcanizable copolymers are made by copolymerizing C₂H₄, a C₃-8 α -olefin, and an alkenyl cycloalkene. As polymerization catalysts, mixts. of organoaluminum compds. and hydrocarbon-sol. V compds. are used. The vulcanized copolymers are elastomeric. Thus, in a reactor at -20° contg. 350 cc. C₇H₁₆ and 5 cc. 4-vinyl-1-cyclohexene (I), a mixt. of C₂H₄ and propylene (II) in a mole ratio of 2:1 was introduced at 200 l./hr. A catalyst soln. made by reaction between 4 millimoles VCl₄ and 10 millimoles trihexylaluminum (III) in C₇H₁₆ was siphoned into the reactor, and addn. of the mixt. of C₂H₄ and II was continued at 400 l./hr. After 7 min., the reaction was stopped by addn. of MeOH. A copolymer (8.6 g.) contg. 5% I was obtained. The copolymer was cured by heating at 150° in a recipe contg. S, phenyl- β -naphthylamine, tetramethylthiuram disulfide, mercaptobenzothiazole, and ZnO. Other copolymers were made with different monomer proportions. III may be replaced by Et₂AlCl or 2-methyl-1,4-bis(diisobutylaluminio)butene.

Bibliographic Information

Catalyst for stereospecific polymerization of propylene. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964), 4 pp. US 3141872 19640721 Patent language unavailable. Priority: IT 19541203. CAN 61:48297 AN 1964:448297 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 73 + U 73/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3141872		19640721	US 1960-22134	19600414

Priority Application

IT

19541203

Abstract

A catalyst for producing isotactic polypropylene that is 70-95% insol. in hot n-C7H16 is made by mixing solid TiCl3 with AIR'R"X in an inert liquid diluent at $\leq 90^\circ$ so that no Ti is reduced below Ti(III). R' and R" are C2-4 alkyls. AlEt2Cl is claimed. In the examples, TiCl3-Pr3Al, TiCl3-Et3Al, TiCl3Et2Be and TiCl3-BeEtCl were used. For example, 7 g. TiCl3, purified of traces of TiCl4 by repeated washing under N in anhyd. n-C7H16, was introduced into a 2080-ml. autoclave and 11.4 g. Et3Al in 500 cc. n-C7H16 and 310 g. pure propylene were added. The vessel was heated to 80° and agitated for 10 hrs., giving 240 g. crude product, which was solvent fractionated with acetone, Et2O, and n-C7H16 (warm) to give 3.5% amorphous, 3.4% amorphous, and 4.0% 50%-cryst. material, resp., and leaving the remainder as a cryst. residue, softening point 165° and viscosity mol. wt. of >100,000.

Bibliographic Information

Olefin copolymers. Natta, Giulio; Mazzanti, Giorgio; Valuassori, Alberto; Sartori, Guido; Turba, Vittorio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1964). 24 pp. BE 634887 19640113 Patent language unavailable. Priority: IT 19620713. CAN 61:18730 AN 1964:418730 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 436)

Patent Family Information

<u>Patent No.</u>	<u>Kind</u>	<u>Date</u>	<u>Application No.</u>	<u>Date</u>
BE 634887		19640113	BE	
FR 1361836			FR	
GB 1010739			GB	
IT 678665			IT	
NL 294989			NL	

Priority Application

IT

19620713

Abstract

High-mol.-wt. chain copolymers from unsatd. α -olefins RCH:CH2, in which R is a C1-6 alkyl are prepd. by the use of ionic-type catalysts prepd. with a V compd. and an organo-aluminum compd. C2H4, propylene and butylene can be co-polymerized, with or without a conjugated diolefin. LiH, NaBH4, and Bu2AlH, may also be used as catalysts. To prep. a low-mol.-wt. polyolefin, VCl4, VOCl3, or VBr4 can be used as the catalyst. But better results are obtained by using a V halideorganoaluminum mixt., preferably VCl4-Al trioxy. Polymerization may be effected at -10° to -50°. A complementary catalyst RYR', where Y is O or S, and RR' can be a C1-14 alkyl, C6-14 aryl, or a tertiary amine RR'R"N, where the R groups are similar to R in RYR'; or a phosphine PR'R'R may be used as an ionic catalyst in an amt. of 0.5-1.0 per mole of alkylaluminum halide. A V oxyhalide may be used with a trialkyl Al chloride in a ratio 2-4:1. A Et2AlCl-V triacetylacetonate in a ratio 4-10:1 may be the catalyst. The polymerization may be effected in the form of monomers sol. in hydrocarbon solvents, CHCl3, chloroethylene, and polycycloalkene. The copolymers which vary from an amorphous to cryst. form may contain $\geq 75\%$ C2H4. In a terpolymer, the polyene may be 0.1-20 mole %. A preferred copolymer can be prepd. from a 2:1 C3H6-C2H4 mixt. in soln. in heptane and 1,4-bis(2-cyclopentenyl)butane at .apprx.-20°. For example, a 100:20 C3H6-C2H4 gas mixt. is fed at a rate of 200 l./hr. and is polymerized with a 4:20 VCl4-Et2AlCl mixt. at room temp. for about 50 min. to produce a copolymer resembling vulcanized rubber in which the C3H6:C2H4 ratio is 1:1.

Bibliographic Information

Ethylene copolymers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazareno. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 30 pp. BE 631580 19630816 Patent language unavailable. Priority: IT 19620427. CAN 61:12071 AN 1964:412071 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 422)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 631580		19630816	BE	
FR 1362094			FR	
GB 1006193			GB	
IT 675070			IT	

Priority Application

IT	19620427
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Abstract

Amorphous vulcanizable copolymers are made by copolymerizing C₂H₄ with a C₃-8 aliphatic α -olefin, and one or more monomers chosen from cyclic non-conjugated dienes, alkenyl cycloalkenes, and dialkenyl and polyalkenyl cycloalkanes. As polymerization catalysts, there are used mixts. of org. Al compds. and hydrocarbon-sol. V compds. The vulcanized copolymers are elastomeric. Thus, in a reactor at -20° contg. 700 cc. heptane and 5 cc. dimeric butadiene contg. cis,cis-1,5-cyclooctadiene and 4-vinyl-1-cyclohexene in a 4:1 vol. ratio, a mixt. of C₂H₄ and C₃H₆ in a molar ratio of 2:1 was introduced at a rate of 200 l./hr. A catalyst soln. made by reaction between 1 millimole VCl₅ and 5 millimoles Et₂AlCl in heptane was siphoned into the polymerization vessel, and the addn. of the C₂H₄-C₃H₆ mixt. was continued at 400 l./hr. After 15 min., the reaction was stopped by addn. of MeOH to give 38 g. copolymer contg. C₂H₄ and C₃H₆ in a 1:1 ratio. A mixt. of 100 parts copolymer and 50 parts carbon black was vulcanized by heating at 150° with S, tetramethylthiuram disulfide, mercaptobenzothiazole, ZnO, and phenyl- β -naphthyl- amine.

Bibliographic Information

Elastomeric olefinic terpolymer. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazareno. ("Montecatini" Societa Generale per l'industria Mineraria e Chimica). (1963), 15 pp.; Addn. to Belg. 623,698 (CA 59, 1821f). BE 633763 19631218 Patent language unavailable. Priority: IT 19620619. CAN 61:4869 AN 1964:404869 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (404/C)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 633763		19631218	BE	
FR AD83842			FR	
GB 1005615			GB	

Priority Application

IT	19620619
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Abstract

Copolymers from C₂H₄, RCH:CH₂, R being a C₁-6 alkyl group, and a nonconjugated polyene are made in the presence of a catalyst contg. a Ti or a Cr compd. and an organometallic compd. from an element of Group I, II, or III. Thus, into a vessel kept at -20°, 350 ml. anhyd. heptane and 15 ml. radioactive 1,5-cyclooctadiene were introduced and a stream of C₂H₄ and propylene (mol. ratio 4/1) was passed in. The catalyst was prepd. sep. at -20° and under N by reacting 4 millimoles TiCl₄ and 10 millimoles (C₆H₁₃)₃Al in 50 ml. anhyd. heptane. It was then introduced into the vessel under N. The gas stream was adjusted to 400 l./hr. After 20 min., the reaction

was stopped by 20 ml. MeOH contg. 0.1 g. phenyl-2-naphthylamine. The product was purified by dild. HCl, washed by H₂O, and coagulated in (Me)₂CO. The dry copolymer (6.5 g.) was amorphous to x-rays, sol. in boiling heptane, contained 2.7% cyclooctadiene, showed the presence of double bonds and a C₂H₄ to propylene ratio of 1/1.

Bibliographic Information

Copolymers of olefins. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio; Pasquon, Italo; Valvassori, Alberto; Zambelli, Adolfo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 18 pp. BE 632725 19631021 Patent language unavailable. Priority: IT 19620523. CAN 61:4868 AN 1964:404868 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 390/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 632725		19631021	BE	
GB 979329			GB	

Priority Application

IT	19620523
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Abstract

Non-vulcanized and vulcanized elastomers are prepd. by copolymerizing C₂H₄ and CH₂: CHR (R = C₁-4 alkyl) with a C₄-8 cycloolefin, which may be substituted with a C₁-8 alkyl radical. The polymerization is carried out in the presence of a catalyst prepd. from a V compd., such as VC14 or V acetylacetonate, and an organometallic compd. of a metal of Groups Ia, II, or IIIa, such as a dialkylaluminum monohalide, at a temp. of -50° to 50°. Thus, 50 ml. anhyd. heptane and 50 ml. cyclopentene-14C are satd. at -30°, under N, with a mixt. of C₂H₄ and C₃H₆ (2:1). A catalyst prepd. by mixing at -30°, under N, a soln. of 9 millimoles (C₆H₁₃)₃Al in 20 ml. anhyd. heptane with a soln. of 3.6 millimoles VC14 in 20 ml. anhyd. heptane is added immediately after its prepn., and after 30 min. the reaction is stopped by addn. of MeOH. The product is treated successively in N atm. with dil. HCl and H₂O, then coagulated by addn. of excess Me₂CO-MeOH. After drying in vacuo, 4.5 g. of a white, rubbery solid, completely amorphous on x-ray examn., is obtained. The copolymer contains 12.5 mole % cyclopentene (by radiochem. analysis) and the C₂H₄:C₃H₇ molar ratio is 1 (by infrared analysis). The copolymer is completely sol. in boiling heptane and has an intrinsic viscosity of 1.6 in Tetralin at 135°. Cycloheptene or 4-methyl-1-cyclopentene may be used in place of cyclopentene and the ratio of C₂H₄:C₃H₆ may be varied or C₃H₆ may be replaced by C₄H₈. Vulcanization occurs on the addn. of phenyl-2-naphthylamine, S, ZnO, and tetramethylthiuram disulfide, after mixing 1 hr. at 150°.

Bibliographic Information

Highly stereospecific catalyst systems for the polymerization of α -olefins to isotactic polymers. Natta, G.; Zambelli, A.; Pasquon, I. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 17 pp. IT 648220 19621027 Patent language unavailable. Application: IT 19610217. CAN 61:4532 AN 1964:404532 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 369)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 648220		19621027	IT	19610217
GB 967832			GB	

Abstract

Isotactic polyolefins are made by using new catalyst compns. of violet $TiCl_3$ and compds. such as $MAI_2RR'X_4X'$ (not necessarily in equimolar ratios), where M is an alkali metal, R and R' are alkyl with a max. of 5 C atoms, X is halogen, and X' is H, halogen, or CN. Examples show the use of $\gamma-TiCl_3$ or $\delta-TiCl_3$ with $KAl_2Et_2Cl_5$, $NaAl_2Et_2Cl_5$, $NaAl_2Et_2Cl_4F$, $NaAl_2Et_2Br_4Cl$, $KAl_2Et_2Br_4Cl$, and $KAl_2Et_2Cl_4Br$. $KAl_2Et_2Cl_5$ was prepd. by heating 2 moles $Al(C_2H_5)Cl_2$ and 1 mole KCl at 80-100° for 15 min. $NaAl_2Et_2Cl_5$ was prepd. similarly by using NaCl. Isotactic polypropylene was obtained by polymerization of C_2H_6 at 70° for 5 hrs. with $\delta-TiCl_3-KAl_2Et_2Cl_5$ with Al:Ti = 2.5. Similar results were obtained with $\gamma-TiCl_3-KAl_2Et_2Cl_5$ with Al:Ti = 3.75 and $\delta-TiCl_3-NaAl_2Et_2Cl_5$ with Al:Ti = 3.5. Isotactic polybutene was obtained by polymerization of 1-butene at 70° for 24 hrs. with $\delta-TiCl_3-KAl_2Et_2Cl_5$, with Al:Ti = 1.4. PhMe was used as a diluent in C_3H_6 polymerization and heptane was used with butene. The polymers are useful in the production of films, fibers, etc.

Bibliographic Information

Vulcanizable copolymers of olefins with polyenes. Natta, Giulio; Mazzanti, Giorgio; Valassori, Alberto; Sartori, Guido; Turba, Viltorio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 48 pp. BE 631165 19630816 Patent language unavailable. Priority: IT 19620418. CAN 60:91750 AN 1964:91750 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 412)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 631165		19630816	BE	
FR 1359982			FR	
GB 1022755			GB	
IT 685869			IT	

Priority Application

IT 19620418

Abstract

Copolymers of C_2H_4 and an α -olefin with dienes or polyenes which have the unsatns. in the aliphatic chains coupled to naphthenic rings, have high mol. wts., are amorphous, essentially linear, and vulcanizable, and can be made by using catalysts that act by an anionically coordinated mechanism. These catalysts are prepd. from transition-metal compounds of Groups IV and V and organometallic compds. of Groups I, II, and III. The α -olefins have the general formula $RCH:CH_2$, R being a C1-6 alkyl group. Esp. good results were obtained by using dialkylenes and dialkenyl and polyalkenyl cycloalkanes in which ≥ 1 of the double bonds is in a terminal position. Each monomer provides 1 double bond in the polymer mol. The preferred mol. wt. of the copolymer is $\geq 20,000$. The polymers have high homogeneity as indicated by the ease with which well-vulcanized products can be obtained. The vulcanized products are insol. in org. solvents, whereas the unvulcanized copolymers are sol. in boiling C_7H_{16} . Catalysts used include VCl_4 , $VOCl_3$, VBr_4 , $NbCl_4$, $NbOCl_3$, or $TaCl_4$ combined with a halogen-containing organometallic compd. The polymerization usually takes place between -80 and +125°, but to obtain a high production yield per unit of catalyst, both the catalyst prepn. and the copolymerization should be performed between -10 and -50°. A further improvement in effectiveness is obtained by the use of complexing agents such as ethers, sulfo ethers, and tertiary amines. Complexing agents are used in amts. of 0.05-1.0 mole/mole of alkyl aluminum halide. The ratio between the trialkyl aluminum and V compd. should be 2-4:1; when Et_2AlCl is used with V triacetylacetonate, the preferred ratios are 4-10:1. Solventless systems are preferred, in which case the monomers are kept in liquid form. To obtain amorphous polymers with elastomeric properties, the diene and polyene content in the polymer should be $>20\%$. The mole ratio between C_2H_4 and C_3H_6 should be $<1:4$ in the liquid phase, corresponding to a 1:1 ratio in the vapor phase. When 1-butene is used instead of propylene, the mole ratio between C_2H_4 and butene in the liquid phase should be $\leq 1:20$. Under these conditions, the terpolymers contain $<75\%$ C_2H_4 units. If this value is exceeded, the copolymers become partially cryst. The lower limit of C_2H_4 content is not crit., but should be $\geq 5\%$. For example, a reactor kept at -20° is charged under N with 200 ml. dry n- C_7H_{16} and 7 ml. trans-1,2-divinylcyclobutane. A 4:1 $C_3H_6-C_2H_4$ mixt. is fed in at 200 l./hr. through a porous disk. The catalyst is prepd. in

advance at -20° in a flask under N. V triacetylacetonate (2.8 millimoles), 40 millimoles Et_2AlCl , and 30 ml. dry toluene are mixed. After 5 min. at -20° , the catalyst mixt. is pumped into the reactor. Subsequently, the feed rate of the C_2H_4 - C_3H_6 mixt. is brought to 400 l./hr. Twenty min. after the start of the reaction, an amt. of catalyst the same as initially is added and, after 80 min., the polymerization is stopped by addn. of 20 ml. MeOH contg. 0.1 g. phenyl- β -naphthylamine. The polymerization product is purified by treating repeatedly with dil. HCl, washed with H_2O , and coagulated with acetone. After drying in vacuo, the yield is 13 g. of an amorphous solid resembling an unvulcanized elastomer, completely sol. in boiling n-C $_7$ H $_16$, intrinsic viscosity 2.1. The C_2H_4 : C_3H_6 ratio in the polymer is 1:1. This polymer (100 parts) is then mixed with phenyl- β -naphthylamine S 2, ZnO 2, tetramethylthiuram disulfide 1, and mercaptobenzothiazole 0.5 part. The mixt. is vulcanized under pressure for 30 min. at 150° . The vulcanized sheet has: tensile strength 23.3 kg./cm. $_2$; elongation at break 500%; 300%, modulus 10.5 kg./cm. $_2$; permanent elongation at break 8%. If, in addn., 50 parts HAF carbon black is used as a filler, the tensile strength is 300 kg./cm. $_2$; the elongation at break 520%; the 300% modulus 125 kg./cm. $_2$; and the permanent elongation at break 8%.

Bibliographic Information

Vulcanizable copolyolefins. Natta, Giulio; Valvassori, Alberto; Sartori, Guido; Giannini, Umberto. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 32 pp. BE 625657 19630604 Patent language unavailable. Priority: IT 19611205. CAN 60:91748 AN 1964:91748 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (LL 405 + LL 405/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 625657		19630604	BE	
GB 983437			GB	

Priority Application

IT	19611205
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Abstract

Linear vulcanizable co- and ter polymers of conjugated diolefins (butadiene, isoprene, 1,3-pentadiene, or 1,3-hexadiene) with C_2H_4 and (or) α -olefins (propylene or 1-butene) are produced by using a catalytic system contg. a hydrocarbon sol. V compd., such as a halide, oxyhalide, alkoxide or acetylacetonate, e.g. VCl_4 , VCl_3 , or VBr_4 , and an organoaluminum compd. contg. ≥ 1 org. group having strong sterical hindrance, e.g. 3-methylbutyl, cycloalkyl, or cyclopentylmethyl. At least one valency of V and (or) Al should be satd. by a halogen atom. The mole ratio Al compd. to V compds. should be 4:1 to 20:1. The reaction temp. is preferably -50 to 0° . The copolymers or terpolymers can be vulcanized in the usual way by means of S, and used for the production of molded products, sheets, tubes, etc. The vulcanized polymers, mol. wt. $>20,000$, have an improved resistance to aging and O. Thus, 350 cc. n-C $_7$ H $_16$ was placed in a glass tube. A 4:1 propylene- C_2H_4 mixt. was added in an amt. of 100 l./hr. and butadiene was added in an amt. of 10 l./hr. at -20° . A fresh catalyst mixt. of 4 millimoles VCl_4 and 10 millimoles 2-methyl-1,4-bis(diisobutylaluminium)butane in 30 cc. n-C $_7$ H $_16$ was added. After 45 min., the reaction was stopped by addn. of 20 cc. MeOH contg. 0.4 g. phenyl- β -naphthylamine as antioxidant. The product was purified with dil. HCl and H_2O under N and then coagulated with an excess of an acetone-MeOH mixt. Drying in vacua gives 10 g. of a white solid amorphous product. Vulcanizing of C_2H_4 propylene-butadiene terpolymer 100 with phenyl- β -naphthylamine 1, lauric acid 2, ZnO 5, S 2, tetramethylthiuram disulfide 1, and mercaptobenzothiazole 0.5 part at 150° during 30 min. on a press gives a film having a tensile strength of 58 kg./cm. $_2$, an extension at rupture of 900%, an extension modulus at 300% of 10 kg./cm. $_2$, and a permanent extension at rupture of 28%. Belg. 625,658; 21 pp. An organoaluminum compd. contg. ≥ 1 unsatd. hydrocarbon group is used, such as trivinylaluminum. Thus, in the same app. and under same conditions, 15 cc. 1,3-butadiene and a propylene- C_2H_4 mixt. (mole ratio 3:1) in an amt. of 100 l./hr. were added. A fresh soln. of 12 millimoles I and 4 millimoles VCl_4 in 30 cc. n-C $_7$ H $_16$ was added. After 10 min., the reaction is stopped by addn. of 20 cc. MeOH contg. 0.2 g. phenyl- β -naphthylamine as antioxidant. Purifying, coagulating with excess acetone, and drying in vacuo gave 5 g. amorphous, solid product. One

hundred parts C₂H₄-propylene-butadiene terpolymer was vulcanized at 150° during 30 min. on a press. The film obtained had tensile strength 60 kg./cm.², extension at rupture 800%, 300% modulus 17 kg./cm.², and permanent extension at rupture 20%.

Bibliographic Information

Ethylene copolymers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 11 pp.; Addn. to Belg. 609,581. BE 631164 19631104 Patent language unavailable. Priority: IT 19620418. CAN 60:91747 AN 1964:91747 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 340/c)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 631164		19631104	BE	
FR AD83527			FR	
GB 985884			GB	

Priority Application

IT	19620418
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Abstract

Linear, amorphous polymers are made by copolymerizing C₂H₄ with higher α -olefins in the presence of a catalyst obtained by mixing a hydrocarbon-sol. V halide and an alkylaluminum dihalide, dialkylaluminum halide, or alkylaluminum sesquihalide. The copolymers are elastomeric. Thus, 0.5 millimole VCl₃ and 2.5 millimoles Et₂AlCl were made to react in 50 cc. n-heptane at -20° in an N atm., held for 1 min. at -20°, then siphoned into a flask contg. 350 cc. n-heptane through which a mixt. of C₂H₄ and C₃H₆ in a 3:1 molar ratio was circulated at the rate of 400 l./hr. After 4 min., the reaction was stopped by the addn. of 10 cc. MeOH. The copolymer was purified by washing with aq. HCl and H₂O, and then coagulated with MeOH. In similar procedures, C₂H₄ and C₃H₆ were copolymerized in a 2:1 molar ratio with catalyst mixts. of VCl₄ and Et₂AlCl, and VCl₃ and Et Al sesquichloride. Comparative expts. showed that the yield of copolymer was decreased by prepg. the catalyst mixt. at 25° and polymerizing at that temp.

Bibliographic Information

Linear ketene-formaldehyde copolymers. Natta, Giulio; Pregaglia, Gianfranco; Mazzanti, Giorgio; Binagli, Marco; Pozzi, Giancarlo; Oddo, Nino; Zamboni, Valentino. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 27 pp. BE 629672 19630701 Patent language unavailable. Priority: IT 19620316. CAN 60:91408 AN 1964:91408 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (D 198 + u 414)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 629672		19630701	BE	
DE 1202495			DE	
FR 1353226			FR	
GB 970018			GB	
IT 665056			IT	

Priority Application

IT	19620316
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Abstract

Copolymers contg. units derived from HCHO and $\leq 10\%$ of the ketene compd. R1C(R2):C:O (I) (R1 and R2 are Me or Ph) are described. Thus, when I is in slight excess of HCHO and R1 = R2, cryst. polyesters consisting of alternate units derived from HCHO and I are obtained. When I is in large excess of HCHO, and when a long reaction time is used, the product consists entirely of monomer chains derived from I. When HCHO is in excess of I, the copolymer obtained consists of polyacetal chains sep'd. by ester groups. For example, 200 g. anhyd. cyclohexyl formal (II) was decompd. at 135-45° to give HCHO gas, which was passed into 10.36 cc. Et3N in 300 cc. PhMe, and maintained at 20°/100 mm., under N. During the subsequent reaction, the decompn. temp. of II was controlled by holding the pressure at .apprx.600 mm., and 5 cc. Me2C:C:O (III) was added gradually. After 20 min., the addn. of monomers was stopped, and the stirred mixt. was held at 20° for 15 min. The copolymer suspension was filtered, and the residue was washed several times with Me2CO and dried 4 hrs. at 60° to give 26 g. of a product (IV) having the following properties [inherent viscosity, wt. loss at 160°, mole/kg. CH2OH groups (by infrared analysis), wt. % III copolymerized, m.p. % cryst. to x-rays given]: 1.3, 2.0%, 0.08, 2.5, 169°, 74. Corresponding data for an analogous prepn. without III, a prepn. in which III was added in two 5-ml. portions, a prepn. in which II and III were added alternately, and a prepn. giving pure poly(oxymethylene) were: 1.2, 8, 0.26, -, 175°, -; 0.9, 5, 0.06, 6.5, 160°, 76; 1.1, 6, 0.12, 3, 167°, 75; 1.2, -, 0.26, -, -, 75. The following data were obtained for 3 copolymers prep'd. as IV, but using a catalyst [catalyst, wt. % catalyst relative to solvent, yield, inherent viscosity, wt. % III copolymerized given]: Bu3N, 0.2, 20 g., 1.0, 3; hexamethylenetetramine, 0.1, 14, 0.7, 3; C5H5N, 0.3, 24, 1.9, 3.5.

The copolymers are useful for the fabrication of shaped plastic articles, and, when compression-molded at 160-80°, give tough, translucent, homogeneous films, showing great resistance to repeated bending.

Bibliographic Information

Succinic acids. Natta, Giulio; Pino, Piero. (Lonza Ltd.). (1962), 6 pp. DE 1133359 19620719 Patent language unavailable. Application: DE 19650324. Priority: DE 19650324. CAN 60:82489 AN 1964:82489 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1133359		19620719	DE	19650324
CH 333913			CH	
GB 828441			GB	
US 2851486		19580909	US 1956-573444	19560323

Priority Application

DE 19650324

Abstract

Co2(CO)8 (10 g.) was suspended in 100 g. H2O with 2.5 l. [standard conditions (S.T.P.)] C2H2, CO added to 200 atm., the mixt. heated 6 hrs. at 140°, cooled, and distd., the residue in H2O acidified, and the soln. concd. to give 2 g. succinic acid (I), m. 182-4°. Similarly, 10 g. Co2(CO)8, 216 g. Me2CO, 72 g. H2O, 14 l. C2H2 (S.T.P.), and CO to a pressure of 200 atm. heated 3 hrs. at 110° gave a small amt. cyclopentanone and 3.8 g. mixt. of acrylic acid (II), and EtCO2H. The residue afforded 60 g. I. Similarly, 4 g. Co2(CO)8, 36 g. H2O, 90 g. dioxane, CO, and 9.5 l. (S.T.P.) C2H2 autoclaved 5 hrs. at 110° and 200 atm. initial pressure gave 1.59 g. crude cyclopentanone and 4 g. mixt. of II and EtCO2H; the residue contained 65% I. Similarly, I, H2O, Me2CO, monophenylacetylene, and CO shaken 4 hrs. at 140° in an autoclave gave monophenylsuccinic acid, m. 166°. Similarly, Fe(CO)5, H2O, Me2CO, and CO with C2H2 gave a mixt. of II and EtCO2H, cyclopentanone, and I. Ni(CO)4 and C2H2 gave II and EtCO2H, but no I. I Co deriv (7.13 g.), 251 g. Me2CO, 45 g. H2O, and C2H2 treated as above gave 45.5% I, some cyclopentanone, and 3.01 g. II and EtCO2H. Similarly, Co2(CO)8, Me2CO, H2O, and 1-hexyne gave heptanoic acid and butylsuccinic acid, m. 81°. Diphenylacetylene treated with Co2(CO)8 in Me2CO gave di-Me meso-diphenylsuccinate, m. 215-20°, on esterification. CO2(CO)8, Me2CO, H2O, and dimethylacetylene similarly gave meso-dimethylsuccinic acid, m. 195-6°.

Bibliographic Information

Molybdenum-iron catalysts. Natta, Giulio; Baccaredda, Mario; Traina, Francesco; Pergolini, Remo; Balcet, Eugenio; Soldano, Umberto. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 5 pp. DE 1144252 19630228 Patent language unavailable. Priority: IT 19581028. CAN 60:82477 AN 1964:82477 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (F 219)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1144252		19630228	DE 1959-M43156	19591023
GB 879888			GB	
US 3152997		19641013	US 1959-846791	19591016

Priority Application

IT 19581028

Abstract

Catalysts for the oxidn. of MeOH to HCHO were prepd. from Mo and Fe compds. Thus, 400 l. H₂O and 20 kg. (NH₄)₆Mo₇O₂₄ at a pH of 4.5-5.0 was heated at 60°. A soln. of 11 kg. FeCl₃.6H₂O in 220 l. H₂O at pH 1.0-1.5 was added to the molybdate and stirred. The ppt. was washed by decantation and vacuum-filtered at 200 mm. The ppt. was dried to a H₂O content of 45-47% and rolled flat between granite rollers moving at 45 r.p.m. By the use of bored rollers, the material was converted to cylinders with a height and diam. of 4.2 mm. The catalyst was dried 6 hrs. at 15-30°, 12 hrs. at 40°, and 6 hrs. at 120°. Activation was carried out by heating 2 hrs. at 150°, 1 hr. each at 200°, 250°, and 300°, and 5 hrs. at 420°. The product, which had overall dimensions of 3.5 mm., was used as follows. The reaction gas of 935:65 air-MeOH was fed into H₂O-cooled reaction tubes contg. 571 kg. catalyst at 270°. During 318 days, 4020 tons 100% MeOH produced 9483 tons 36% HCHO in 90.6% yield. Analysis of the product showed in addn. 0.7% MeOH and 0.006% HCO₂H.

Bibliographic Information

Isotactic polypentadiene. Natta, Giulio; Porri, Lido; Stoppa, Gianfranco; Carbonaro, Antonio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1963), 21 pp. BE 628238 19630529 Patent language unavailable. Priority: IT 19620212. CAN 60:69066 AN 1964:69066 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 396/Bis + U 396/Bis A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 628238		19630529	BE	
FR 1350979			FR	
GB 961269			GB	

Priority Application

IT 19620212

Abstract

The polymerization of trans-1,3-pentadiene (I) takes place in the presence of a catalyst contg. an aluminum alkyl and a Ti deriv. (II) to form a polymer (III) having mainly the cis-1,4 structure, which is different from syndiotactic polypentadiene (CA 58, 6943a) of the same steric configuration when they are compared by infrared absorption and x-ray diffraction. II is Ti(OR)₄, in which R is an alkyl, cycloalkyl, or aromatic group. III is a rubberlike material having a high elasticity, which is very similar to natural rubber. When vulcanized, it is amorphous at room temp. and becomes cryst. if it is stretched. Thus, anhyd. C₆H₆ 80, Ti(OBu)₄ 0.6, and Et₃Al 1.8 ml. were

introduced into a reagent glass under an anhyd. N stream. The temp. was brought to 0° and 2-4 min. later, 15 ml. I was added. After 18 hrs. at 0°, the polymerization was stopped by addn. of MeOH which pptd. 3 g. crude III. When dried in vacuo, it was purified 2 times by soln. in IV and pptn. by MeCOEt. The pure resin was cryst. (by x-ray examn.) and contained cis 85, trans 12, and vinyl-type double bonds 3% (by infrared analysis). Its intrinsic viscosity in PhMe (100 ml./g. at 30° was 7.04, while its m.p. was 43°.

Bibliographic Information

Rubberlike terpolymers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 16 pp. IT 648817 19621113 Patent language unavailable. Application: IT 19610322. Priority: IT 19610322. CAN 60:61763 AN 1964:61763 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 364)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 648817		19621113	IT	19610322
GB 957105			GB	

Priority Application

IT	19610322
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Abstract

High-mol.-wt. (.apprx.20,000) linear amorphous terpolymers of cyclo- or alkylcyclopentadienes, C₂H₄, and a 1-olefin, such as propylene or 1-butene, are prepd. at -20° in the presence of a hydrocarbon-sol. catalyst system obtained at this same temp. from a dialkylaluminum monohalide, a monoalkylaluminum dihalide or an alkylberyllium halide, or their mixt. and a V compd. which is either hydrocarbon-sol., e.g. V tris(acetylacetonate) or bis(acetylacetonate), or vanadyl haloacetylacetonate, or able to give sol. compds. by reaction with Al or Be compds., e.g. acids and oxy acids of V³⁺ and V⁴⁺. When the copolymerization is done at higher temps. (0-125°), a complexing agent, e.g. an ether or thio ether contg. ≥1 branched alkyl group or an aromatic nucleus must be added. The activity of the catalyst varies with the mole ratio of its components. For example, in the case of Et₂AlCl and V tris(acetylacetonate), the best results are obtained by using them in a 4:10 mole ratio. Very high yields of homogeneous products are obtained by using the monomers in their liquid state (thus eliminating solvents) and by maintaining the ratio of their concns. fairly const.; for this purpose, the copolymerization is done continuously and the catalyst is added in the same way or periodically. For example, C₃H₆ and C₂H₄ were copolymerized in a 4:1 mole ratio at -20° with 0.183 mole of freshly distd. cyclopentadiene; the catalyst, also prepd. at -20° from a soln. of 14 millimoles Et₂AlCl and 2.8 millimoles V tris(acetylacetonate) in anhyd. toluene, was added periodically; after 35 min., the reaction was interrupted by addn. of 20 cc. MeOH contg. 0.2 g. antioxidant (phenyl-naphthylamine). After washing with aq. HCl and then H₂O, the mixt. was coagulated with an excess of a Me₂CO-MeOH mixt.; after drying, 20 g. of a solid, white, rubbery compd. was obtained, which had properties similar to those of nonvulcanized rubber and could be vulcanized by the customary methods.

Bibliographic Information

Copolymers of ethylene with other α -olefins. Natta, Giulio; Mazzanti, Giorgio. ("Montecatini" Societa-Generale per l'Industria Mineraria e Chimica). (1962), 24 pp. IT 638375 19620404 Patent language unavailable. Application: IT 19601026. Priority: IT 19601026. CAN 60:61761 AN 1964:61761 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 340)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 638375		19620404	IT	19601026
GB 957068			GB	

Priority Application

IT

19601026

Abstract

High-mol.-wt., linear, amorphous copolymers of C₂H₄ and α -olefins (C₃H₆ or 1-butene) contg. 70% by wt. C₂H₄ are prepd. in the presence of a hydrocarbon-sol. catalyst system obtained from a mixt. of a hydrocarbon-sol. V compd. [V tris(acetylacetonate) or vanadyl acetylacetonate or haloacetylacetonate] and a dialkylaluminum halide (I). For the highest activity, a mole ratio very close to 5 of I to V compd. is used. The catalyst is best prepd. at -20° and in the presence of the monomers to be copolymerized; copolymerization is done at this same temp., in the absence of a solvent, by using the monomers in their liquid state. For the best yields of products of good homogeneity, the process is carried on continuously, the catalyst is added in the same way, and the ratio of the molar concns. of the monomers is kept fairly const. In the case of C₂H₄-C₃H₆ copolymers, the mole ratio of C₃H₆ to C₂H₄ should be kept at 4, when using 1-butene, the mole ratio of 1-butene to C₂H₄ should be kept at 25. The products of the invention can be used as synthetic rubbers. Under certain conditions, it is possible to obtain cryst. copolymers.

Bibliographic Information

Ketone-ketene copolymers. Natta, Giulio; Mazzanti, Giorgio; Pregaglia, Gianfranco; Binaghi, Marco. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 11 pp. BE 623181 19630403 Patent language unavailable. Priority: IT 19611004. CAN 60:61411 AN 1964:61411 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 288/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 623181		19630403	BE	
FR AD82390			FR	
GB 1015395			GB	

Priority Application

IT 19611004

Abstract

Copolymers having the structure of linear polyesters are made by copolymerizing ketones and ketenes with the use, as catalysts, of Li or its hydrides, alkoxides, or amides, Li alkenyls, or polycyclic Li hydrocarbons. Thus, 9.2 g. acetone, 10 g. dimethylketene (II), 0.2 g. LiOEt, and 40 cc. C₇H₁₆ were mixed at -40° for 2.5 hrs. MeOH was added and a powd. copolymer was obtained having strong infrared absorption at 5.80 μ . In similar procedures, I and II were copolymerized by using metallic Li, MeOLi, n-BuOLi, naphthyl Li, and LiAlH₄ as catalysts, heptane, toluene, and propylene as solvents, and temps. of -78 to -28°. In one expt., the solvent was omitted.

Bibliographic Information

Isotactic polypropylene and crystalline polymers of higher homologs of ethylene. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 9 pp. US 3112301 19631126 Patent language unavailable. Application: US 19580505. CAN 60:39188 AN 1964:39188 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 59 + U 63)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3112301		19631126	US 722 808	19580505

Abstract

The disclosure is similar, but the claims are different.

Bibliographic Information

Isotactic polypropylene and crystalline polymers of higher homologs of ethylene. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 9 pp. US 3112300 19631126 Patent language unavailable. Application: US 19550608. CAN 60:39187 AN 1964:39187 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 59 + u 63)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3112300		19631126	US 1957-701332	19550608

Abstract

Films and textile fibers were made from isotactic polypropylene macromols. which are insol. in boiling n-heptane, Et₂O, and acetone. Thus, 1.8 g. TiCl₄ in 50 mL. anhyd. gasoline b. 98° was added dropwise at 5-10° to 11.4 g. Et₃Al in 150 mL. gasoline. The soln. was further dild. to 500 mL. with gasoline and introduced into a 2-1. oscillating, dried, and evacuated stainless steel autoclave. Carefully dried, liq. C₃H₆ (190 g.) was pumped into the autoclave, and the mixt. heated, while agitating, to about 55-60°. After the pressure had fallen from about 10 atm. to about 2 atm., an addnl. 160 g. C₃H₆ was added. The pressure thereafter dropped at a lower rate and after about 20 h. no further decrease could be obsd. The residual gases were vented, and consisted chiefly of C₃H₆ (72.51.) and C₂H₄ (0.21.). MeOH (95 g.) was pumped into the autoclave to decomp. the catalyst; 5.7 l. gas was evolved, >50% of which was C₃H₆. The polymn. product, comprising a solid mass drenched with gasoline and MeOH, was extd. from the autoclave, suspended in (iso-Pr)₂O, and heated under strong stirring, while bubbling through gaseous HCl, to render sol. all inorg. compds. resulting from decompn. of the catalyst. After 4 h., a little MeOH was added to ppt. the polymer which may have been dissolved, the suspension filtered under suction, dried at 100° under reduced pressure to give 180 g. of a white, spongy solid comprising a mixt. of polypropylenes (I) of a wide range of mol. wts., and having a transparent, rubber-like appearance at 140°, and m. 155°. The polymer mixt. could be molded at 130° to flexible sheets contg. amorphous and cryst. portions, as shown by x-ray diffraction pattern. A few g. of a very viscous oil was recovered from the filtered liq., after distrn. of the solvent. The solid I mixt. was sepd. into a small amt. of oily, low-mol.-wt. products and several larger fractions of amorphous and cryst. products by fractional dissoln. using, successively, boiling acetone, Et₂O, and n-heptane. The acetone-extd. fraction (A) consisted of the oily, low-mol.-wt. products amounting to 2.8% of the solid I obtained. The ether-extd. fraction (B) amounted to 39% of the total I, and, after evapn. of Et₂O in vacuo, had an intrinsic viscosity of 1, and was completely amorphous, similar to an unvulcanized elastomer. The n-heptane extd. fraction (C), amounting to 19% of the total I, had, after evapn. of the solvent in vacuo, an intrinsic viscosity of 1.2-1.3 and was, at room temp., a partially crystn. solid m. 150°, which also had the properties of an elastomer but up to temps. higher than those at which fraction (B) showed elastomer-like properties. The residue (D), insol. in all 3 solvents, had a d. of about 0.92 and an intrinsic viscosity, of 3.33 (100 mL./g.) (in tetrahydronaphthalene soln.). A 1% Tetralin soln. had a sp. viscosity of 0.374. Fraction D underwent syneresis at 120°, lost its crystallinity >150°, and, at 170° was wholly converted into a transparent, very viscous mass. Upon molding fraction D in a flat press at 140-50°, plates or sheets were obtained which appeared cryst. upon x-ray anal., showed a 700% elongation, and a breaking load of 350 kg./cm.² Fraction D could be formed into filaments or threads by extrusion in a softened condition, and the extruded filaments being warm- or cold-stretched. The stretched filament was highly cryst. and had a very high breaking load e.g., a cold stretched thread of 0.3 mm. diam., after stretching, had a breaking load of 32 kg./mm.² and an elongation of 40%. The residue of the ether extn. had similar characteristics but a lower tensile strength, and its properties were intermediate to those of the n-heptane

ext. and the n-heptane residue. Other cryst. high-mol.-wt. polymers prepd. were: a fiber-forming 2-butene-1-butene polymer (30:70) softening at 125°; a 1-hexene polymer; a polypropylene; a polystyrene of mol. wt. 2,800,000 (calcd. from viscosity measurements in C6H6 at 25°), a d. of 1.08, and a 1st-order transition pt. >210°; in place of TiCl4, Cr acetylacetonate, VCl4, TiBr4, TiI4, and ZrCl4 were used. In place of Et3Al, Pr3Al, and Et2Zn were used.

Bibliographic Information

Catalysts for copolymerization of ethylene with γ -olefins. Natta, Giulio; Mazzanti, G. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 26 pp. IT 638656 19620418 Patent language unavailable. Application: IT 19601024. Priority: IT 19601024. CAN 60:24086 AN 1964:24086 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 334)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 638656		19620418	IT	19601024
GB 956875			GB	

Priority Application

IT	19601024
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Abstract

C2H4 is copolymerized with γ -olefins at room temp. in the presence of a hydrocarbon-sol. V compd., such as a vanadyltrialkoxide or a compd. of the general formula VO(OR)X2, in which R is an alkyl group and X is a halogen atom and a complex of a dialkylaluminum halide and an ether or thioether. Thus, a 4:1 mole ratio of C3H6 to C2H4 is introduced at 200 l./hr. into a reactor contg. 350ml. anhyd. n-C7H16 under N at 25°. A soln. of 7 millimoles Et2AlCl and 1.4 millimoles iso-Pr2O in 25 ml. anhyd. C6H6 is added, followed by a soln. of 1.4 millimoles V triacetylacetonate in 25 ml. C6H6 after 1 min. The introduction of the C3H6-C2H4 is continued for 18 min. at 200 l./hr. Fifty ml. MeOH is then added and the mixt. is washed with HCl. The org. soln. is washed with H2O; and Me2CO and MeOH are added to give 12 g. C2H4-C3H6 copolymer contg. 53.5 mole % C2H4. Copolymerization of C2H4 with 1-butene is also mentioned.

Bibliographic Information

Olefin-diolefin copolymers. Natta, G.; Mazzanti, G.; Valvassori, A.; Sartori, G.; Crespi, G. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 28 pp. IT 638953 19620430 Patent language unavailable. Application: IT 19601114. CAN 60:17691 AN 1964:17691 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 344)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 638953		19620430	IT	19601114
GB 957103			GB	

Abstract

α -Olefins of the general formula RCH:CH2, where R is H or a C1-6 alkyl group, are co-polymerized with an unconjugated diolefin, which ≥ 1 of the double bonds is in a terminal position, in the presence of a mixt. of an alkylaluminum halide and a V compd., such as V tris(acetylacetonate) (I) or a vanadyl trialkoxide, to give linear, amorphous copolymers. Thus, 350 ml. anhyd. n-C7H16 is satd. at -20° with a C2H4-C3H6 mixt., mole ratio 1:4, at 200 l./hr. and 0.168 mole 1,5-hexadiene (II) is added. A mixt. is prepd., at 20° from a soln. of 14 millimoles

Et₂AlCl in 20 ml. anhyd. PhMe and a soln. of 2.8 millimoles I in 20 ml. PhMe. The catalyst mixt. is added to the n-C₇H₁₆ mixt. and the introduction of the C₂H₄-C₃H₆ mixt. is continued at 300 l./hr. Then, 0.067 mole II is added and 20 ml. MeOH contg. 0.2 g. phenylnaphthylamine is added 12 min. after the introduction of the catalyst. The mixt. is treated with HCl and H₂O under N, a Me₂CO-MeOH mixt. is added, and the ppt. that forms is sepd. and dried in vacuo to give 25 g. copolymer, intrinsic viscosity (135°, Tetralin) 3.0, infrared bands 6.08, 10, and 11μ, contg. .apprx.9-10% by wt. II. A mixt. of the terpolymer 100, phenyl-β-naphthylamine, 1, S 2, tetramethylthiuram disulfide 1, and mercaptobenzothiazole 0.5 part is vulcanized for 30 min. at 150° in a press to give a product of rupture resistance 43 kg./sq. cm., elongation at break 380%, modulus at 300% elongation 24 kg./sq. cm., residual deformation after rupture 4%, Shore hardness (A scale) 57, and elasticity (25°) 65%.

Bibliographic Information

Vulcanized elastomers. Natta, Giulio; Mazzanti, Giorgio; Boschi, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1962), 2 pp. DE 1139637 19621115 Patent language unavailable. Priority: IT 19560711. CAN 59:55991 AN 1963:455991 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 117)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1139637		19621115	DE 1957-M48901	19570704

Priority Application

IT	19560711
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Abstract

Copolymers are made as described in Brit. 858,067 (CA 55, 12937b) from C₂H₄, ≥1 olefin of the formula CH₂:CHR (R = lower alkyl), and ≥1 diolefin contg. ≥1 vinylic double bond. Vulcanized by the usual methods, these polymers have better resilience than copolymers made without C₂H₄. For example, a copolymer was used which had an intrinsic viscosity of 4.2 (dtd. in tetrahydronaphthalene at 135°), an I no. of 40, and was free of polyethylene and polypropylene. This polymer was extd. with Et₂O, removing 36%, while the C₇H₁₆-sol. residue was vulcanized by addn. of 3% S, 2% Zn diethyldithiocarbamate, 2% mercaptobenzothiazole, and 2% tetramethylthiuram disulfide during 15 min. at 180°. The vulcanizate obtained had 0.3 kg./mm. tensile strength, an elongation of 480%, and a deformation at break of 60%. The resilience was 60-5%, while that of a polymer from propylene and iso-propylene was 20% and that from butyl rubber was 17%.

Bibliographic Information

Stereospecific polymerization of α-olefins. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo; Figini, Gianfranco. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 13 pp. FR 1322041 19630322 Patent language unavailable. Priority: IT 19610518. CAN 59:22168 AN 1963:422168 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 384)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 1322041		19630322	FR 1962-897830	19620517
GB 963379			GB	
IT 651547			IT	

Priority Application

IT	19610518
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Abstract

α -Olefins, esp. propylene, were polymerized in the presence of an organometallic compd. of a metal of Group II or III, a compd. of a transition metal of Group IV or V, and a simple or complex hydride of an alkali metal, esp. Na or Li. Thus, 1.1 g. Et₂AlCl, 0.33 g. TiCl₃ (obtained by reducing TiCl₄ with Al and contg. about 25 mole % cocrystd. AlCl₃), 0.35 g. LiAlH₄, and 1.6 g. Me₂SiCl₂ in 300 cc. anhyd. n-heptane were added under N to a 1 l. oscillating autoclave preheated to 75°. Gaseous propylene was added, while agitating, until a pressure of 5 atm. was reached and held for 5 hrs. Excess propylene was removed, 400 cc. of a 1:1 MeOH-acetone mixt. was added, and the resulting polymer was filtered. After drying, 144 g. of a finely divided white powder was obtained. The polymer had an intrinsic viscosity of 1.7, as detd. in tetrahydronaphthalene at 135°. Ninety-one percent of the polymer was not extractable by boiling n-heptane, and x-ray examination revealed a very high crystallinity. In place of Me₂SiCl₂, BCl₃, PCl₅, and SbCl₅ were used. In place of LiAlH₄, NaI and LiH were used in mixt. with AlCl₃.

Bibliographic Information

Elastomeric copolymers of α -olefins and nonconjugated, cyclic polyenes. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Dall'Asta, Gino; Sartori, Guido; Cameli, Nazareno. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 21 pp. BE 623741 19630214 Patent language unavailable. Priority: IT 19620430. CAN 59:9648 AN 1963:409648 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 404/A + U 404/B)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 623741		19630214	BE	
FR AD82562			FR	

Priority Application

IT	19620430
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Abstract

The catalysts and polymn. conditions of Belg. 623,698 (preceding abstr.) are employed in the copolymn. of C₂H₄ or a higher α -olefin with a nonconjugated, cyclic polymer or alkyl polyene to form unsatd., linear copolymers which can be amorphous or partially cryst., depending upon the proportion of α -olefin in the polymer. Thus, when C₂H₄ and 1,5-cyclooctadiene are copolymd. at -20° with VCl₄-Et₂AlCl or VCl₄-Al(C₆H₁₃)₃ (I) as catalysts to form polymers contg. 55 and 60 mol % C₂H₄, resp., the polymers are amorphous. With I or V/triacetylacetonate-Et₂AlCl at -30°, partly cryst. polymers contg. 89 and 85 mol % C₂H₄, resp., are formed. A partly cryst. polymer of C₂H₄ and 1,5,9-cyclododecatriene, contg. 99 mol % I, is formed at -30° with the I catalyst.

Bibliographic Information

Elastomeric olefinic copolymers containing cyclic nonconjugated dienes. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido; Cameli, Nazareno. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 40 pp. BE 623698 19630214 Patent language unavailable. Priority: IT 19611018. CAN 59:9647 AN 1963:409647 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 404)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 623698		19630214	BE	
GB 977839			GB	
IT 660432			IT	
US 3260708		19660712	US 1962-231031	19621016

Abstract

Copolymers of C₂H₄ and C₃H₆ with 1,5-cyclooctadiene (I) are prepd. in the presence of catalysts comprising compds. of V and either organometallic compds. of Al, Be, or Li or organometallic complexes of Al and Li. Thus, 350 cc. n-heptane and 15 cc. I are introduced into a reactor maintained at -20°, and a mixt. of C₂H₄ and C₃H₆, in a ratio of 1:2, is circulated through the reactor at a rate of 200 l./h. A catalyst formed by causing 0.8 mmol VCl₄ and 4 mmol Et₂AlCl to react in 50 cc. n-heptane at -20° is introduced, and the circulation of the mixt. of C₂H₄ and C₃H₆ is continued at a rate of 400 l./h. After 10 min., the reaction is stopped and 13.5 g. of an amorphous, solid polymer, having an intrinsic viscosity in Tetralin at 135° of 2.35, is recovered. The polymer is vulcanizable with S. Cf. Belg. 623,741 (following abstr.)

Author Name task started on Wed May 9, 2007 at 10:15 AM

Explored by Author in CAPLUS and MEDLINE.

Natta, Giulio

Selected 2 of 3 candidates

NATTA G (325 references)

NATTA GIULIO (410 references)

Refine by Document Type started

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239 references were found when refined by Document Type "Patent"

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Bibliographic Information

Crystalline poly(isopropenylpyridines). Natta, G.; Mazzanti, G.; Longi, P.; Sempio, C. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 11 pp. IT 632822 19620202 Patent

language unavailable. Application: IT 19600719. Priority: IT 19600719. CAN 59:9505 AN 1963:409505
CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 306)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 632822		19620202	IT	19600719
DE 1155245			DE	
GB 920559			GB	
US 3208983		19650928	US 1961-124652	19610717

Priority Application

IT 19600719

Abstract

Title compds. are prepd. from 2- and 4-isopropenylpyridine with Group I-III metal derivs. Suitable catalysts are alkyl, aryl, and alkyl halides of Mg and Be, alkyl or aryl derivs. of the alkali metals, hydrides of the Group I-III metals, and org. derivs. with metal-N bonds. Thus, 0.35 g. Et₂NMgBr [or LiAl(NPh₂)₃HOEt₂] in 20 ml. toluene is stirred at 45° under N. 2-Isopropenylpyridine (10 g.) in 10 ml. toluene is added slowly and stirred 2 hrs., the mixt. mixed with 200 ml. 5% HCl, and the polymer pptd. from the aq. layer with 200 ml. water contg. 5% NH₃ and 5% NH₄Cl. The product is extd. with benzene and pptd. with heptane to yield 9.5 g. poly(2-isopropenylpyridine) (I), softens at 190°, intrinsic viscosity 0.1 (HCONMe₂, 30°). I (5% and 95% isotactic polypropylene are extruded at 220-40° to give fibers with good dyeability and excellent mechanical properties. Similarly prepd. is poly(4-isopropenylpyridine), softens 220-30°, with Et₂Be as catalyst.

Bibliographic Information

Thermoplastic resins. Natta, Giulio; Donati, Mario; Farina, Mario. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1963), 10 pp. BE 620901 19630131 Patent language unavailable. Priority: IT 19610801. CAN 59:9429 AN 1963:409429 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 394)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 620901		19630131	BE	
DE 1180134			DE	
GB 948718			GB	
IT 683008			IT	

Priority Application

IT 19610801

Abstract

The title compds. are obtained by polymerizing (between -70° and 20°) and in the presence of an organometallic catalyst, such as BuLi, PhMgBr, or LiNEt₂, or a hydrocarbon solvent, such as heptane, PhMe, or Et₂O, esters of nonsatd. acids and alcs. of the type: R₁(CH:CR₂)_nCOO(CH₂)_m-CR₃:CHR₄ (where R₁, R₂, R₃, R₄, alike or not, are H or an alkyl, aryl, or cycloalkyl group with 1-10 C atoms; n = 1 or 2; R₂ = H if n = 2; m = 0-6). These polymers are cryst. and have a great structural regularity; they present a strong unsatn. in the alkoxy-carbonylic side chain and can be processed into articles, such as fibers and films, whose properties (soly. and heat resistance) can be greatly modified by cross-linking.

Bibliographic Information

Stereoregular poly(tert-butyl vinyl ether). Natta, Giulio; Dall'Asta, Gino. (Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 11 pp. BE 619277 19621224 Patent written in French. Priority: IT 19610623. CAN 59:3964 AN 1963:403964 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (4389)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 619277		19621224	BE	
GB 944089			GB	
IT 652139			IT	
US 3278507		19661011	US 1962-203745	19620620

Priority Application

IT	19610623
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Abstract

Cryst. polymers from tert-Bu vinyl ether (I) were obtained by using as catalysts compds. of the formula RBF₂, where R is an alkyl, aryl, or alkoxy radical. Thus, to a soln. of 2.5 millimoles BuBF₂ in 250 ml. PhMe 100 g. C₃H₆ was added at -78°, and 25 g. I, freshly distd. over Na, was then added dropwise in 5 hrs. at the same temp. (-78°) under N. After 20 hrs., the reaction was stopped by the addn. of 10 ml. MeOH, the solvent evapd., and the residue slowly poured into 1.5 l. MeOH. The pptd. polymer was filtered, washed with MeOH, and dried at 80° in vacuo to give 21.5 g. poly-I, m. 170-80°, intrinsic viscosity 0.3 at 30° (in PhMe) and sol. in aromatic hydrocarbons, CHCl₃ and Et₂O.

Bibliographic Information

Copolymers of ethylene with cycloolefins. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio; Pasquon, Italo; Valvassori, Alberto; Zambelli, Adolfo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 37 pp. BE 619877 19621031 Patent language unavailable. Priority: IT 19610708. CAN 58:53817 AN 1963:53817 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (4390)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 619877		19621031	BE	
GB 967836			GB	
IT 659327			IT	

Priority Application

IT	19610708
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Abstract

C₂H₄ is copolymerized with cycloolefins at -50 to +50° by using catalysts prepd. from transition metals of Groups IV, V, or VI or organometallic compds. of Groups IA, II, or IIIA to yield linear thermoplastic compns. contg. ≤50 mole % cycloolefins alternating with polyethylene units. The reaction products were characterized by fractional extrn., infrared, x-ray, and radioanalysis by use of radioactive C₂H₄ for polymerization. The polymer fractions obtained were of waxy or polyethylene-like consistency. For example, under N, to 100 ml. dry toluene and a catalyst prepd. at -30° from 40 ml. anhyd. toluene, 3.6 millimoles V acetylacetonate, and 18 millimoles Et₂AlCl was added at -60°, 3.9 g. cyclobutene in 50 ml. toluene (-78°) followed by 150 l. C¹⁴-labeled C₂H₄ during 3 hrs. After 2 hrs., the reaction was stopped by addn. of 10 ml. MeOH and the reactor allowed to attain room temp. The gelatinous reaction product, when mixed with 1 l. MeOH contg. 10 ml. 38% of HCl, can be

filtered. It yields, after washing with hot MeOH and vacuum drying, 5.15 g. (88%) of a powd., white thermoplastic material.

Bibliographic Information

Ketene-aldehyde and ketone-aldehyde linear copolymers. Natta, Giulio; Mazzanti, Giorgio; Pregaglia, Gianfranco; Pozzi, Giancarlo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 18 pp. BE 616909 19620515 Patent language unavailable. Priority: IT 19610427. CAN 58:21074 AN 1963:21074 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 386)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 616909		19620515	BE	
DE 1197625			DE	
GB 950508			GB	
IT 649439			IT	

Priority Application

IT 19610427

Abstract

Copolymers prepd. from ketones and ketenes have been described in Belg. 600,910 in which a part of the repeating units are formed by the opening of the carbonyl unsatn. In continuing this work, the carbonyl unsatn. is supplied by aldehydes. For example, 15 cc. of a 4M soln. of di-methylketene (I) in toluene is mixed with 6 cc. of BzH. After blanketing with N and cooling to -78°, 1 millimole BuLi in 10 cc. toluene is added. The rapid exothermic reaction causes an increase in viscosity, thus forming a gel in a few min. After 29 min., the catalyst is decompd. with MeOH and a white powder, partially sol. at the b.p. in CHCl₃, PhNO₂, and C₆H₆, is pptd. A 62% yield (6.5 g.) of polymer based on I is obtained. The crude polymer has a slight crystallinity that increases when the material is taken up in boiling n-C₇H₁₆ or cyclohexanone. Fractionation by extrn. with solvents at the boil gives 23.4% sol. in Et₂O, 17.9% sol. in C₆H₆, and 58.7% residue. Molded samples of the 3 materials show different dimensional stability at different temps. The material extd. by C₆H₆ is liquid at 250°, while the residue m. 290°. The C₆H₆-insol. polymer contains 74.59% C and 6.81% H. The crude polymer contains 76.35% C; 6.63% H

Bibliographic Information

Controlled medium-molecular-weight cis-1,4-polybutadienes. Natta, Giulio; Porri, Lido; Pasquon, Italo; Mazzei, Alessandro. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), 5 pp. DE 1117878 19611123 Patent language unavailable. Priority: IT 19590803. CAN 58:21035 AN 1963:21035 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 256)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1117878		19611123	DE 1960-M46114	19600801
GB 924427			GB	
IT 613456			IT	

Priority Application

IT 19590803

Abstract

By controlled concn. proportions of various aliphatic solvents (butane, pentane, etc.) with C₆H₆ and toluene in the presence of dialkylaluminum monohalides and combinations of Group VIII metals, polymers of fixed, moderate (65,000-500,000) mol. wt. are produced.

Bibliographic Information

Copolymers from unsaturated endomethylene compounds, ethylene, and α -olefins. Natta, Giulio; Pasquon, Italo; Zambelli, Adolfo; Giustiniani, Pier A. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 15 pp. BE 616851 19620515 Patent language unavailable. Priority: IT 19610426. CAN 58:15167 AN 1963:15167 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4353)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 616851		19620515	BE	
GB 951022			GB	

Priority Application

IT	19610426
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Abstract

Copolymers of norbornene (I) or dicyclopentadiene (II) and C₂H₄ and (or) propylene, or 1-butene, or 4-methyl-4-pentene were prepd. at -15° in the presence of Et₂AlCl, EtAlCl₂, or Et₂Al, and vanadium tris(acetylacetonate) (III), vanadium stearate, a VCl₄-pyridine complex, or other components. Some of the rubberlike copolymers were vulcanized. Thus, in a glass-lined reactor, 20 ml. PhMe, 10 ml. I labeled with C¹⁴, 1.5 millimoles Et₂AlCl, and 1.4 × 10⁻⁴ moles III were mixed at -15°. The clear mixt. was satd. with C₂H₄ at 20 mm.; this pressure was maintained 2 hrs. The polymerization was stopped by addn. of MeOH to give a powd. polymer. According to radiation measurements, the polymer contained 50% of each monomer. The x-ray spectrum showed no crystallinity, but the Geiger spectrum revealed a max. at the angle 2 θ = 17° (Cu K α). In the absence of C₂H₄, no polymer was formed. If, instead of the above catalyst, TiCl₄ and Et₃Al were used, a spongy homopolymer of I was formed. In another example, 300 ml. PhMe, 4 mole Et₂AlCl, and 2 g. II were stirred. A mixt. of 2 vols. C₂H₄ and 5 vols. propylene was bubbled through the soln. for 20 min. Then a mixt. of 0.3 millimole III and 3 g. II in 30 ml. PhMe was added dropwise for 1 hr. Simultaneously, C₂H₄ and propylene were introduced. Finally, excess MeOH was added. Filtering and drying gave 10 g. copolymer contg. 5% II by infrared analysis. A sample was treated with abrasion-resistant C 50, ZnO 5, stearic acid 2.5, mercaptobenzothiazole 0.5, tetramethylthiuram disulfide 1, and S 2 parts and vulcanized at 143.5° for 40 min. The product had a tensile strength of 180 kg./sq. cm., an elongation at break of 500%, and a modulus of 280 kg./sq. cm. at 300%.

Bibliographic Information

Linear polymers of increased molecular weight. Natta, Giulio; Dall'Asta, Gino; Mazzanti, Giorgio; Pasquon, Italo; Valvassori, Alberto; Zambelli, Adolfo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 31 pp. BE 615314 19620413 Patent language unavailable. Priority: IT 19610321. CAN 58:3581 AN 1963:3581 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4378)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 615314		19620413	BE	
GB 932658			GB	
IT 648813			IT	
US 3250755		19660510	US 1962-181234	19620319

Priority Application

IT	19610321
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Abstract

The prepn. of copolymers is described which are composed of C₂H₄ and olefins contg. an internal double bond, e.g. 2-hexene, 2-heptene, stilbene, and phenyl-2-butene. As catalysts serve colloidal dispersions or solns. composed of compds. of transition metals from Groups IV, V, and VI, and organometallic compds. from metals of Groups IA, II, IIIA. The preferred combination is a V halide with an org. Al compd. Thus, into a reactor, purged with N and cooled to -30°, there were introduced 10 g. cis-2-butene and a catalyst mixt. prepd. by dissolving 3.6 mmol VCl₄ and 9.0 mmol (trihexyl)aluminum in 30 cc. anhyd. heptane. After shaking, radioactive polyethylene (of known specific activity) was introduced under partial pressures of 50, 100, 200 mm., resp., for 8.5 h. Then the reaction product was poured into 500 mL. MeOH contg. 5 mL. HCl, filtered, washed with MeOH, and dried at reduced pressure and 50-60° to recover 2.16, 3.83, 6.14 g., resp., of copolymer. In a similar series of expts., by using trans-2-butene, the wt. of copolymer recovered was 1.26, 2.44, 4.63 g., resp. In all samples, the content of C₂H₄ was detd. radiochem. and the content of 2-butene by IR anal. The latter was found in the cis-series to be 40.5, 38, 22 mol %, and in the trans-series 19, 16, 10.5 mol %, resp. In all samples, the crystallinity (polyethylene type) was low compared with a polyethylene sample prepd. under the same conditions. Through successive extrn. with Et₂O, n-hexane, and n-heptane, the above copolymers were divided into 3 fractions and a residue each. All the residues contained 2-5 mol % butene; the n-heptane exts. contained 5-15 mol % butene and both showed light crystallinity (of the polyethylene type). The n-hexane exts. were either powdery or waxy and contained 14-50 mol % butene; from 14-25 mol % butene, there was light crystallinity, but from 45-50 mol % butene, the copolymer was powdery and showed some elastic properties; the degree of crystallinity was high and of a type different from polyethylene.

Bibliographic Information

β-Chlorovinyl ether polymers. Natta, G.; Farina, M.; Bressan, G.; Peraldo, M. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), 13 pp. IT 630655 19611218 Patent language unavailable. Application: IT 19600517. CAN 57:84244 AN 1962:484244 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 298)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 630655		19611218	IT	19600517

Abstract

Unsaturated halogenated polyethers having sterically regular structure are prepd. by using catalysts of the type MeXⁿYmZp (Me is a metal of Group II-III, IV, or V; X' is a halogen; Y is alkyl, alkoxy, aryl, aralkyl, or cycloalkoxy; Z is a Lewis base; n and m are 0 or integers; m + n is the valence of Me; p is 0 or an integer) at +20° to -120°. Thus, 5.6 g. β-chlorovinyl Bu ether (90% cis) was polymerized at -78° by using 0.25 cc. EtAlCl₂ in 40 cc. toluene. A fibrous, white solid (5.6 g.) was obtained having high crystallinity as shown by x-ray examn. Intrinsic viscosity in toluene at 30° was 0.8-100 cc./g. and m.p. was 200°.

Bibliographic Information

Polymers with regular structure. Natta, Giulio; Farina, Mario; Donati, Mario. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 6 pp. DE 1133554 19620719 Patent language unavailable. Priority: IT 19600801. CAN 57:84181 AN 1962:484181 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 322)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
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DE 1133554	19620719	DE 1961-M48622	19610407
GB 907821		GB	
IT 637612		IT	
US 3277067	19661004	US 1961-101475	19610407

Priority Application

IT 19600801

Abstract

By polymerizing monomers of the formula $RCH:CHCH:CHCOOR'$, in which R and R' are C1-16 substituted or unsubstituted alkyl, cycloalkyl, aryl, or aralkyl groups and R may also be H, at -100 to +20° in the presence of org. Li compds., 1,4-polymers are obtained having a regular structure and mainly trans at the double bond. X-ray examn. shows a high degree of crystallinity. The polymers have asym. C atoms. They are a new group of tritactic polymers and may be called erythro- or threo-trans-diisotactic polymers. Fibers obtained from some of the polymers are very elastic. The polymers can be cross-linked to insol. and thermosetting polyesters. The polymerization is carried out in an anhyd., inert or basic solvent and under an inert gas. Thus, 9.6 g. Me sorbate in 40 cc. anhyd. toluene under N is cooled to -70°; then 2 cc. BuLi in pentane (6 millimoles) is added, and the mixt. polymerized at -40° for 16 hrs. and then mixed with MeOH. The polymer m. 210° and has an intrinsic viscosity of 50 cc./g. (in tetrahydronaphthalene at 135°).

Bibliographic Information

Vulcanizable compounds based on terpolymers and butyl rubber. Crespi, Giovanni; Natta, Giulio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 17 pp. BE 614316 19620315 Patent language unavailable. Priority: IT 19610224. CAN 57:83983 AN 1962:483983 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 367)

Patent Family Information

<u>Patent No.</u>	<u>Kind</u>	<u>Date</u>	<u>Application No.</u>	<u>Date</u>
BE 614316		19620315	BE	
GB 957104			GB	
IT 659324			IT	

Priority Application

IT 19610224

Abstract

A copolymer of low unsatn. obtained essentially from C₂H₄ and α -olefins, i.e. a terpolymer (I), forms with a copolymer of isobutylene and small amts. of isoprene, i.e. butyl rubber (II), in any proportions, a homogeneous mixt. suitable for compounding with the usual ingredients and vulcanizing in the usual way to obtain a good rubber product. Generally, the modulus at 300% elongation, the tensile strength, and the hardness are improved, as compared with those of the component copolymers. Thus, samples with 100, 70, 50, 30, and 0 part I obtained from C₂H₄, C₃H₆, and 8-10% of dicyclopentadiene and 0, 30, 50, 70, and 100 parts, resp., of II were homogenized on a lab. mixing mill, mixed with phenyl- β -naphthylamine 1, lauric acid 2, ZnO 5, S 2, tetramethylthiuram disulfide 1, and mercaptobenzothiazole 0.5 part and vulcanized in a press for 30 min. at 150°. The tensile strengths of the products were 49, 69, 72, 49, and 44 kg./sq. cm.; the elongations at rupture 410, 385, 390, 450, and - %; the moduli at 300% elongation 21.5, 31.0, 30.0, 20.5, and 15.0 kg./sq. cm.; the Shore hardnesses 49, 50, 49, 47, and -; and the resiliences at 20° 37, 32, 30, 27, and 22%, resp.

Bibliographic Information

Control of molecular weight during the polymerization of butadiene to cis-1,4-polybutadiene. Natta,

Giulio; Porri, Lido; Pasquon, Italo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 3 pp. DE 1135664 19620830 Patent language unavailable. Priority: IT 19600607. CAN 57:76923 AN 1962:476923 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 287)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1135664		19620830	DE 1961-M49272	19610606
GB 941739			GB	

Priority Application

IT	19600607
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Abstract

When butadiene is polymerized in C₆H₆ by using Co acetylacetonate or CoCl₂-pyridine complex with Et₂AlCl, the mol. wt. of the product is controlled by varying the concn. of butadiene in the reaction mixt.; the higher the concn., the higher the mol. wt.

Bibliographic Information

Copolymers from at least one compound containing conjugated double bonds. Natta, Giulio; Farina, Mario; Donati, Mario. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 19 pp. BE 611901 19620622 Patent language unavailable. Priority: IT 19601223. CAN 57:70111 AN 1962:470111 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 357)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 611901		19620622	BE	
DE 1171159			DE	
GB 921512			GB	
IT 642096			IT	

Priority Application

IT	19601223
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Abstract

Copolymers were prepd. from 1 compd. of type R₁(R₂)C:C(R₃)C(R₄)C(K₅)R₆ (R₁, R₂, R₃, R₄, and R₅ are H, alkyl, cycoalkyl, or aryl radicals contg. 1-8 C atoms, and R₆ is a carboxyl, ester, amide, or CN group) and 1 compd. of type R₁(R₂)C:C(R₃)R₄ (R₁, R₂ and R₃ are H, alkyl, cycloalkyl, or aryl radicals with 1-8 C atoms, and R₄ is a carboxyl, ester, amide, or CN group) in the presence of anionic catalysts, such as (a) alkyl or aryl Mg or Be compds., or the corresponding alkyl metal hydrides; (b) alkyl or aryl compds. of alkali metals; or (c) compds. of the general formula M₁pM₂l[N(R₁)R₂] mX_n (R₁ and R₂ are alkyl, cycloalkyl, aryl, or alkylaryl radicals, or form a heterocyclic nucleus with N; M₁ is an alkali metal; M₂ is a metal of Group I, II, or III; and x is H or halogen). Esp. active compds. were alkylolithiums, PhMgBr, and Et₂NMgBr. Polymerization was done between -80° and 20° under an inert atm. in a solvent, such as heptane, toluene, Et₂O, or tetrahydrofuran. The copolymers were obtained in optically active form when the reaction was done in the presence of an optically active form of the catalyst. X-ray investigation showed the copolymers to be amorphous, which represented a true asym. structure owing to the C atoms of the chain. Products with a high proportion of one monomer were easily extruded into threads with high m.p. and transition temp. lower than that of the corresponding homopolymer. Sol. products in volatile solvents were used for the manuf. of transparent coatings for metals. The products showed a great affinity for acetate dyes and also, when partially sapond., for basic dyes. The copolymers were optionally cross-linked. For example, reaction of 0.9 g. Me sorbate and 4.1 g. Bu sorbate in 20 cc. anhyd. toluene at -40° in the

presence of 0.003 mole BuLi under N yielded, after 2 hrs., 0.8 g. copolymer contg. 35 mole % Me sorbate. Similarly, Bu β -styrylacrylate, Me methacrylate, acrylonitrile, N,N-diethylsorbamide, and sorbonitrile were copolymerized with Me or Bu sorbate.

Copolymerization at -40° for 3 hrs. of 1.9 g. Bu sorbate (ester of trans,trans-sorbic acid) and 1.9 g. Bu β -styrylacrylate in 20 cc. toluene in the presence of 0.003 mole iso-AmLi (prepd. from S(+)-methyl-1-chlorobutane, $[\alpha]_{20D} = 1.65$, and Li in petr. ether) yielded a product with $[\alpha]_{20D} = 0.60$.

Bibliographic Information

Polymer compositions for crystalline textile fibers. Giustiniani, Piero; Natta, Giulio; Farina, Marlo; Mazzanti, Giorgio; Crespi, Giovanni. ("Montecatini" Societa Generale per l'Industria Mineraria Chimica). (1962), 12 pp. BE 612488 19620131 Patent language unavailable. Priority: IT 19610111. CAN 57:63776 AN 1962:463776 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 359)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 612488		19620131	BE	
DE 1216480			DE	
GB 929769			GB	
IT 647959			IT	
US 3151185		19640929	US 1962-165473	19620109

Priority Application

IT 19610111

Abstract

Polymer mixts. of isotactic poly- α -olefins and polymers from RCH:CHCH:CHCO₂R' compds., where R is H, alkyl, or aryl, and R' is alkyl, are prepd. for use as dyeable textile fibers. Thus, 50 parts of 94% isotactic polypropylene (intrinsic viscosity 1.9 in Tetralin at 135°) is mixed with 50 parts of poly(Me sorbate) (intrinsic viscosity 0.46; same conditions), and extruded at 230-5° to give a fiber with a tenacity of 3-4 g./denier (elongation at break 20-5%), which is dyed in a bath of (f) 5 g./l. Celanthrene Brilliant Blue for 40 min. at 80-90° to obtain a strong and homogeneous color. The fibers may also be dyed with basic dyes by previous hydrolysis with 2N HCl at 70-80° for 1 hr.

Bibliographic Information

Vinyl chloride polymers. Natta, Giulio; Mazzanti, Giorgio; Giannini, Umberto; Cesca, Sebastiano. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 16 pp. BE 611654 19620115 Patent language unavailable. Priority: IT 19601219. CAN 57:63662 AN 1962:463662 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 350)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 611654		19620115	BE	
GB 944741			GB	

Priority Application

IT 19601219

Abstract

Cryst. polymers of mol. wt. >10,000 and a Vicat softening point >90° are prepd. by polymerization of the

monomer either in soln. in an aliphatic, cycloaliphatic or aromatic hydrocarbon, or a halogen deriv. thereof (e.g. n-heptane or C₆H₆), or in the fused state. The catalyst system used consists of a transition metal compd. (e.g. TiCl₃ or BuOTiCl₃) with an org. Al compd. of the general formula AlR'ⁿ(OR'')^mX^p, in which R' is an aliphatic or aromatic hydrocarbon radical with ≥10 C atoms; R'' is similar to R' or is an alkyl, aryl, or cycloalkyl radical which may contain an ether-O atom; X is F, Cl, Br, or I; m is 1-2; n is 1-2; p is 0 or 1; and m + n + p = 3. The mole ratio of the org. Al compd. to the transition metal compd. is 1-10:1. The transition metal compd. may also be a V compd.

Bibliographic Information

Polyolefins with optical activity in solution. Natta, Giulio; Pino, Piero; Lorenzi, Gian P. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 6 pp. DE 1131888 19620620 Patent language unavailable. Priority: IT 19590115. CAN 57:63643 AN 1962:463643 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 222)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1131888		19620620	DE 1960-M43971	19600113
GB 903647			GB	
GB 903648			GB	
US 3193544		19650706	US 1960-2607	19600115

Priority Application

IT	19590115
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Abstract

To obtain the title polyolefins, optically active olefins (I) of the formula CH₂:CHR, where R is an optically active, branched C₄-8 alkyl group or an alkaryl group with an asym. C atom, are polymerized by catalysts (II), which are formed by reaction of metal compds. from Groups IV-VI with optically inactive metal alkyls from Groups I-III; or the polyolefins are prepd. from optically inactive olefins and the same type of catalysts, when the latter are made from optically active metal alkyls (III). Esp. suitable I are (+)-(S)-3-methyl-1-pentene, (-)-(S)-4-methyl-1-hexene, (+)-3-phenyl-1-pentene, and (+)-5-methyl-1-heptene, or their optical antipodes. A preferred II is obtained from trialkylaluminum compds. and TiCl₃, while III is made from metal alkyls of the formula MeR_n, where Me is Al, Be, Mg, or Li; R is an optically active alkyl group, and n the valency of the metal. A preferred III is made from TiCl₃ and (+)-tris [(S)-2-methylbutyl]aluminum etherate. For example, with N as inert gas, 3.38 g. freshly distd. iso-Bu₃Al was treated with 0.88 g. TiCl₄. After the formation of the catalyst, (+)-(S)-3-methyl-1-pentene (b.p. 54°, n_D 1.3845) was added and polymerized at 80° until no reflux was observed. The catalyst was destroyed with 50 cc. abs. EtOH. Then, the polymer was boiled for several hrs. with 300 cc. MeOH, filtered, and dried on a water bath at 20 mm. The 6.92 g. olefin used gave, after 490 min. reaction period, 3.16 g. (+)-poly[(S)-3-methyl-1-pentene]. The polymerization was compared with racemic 3-methyl-1-pentene, 6.68 g. of which gave 2.61 g. polymer. The amts. of exts. with Me₂CO, Et₂O, isooctane, and C₆H₆ were detd. The optical rotation, [α]_D²⁷, in decahydronaphthalene varied from +45.4 to +112° for the different fractions of the polymer from the optically active olefin.

Bibliographic Information

Butadiene copolymers. Natta, Giulio; Porri, Lido; Carbonaro, Antonio; Pasquon, Italo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 22 pp. BE 612847 19620215 Patent language unavailable. Priority: IT 19610120. CAN 57:63414 AN 1962:463414 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 363 + U 363/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
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BE 612847
GB 968899

19620215 BE
GB

Priority Application

IT 19610120

Abstract

Copolymers are prepd. comprising butadiene, principally of trans-1,4 structure, and diolefins which are partially of trans-1,4 and partially of 1,2 structure. The diolefms have the general formula $CH_2:CHCH:CHR$, where R is an alkyl, aryl, or alkylaryl group, e.g. 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene, 5-phenyl-1,3-pentadiene, or 6-methyl-1,3-heptadiene. The copolymers contain 65-90% moles of butadiene and melt at 0-30°. Elastomers obtained by vulcanization of the copolymers crystallize by elongation at ambient or elevated temp. The copolymers are prepd. by contact between the monomer mixt. and a homogeneous catalyst obtained by treating a V compd. with an alkylaluminum halide of the general formula $R(R')AlX$, in which R and R' are the same or different alkyl, aryl, or alicyclic groups, and X is a halogen. The V compd. is a hydrocarbon-sol, or -insol. compd., e.g. V tris(acetylacetonate). The catalyst is prepd. by the reaction between the V compd. and an alkylaluminum halide of general formula $RAIX_2$ (R being an alkyl, aryl, or alicyclic group, and X a halogen) which may be complexed by an electron-donor, e.g. Me₂O or pyridine. The polymerization temp. is between -80° and +50° and may be carried out in a soln. in aliphatic or aromatic hydrocarbons or their mixt.

Bibliographic Information

Stereoregular polymers of methacrylonitrile. Natta, Giulio; Mazzanti, Giorgio; Dall'Asta, Gino. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), 21 pp. BE 611491 19611229 Patent language unavailable. Priority: IT 19601214. CAN 57:50105 AN 1962:450105 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 347)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 611491		19611229	BE	
GB 933595			GB	
US 3231552		19660125	US 1961-158343	19611211

Priority Application

IT 19601214

Abstract

$CH_2:C(Me)CN$ (I) is polymerized by means of an organometallic catalyst of the formula $MR^aR^bX_c$, in which M is a Group IA, II or III metal, R' and R'' are similar or different alkyl, aryl or alkaryl groups, A = 0-3, b = 1-3, and c is a no. such that a + b + c = valence of M. The polymerization is carried out in an inert solvent at 0-100°; O- or N-contg. solvents capable of complex-formation with the catalyst should not be used. The resulting linear polymers of I differ in their phys. and mech. properties from the amorphous polymers of I known hitherto. Organometallic catalysts contg. Mg or Be give cryst. polymers; the other catalysts give amorphous polymers. Thus, 10 g. anhyd. I is added with stirring during 30 min. to a mixt. comprising 410 mg. Et₂Mg in 100 cc. PhMe free from S at 70°; the mixt. is maintained for 6 hrs. at 70° and then poured into 500 cc. MeOH contg. 2-5% HCl; when the ppt. has become completely bleached, the liquid is decanted, the polymer washed with MeOH, and dried to yield 9.5 g. poly-I as a white powder, insol. in most org. solvents, but swollen by some solvents, such as PhCN, PhCOMe, PhNO₂ and Me₂NCHO, which dissolve 10-20% of an amorphous fraction; the residual, cryst. polymer has x-ray diffraction spacings d = 7.85, 5.95, and 4.55 Å. The polymer, m. 220-50°, can be extruded as hot-drawable filaments, or molded by injection or compression; it resists org. and mineral acids, but is readily hydrolyzed by 50% aq. KOH. On heating to > 150° it turns a red color which is eliminated by a short treatment with MeOH contg. 5-10% HCl.

Bibliographic Information

Catalysts for the polymerization of unsaturated hydrocarbons. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo; Bernardini, Francesco. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1960), 6 pp. IT 601433 19600120 Patent language unavailable. Application: IT 19581128. Priority: IT 19581128. CAN 57:50034 AN 1962:450034 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 220)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 601433		19600120	IT	19581128

Priority Application

IT	19581128
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Abstract

Hydrocarbons of vinylic type can be polymerized with catalysts prepd. from halides of metals of Group I-III, free from C-metal bonds, contg. N-metal bonds, and having the formula $X_nM[N(R_1)R_2]_m$, where M is a metal as described, X is Cl, Br, or I, R₁ and R₂ are alkyl, cycloalkyl, aryl, or alkylaryl radicals, n = 0 or ≥ 1, m ≥ 1, and n + m is the valence of M. R₁ and R₂ can also form with N heterocyclic rings. As catalysts, products of the formula (XM)₂NR, where M is Be or Mg, and X and R have the above indicated meaning, as well as products contg. the N-M bond, but free from org. groups, can also be used. Catalysis is carried out in mixt. with halogenated derivs. of metals of Groups IV-VIII, in which the valence of the metal is preferably not the highest possible. The polymers obtained have linearity and crystallinity higher than those prepd. with the Ziegler catalysts, and, in the case of propylene, 1-butene, and other α-olefins, are highly isotactic. Thus, 5 g. of a mixt. of Al(NPh₂)₃ (I) and 2 g. TiCl₃ in 250 cc. anhyd. C₆H₆ is poured under N into a pressure vessel. With stirring C₂H₄ is introduced until the pressure reaches 45 atm. After 8 hrs. at 110° and cooling to 40°, 130 g. polyethylene is obtained. The product, washed with MeOH contg. HCl and MeOH, has a mol. wt. of 780,000, a crystallinity of 80%, and a m.p. of 134°.

Bibliographic Information

Elastic copolymers. Natta, Giulio; Mazzanti, Giorgio; Valvassori, Alberto; Sartori, Guido; Crespi, Giovanni. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 31 pp. BE 610221 19620514 Patent language unavailable. Priority: IT 19601114. CAN 57:49925 AN 1962:449925 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 344)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
BE 610221		19620514	BE	

Priority Application

IT	19601114
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Abstract

Linear amorphous elastomers of high mol. wt. are prepd. by copolymerization of C₂H₄ or α-olefins having 3-8 C atoms and diolefins contg. 1 terminal unconjugated double bond. The catalyst used is a mixture of an alkylaluminum dihalide or alkylberyllium halide and a hydrocarbon-sol. org. V compd. in which one or more of the metal valences are coupled to an org. group by an O atom, such as vanadyl haloalkoxides or V tris-(acetylacetonate). These elastomers are vulcanized with S or S compds.

Bibliographic Information

Aldehydes. Natta, Giulio; Ercoli, Raffaele; Castellano, Salvatore. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), 5 pp. US 3008996 19611114 Patent language unavailable. Priority: IT 19540410. CAN 57:48929 AN 1962:448929 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 51)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3008996		19611114	US 1955-498693	19550401

Priority Application

IT	19540410
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Abstract

The synthesis of aldehydes by the oxo process makes use of $[\text{Co}(\text{CO})_4]_2$ catalyst. Thus, using 1.2 g. $\text{Co}_2(\text{CO})_8$ and 11.6 g. cyclohexene in 43 g. n-heptane under 20 atm. CO and 100 atm. H at 115° 30 min. yields 46.5 g. liquid product contg. 10.3 g. hexahydrobenzaldehyde.

Bibliographic Information

Diolefin polymerization and catalyst. Natta, Giulio; Porri, Lido; Fiore, Leonardo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1962), 4 pp. US 3016371 19620109 Patent written in English. Priority: IT 19590226. CAN 57:36895 AN 1962:436895 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 202)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3016371		19620109	US 1959-794730	19590220
GB 908778			GB	

Priority Application

IT	19590226
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Abstract

$\text{Co}(\text{NO})_2\text{Cl}$, when combined with organometallic compds. of Groups II and III forms aliphatic and aromatic hydrocarbon-sol. catalysts of high efficiency and cis-1,4 directivity for polymerizing butadiene. Thus, to an air- and moisturefree mixt. of 100 cc. n-heptane, 0.1 cc. Et_2AlCl , and 0.001 g. of $\text{Co}(\text{NO})_2\text{Cl}$, there is added 99% butadiene (20 g.) during 20 min. at $10-20^\circ$. The reaction is terminated with 50 cc. MeOH, the polymer coagulated with MeOH.HCl, washed, and dried. Approx. 10.5 g. of polymer having 95.3% cis-1,4 structure (detd. by infrared) is obtained. Polybutadienes produced in this manner crystallize readily (m.p. 0° in the unstretched state) and, after vulcanization, have tensile strengths corresponding to those of natural rubbers.

Bibliographic Information

Unsaturated gaseous hydrocarbons from ternary gas mixtures by solvent extraction. Natta, Giulio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), 9 pp. DE 1114475 19611005 Patent language unavailable. Priority: IT 19520521. CAN 57:22714 AN 1962:422714 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (F 84)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1114475		19611005	DE 1953-M18597	19530515

Priority Application

IT 19520521

Abstract

Continuous sepn. of gas (a) from gases (b) + (c) is based on soln. of (a) at above-atm. pressure in a solvent in which (b) is less sol., and (c) is insol. The passage of (c) contg. some (a) through the soln. removes (b) but not (a), which is then recovered. Thus, butadiene can be sepd. from 2-butene by using N and HCONMe₂, and C₂H₂ can be sepd. from CO₂ by using CO or H and ethylene glycol diacetate.

Bibliographic Information

Polymerization of vinylpyridines. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo; Dall'Asta, Gino; Bernardini, Francesco. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), 7 pp.
 DE 1114638 19611005 Patent language unavailable. Priority: IT 19590625. CAN 57:4888 AN 1962:404888 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (u 248)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1114638		19611005	DE 1960-M45635	19600614
GB 898312			GB	
IT 611357			IT	
US 3182045		19650504	US 1960-38580	19600624

Priority Application

IT 19590625

Abstract

Vinylpyridine (I) polymers with sterically regular structure were prepd. with alkyls, awls, hydrides, alkyl amides, and aryl amides of Group I, II, and III metals and halo-metal derivs. Thus, a soln. of 170 g. Ph₂NH in 300 ml. dry Et₂O was dropped into a stirred suspension of 9 g. LiAlH₄ (II) in 150 g. Et₂O and stirred 6 hrs. at the b.p. Most of the EtO was decanted, the product dissolved in 3.21. hot C₆H₆, filtered, and cooled to give 84 g. large crystals of LiAl(NPh₂)₃H.Et₂O which changed to the ether-free compd. (III) at 150°/1 mm. Similarly, iso-Bu₃Al and Me₂NH heated at 190-200° for 15 hrs. gave [Al(NMe₂)₃]₂ (IV) the dimeric constitution of which was shown by cryoscopic detn. of the mol. wt. Freshly distd. 2-1 (10 g.) was introduced into a stirred mixt. of 100 ml. of dry, O-free toluene and 1 g. PhMgBr (V) at 70°. After 5 hrs., a white ppt. produced by addn. of 200 ml. heptane was dissolved in 150 ml. N HCl, neutralized by pouring into aq. NH₄Cl, dried by dissolving in boiling C₆H₆ and distg., and repptd. with heptane. The product obtained in quant. yield consisted of 75-80% cryst. polymer insol. in boiling Me₂CO, softening at 173°, intrinsic viscosity 0.15 (in CH₆ at 30°). In similar expts. the following polymers of 2-1 were prepd. [catalyst (% of 2-1), temp., % insol. in hot Me₂CO, intrinsic viscosity in C₆H₆ at 30° given]: V (10), 40°, 90, 0.45; V (10), 15°, 80, 0.75; Et₂Mg (1.67), 30% -, 0.61; Et₂NMgBr (5), 65° 82, -, V (5), 40°, 87, 0.49 [in HCONMe₂ (VI)]; Be(NMe₂)₂ (1.33), 45°, -, 0.45 (in VI); Ph(Me)NMgBr (8), -, -, 0.6 (in VI); II (3), 70°, 83, -, III (5), 65°, 80, -, IV (4), 80°, -, -. A polymer of 4-1 prepd. similarly with 4% Et₂Mg at 70° was slightly cryst., viscosity 0.45 (in VI), softening at 195-200°.

Bibliographic Information

Crystallizable organometallic complex compounds containing titanium and aluminum. Natta, Giulio; Mazzanti, Giorgio; Giannini, Umberto; Cesca, Sebastiano. ("Montecatini" Societa Generale per l'Industria

Mineraria e Chimica; Karl Ziegler). Patent language unavailable. Priority: IT 19590113. CAN 56:82690 AN 1962:82690 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (U 226)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1105416			DE	

Priority Application

IT	19590113
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Abstract

A procedure for the prepn. of $[(C_5H_5)_2TiAIR_2]_2$ (R = alkyl, C_5H_5 = cyclopentadienyl) was described. For R = Et, e.g., 150 ml. C_6H_6 , contg. 12.52 g. $(C_5H_5)_2TiCl$ and 20 g. $Al(Et)_3$ was heated 8 hrs. in N. After evapn. in vacuo, the residue was twice dissolved in n- C_6H_{14} at 50° and crystd. at -30° to give 7.1 g. $EtAl[Ti(C_5H_5)_2]_2AlEt_2$, m. 170-1°. The compd. was diamagnetic and a very stereospecific catalyst for the polymerization of olefins and hydrocarbons contg. a vinyl group.

Bibliographic Information

Polymerization of α -olefins. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), US 3014018 19611219 Patent language unavailable. Priority: IT 19570228. CAN 56:61350 AN 1962:61350 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (U 154)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 3014018		19611219	US 1958-717339	19580225
GB 890078			GB	

Priority Application

IT	19570228
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Abstract

Linear, regular head-to-tail polypropylene of regular structure is prepd. by contacting propylene in an inert solvent with $TiCl_4$ and a tri-alkyl aluminum or dialkyl aluminum monohalide in which the alkyls contain 2-16 C atoms, as a reducing agent for $TiCl_4$, and controlling the polymerization rate by using the $TiCl_4$ and Al compd. in a molar ratio of 1: 15 to 1:20. Thus, a polymerization autoclave, kept at 60°, was flushed with N_2 , and evacuated until it was completely free of air and moisture. A soln. of 2.75 g. $AlEt_3$ (free of alkyl Al hydrides and of halogens and contg. only 5% diethylaluminum monoethylate as an impurity) in 100 cc. heptane and successively a soln. of 1.73 g. $TiCl_4$ in 200 cc. heptane were introduced into the autoclave within about 10 sec. The autoclave was shaken and after various given times, propylene was quickly introduced from a tank (where it was kept at 7 to 6 atm. pressure and connected to the polymerization vessel by a stainless steel coil) until a pressure of 5 atm. was obtained in the autoclave. (In the tank, the pressure was then brought again to 7 atm. by means of a cylinder connected thereto and contg. liquid propylene). The pressure in the autoclave was kept constant at 5 atm., and the course of the polymerization followed by observing the pressure drop in the tank, from which the wt. in grams of propylene absorbed in 5 min. intervals was calculated. Every time the pressure decreased to 6 atm., it was brought again to the initial value of 7 atm. by means of the cylinder contg. propylene. A table shows the course of the instantaneous polymerization rates, in runs carried out introducing the monomer at various times after the prepn. of the catalyst. Other tables were given showing the variations in the amt. of propylene absorbed in 30 min. by varying the aluminum compd. : $TiCl_4$ molar ratio, the amt. of residue after extrn. of the crude polymerizate with n-heptane, and the intrinsic viscosity of the polypropylenes obtained (varied from

1.7 to 3.26). Other metal alkyl compds.

used were: $\text{Al}(\text{C}_6\text{H}_{13})_3$, LiC_4H_9 , and Et_2AlCl . The tables show that in the case of α -olefins and for optimum results with respect to both the rate at which the α -olefin polymerizes and the stereospecificity of the catalyst for orienting the polymerization to the production of polymers comprising the isotactic structure, the molar ratios of the TiCl_4 and metal alkyl are critical and different from the molar ratios which have been disclosed for use in prep. the catalyst to be used in the polymerization of C_2H_4 . It is possible to select the metal alkyl (on the basis of its alkylating capacity) and the molar ratio thereof to the TiCl_4 , which will result in the production of polymeric α -olefin in the shortest possible time consonant with the desired proportion of isotactic structure content.

Bibliographic Information

Polymerization of conjugated diolefins. Natta, Giulio; Porri, Lido; Fiore, Leonardo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1959), IT 588861 19590219 Patent language unavailable. Application: IT 19580122. CAN 56:61184 AN 1962:61184 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 197)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 588861		19590219	IT	19580122
DD 24063			DD	
GB 903588			GB	

Abstract

Linear, high-mol.-wt. polymers of conjugated diolefins with at least 1 vinyl double bond (isoprene, butadiene) which are linked at the 1- and 4-positions and predominantly in cis-configuration, are prepd. with solid catalysts, obtained by treating alkyl compds. of Al with TiCl_3 . Such catalysts are prepd. from dialkyl Al halide and TiCl_3 (mole ratio Al:Ti = 0.5-5) or from trialkyl Al and TiCl_3 (mole ratio ≤ 0.3 or 0.3:1.5). The polymerization is carried out between -20° and 40° . For example, 0.97g. TiCl_3 (obtained as brown, needle-shaped crystals by action of dark discharges on a gaseous mixt. of TiCl_4 and H, washed repeatedly with anhyd. petr. ether, and dried in vacuo at $50-60^\circ$) is suspended in 80 ml. nheptane. Then 1.1 ml. Et_2AlBr is added, and the mixt. is introduced into an evacuated, 250-ml., jacketed shaking autoclave, cooled to 14° . Approx. 41 g. 98% butadiene is gradually added from a storage bottle. The reaction is stopped after 10 hrs. by introducing 40 ml. MeOH, discharging the mixt., and pptg. the polymer by methanolic-HCl. A yield of 21 g. solid, amorphous polymer results after washing and drying, which consists of 40% 1,4-trans-, 55% cis-, and 5% 1,2-polymer by x-ray analysis. Similarly, 10.5 g. polyisoprene (90-4% 1,4-cis-) is prepd. by making a suspension of 0.75 g. brown TiCl_3 in 40 ml. n-heptane, adding a soln. of 0.34 ml. Et_3Al in 50 ml. n-heptane, and 50 ml. 99% isoprene, the product resembling natural rubber, under the conditions of the 1st example. Cf. CA 53, 3756k.

Bibliographic Information

Alkyl esters of γ -oxopimelic acid. Natta, Giulio; Pino, Piero. (Lonza Elektrizitaetswerke und Chemische Fabriken A.-G.). (1961), DE 1105864 19610504 Patent language unavailable. Priority: CH 19510707. CAN 56:60313 AN 1962:60313 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1105864		19610504	DE 1952-L12721	19520628

Priority Application

CH 19510707

Abstract

Alkyl esters of γ -oxopimelic acid are prepd. by heating a mixt. of C_2H_2 , CO_2 , and alkanol under pressure in the presence of a catalyst of the iron group. Thus, a mixt. of 80 g. MeOH and 5 g. Raney Co is placed in a 300 ml. autoclave and treated with 7 l. C_2H_2 and 250 atm. CO_2 . The mixt. is shaken at 85° until no further absorption, and the pressure of CO_2 is again increased to 250 atm. The process is repeated 4 times, and the mixt. is cooled and fractionated. The fraction b15 150-70° solidified and was washed with petr. ether-benzene to give 20 g. di-Me γ -oxopimelate, m. 56° , b. $276-7^\circ$ (decompn.).

Bibliographic Information

Copolymers of 1,3-butadiene and isoprene. Natta, Giulio; Pasquon, Italo; Porri, Lido; Zambelli, Adolfo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1961), DE 1113822 19610914 Patent language unavailable. Priority: IT 19590424. CAN 56:54079 AN 1962:54079 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 236)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1113822		19610914	DE 1960-M45080	19600422
GB 935425			GB	
IT 611230			IT	

Priority Application

IT 19590424

Abstract

Linear copolymers of high mol. wt. having mostly cis-1,4 structure are obtained by reaction of highly purified 1,3-butadiene (I) and isoprene (II) at -50 to $+50^\circ$. Co diacetylacetonate (III) and Et_2AlCl are used as catalyst mixts. Thus, a soln. of 1 ml. Et_2AlCl and 0.0045 g. III in 65 ml. PhMe was added to a soln. of 19.6 g. I, 23.2 g. II, and 1 ml. Et_2AlCl in 140 ml. PhMe at 13° . Samples taken at different time intervals showed that the copolymer product contained 54% II in all cases.

Bibliographic Information

Styrene-conjugated diolefin block copolymers. Natta, Giulio; Beati, Enrico; Severini, Febo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1957), DE 1104702 19570802 Patent language unavailable. Priority: IT 19580725. CAN 56:39330 AN 1962:39330 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (D 139)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1104702		19570802	DE	
GB 880928			GB	

Priority Application

IT 19580725

Abstract

A polymer having a high impact strength is prepd. by polymerizing styrene with a high-mol.-wt. linear polymer of a conjugated diolefin having an essentially 1,2- or 3,4 interlinking, the conjugated diolefin having the formula $CH_2:CHC(R):CH_2$, where R is H or a lower alkyl radical. Thus, 4 g. of an amorphous, noncrystallizable

polybutadiene with a 1,2-interlinking and an intrinsic viscosity of 1.41 was dissolved in 96 g. styrene. p-Chlorobenzoyl peroxide (0.4 wt. % based on the mixt.) was added, and the mixt. polymerized in the absence of a solvent by keeping at 80° for 22 hrs. The product was a glossy, transparent mass that could easily be worked in the same manner as styrene. Lamina (3 mm. thick) of the polymer were sufficiently transparent that printing could be read through them.

Bibliographic Information

Polymerization of acrylic monomers. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo; Bernardini, Francesco. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1959), DE 1113089 19590630 Patent language unavailable. Priority: IT 19600621. CAN 56:39313 AN 1962:39313 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 242)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1113089		19590630	DE	
IT 612117			IT	
US 3240772		19660315	US 1960-39219	19600628

Priority Application

IT	19600621
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Abstract

Polymn. of acrylic and methacrylic monomers and CH₂:CHR compds., in which R is H or an hydrocarbon group, can be catalyzed with amides of general formula MpM'[N(R)R']_mXn[O(R'')R''']_g; M is Li, M' is Be, Mg or Al; R and R' are the same or different and are alkyl, cycloalkyl, aryl, or aralkyl groups, or form with the N a heterocyclic ring; X is H or a halogen; R'' and R''' are alkyl, aryl, or aralkyl groups; n is zero or an integer; m + n is equal to the sum of the valences of M and M'; m is at least 1; p and g are 0 or 1. Such catalyst is prepd. by dispersing under N 9 g. LiAlH₄ (purity 80%) in 150 cc. dry ether, adding slowly 170 g. Ph₂NH in 300 cc. dry ether with stirring, and boiling for 6 h. The ether is decanted from the ppt., which is dissolved in 3.2 l. boiling C₆H₆ to give a 1st crop of cryst. LiAl(NPh₂)₃H.OEt₂ (I). Concg. and adding 100 cc. dry ether gives a total yield of 84 g. I. Polymn. is accomplished at -100° to +100° in an inert solvent. Thus, 0.05 g. I in 20 cc. toluene is cooled under N at -70°. Adding 10 g. tert-Bu acrylate in 30 cc. toluene during 1 h., stirring for another 2 h., pouring the mixt. into boiling Me₂CO acidified with some HCl, filtering, and drying gives 8 g. of a white powd. polymer with a crystallinity of 60% and an intrinsic viscosity in CHCl₃ at 30° of 6.1.

Bibliographic Information

Fiber-reinforced rubbers. Natta, Giulio; Crespi, Giovanni; Borsini, Giancarlo. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). Patent language unavailable. Application: IT 19571127. CAN 56:13395 AN 1962:13395 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 190)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 588803			IT	19571127

Abstract

Elastomers of ethylene-propylene copolymers reinforced with polypropylene fibers are prepd. by covulcanizing the 2 components and causing the formation of bridge bonds between them. The fiber can be previously peroxidized. Thus, a mix of a linear copolymer ethylene-propylene (100 parts) and divinylbenzene (60.5%),

alkylarene hydrocarbons (25.1%), ethylvinylbenzene (15%), MPU bone charcoal (25 parts), Dutrex (5 parts), and dicumyl peroxide (7.5 parts) was applied on a polypropylene fabric and heated at 130° for 1 hr. The adhesion at 20° was 3.8 kg./cm.

Bibliographic Information

Polymerization of silicon-, germanium-, lead-, or tin-containing vinyl compounds. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo; Bernardini, Francesco. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1960), DE 1091760 19601027 Patent language unavailable. CAN 55:134760 AN 1961:134760 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 196 + U 196 / A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1091760		19601027	DE 1958-M40018	19581222

Abstract

Monomers of the formula $RM(R')(R'')(CH_2)_nCH:CH_2$ polymerize with catalysts which are used for stereospecific polymn. of α -olefins. to give linear, highly cryst. (>40%), isotactic polymers. In this formula, R, R', and R'' are H, aliph., cycloaliph., or arom. residues, and M is Si, Ge, Sn, or Pb, and n = 0-4. Copolymn. of such compds. with other vinyl compds. is possible. The catalysts are obtained from compds. of the transition elements of the Group IV-VI with an organometallic compd. of Group I-III, e.g. $TiCl_4$ and $(alkyl)_3Al$. Solvent extn. below the m.p. of the cryst. portion gives higher crystallinity. Polymers which derive from $H_3Si(CH_2)_nCH:CH_2$ (I) have the same m.p. as the corresponding C-polymers. The polymers obtained have high m.p. and good heat resistance.

Copolymers from I with C_2H_4 give high-mol.-wt. polymers which resemble unvulcanized elastomers and can be vulcanized because of the reactive SiH group. Sn-contg. polymers may be cross-linked by HCl, or the Cl compds. obtained may react with multivalent bases. Pb or Sn contg. polymers decomp. forming free radicals and thus cross-link to give unmeltable polymers. Further transition metal halides react with the Pb and Sn polymers and catalyze the polymn. of C_2H_4 . Copolymers of α -olefins or vinyl compds. which contain organotin monomers are heat stabilizers for olefin polymers. For example, under N, 1.37 g. Et_3Al , dissolved in 14 g. trimethylallylsilane, was heated for 10 min. to 80°, and 0.865 g. $TiCl_4$ in 10 mL. heptane was added. After 4 h. at 80°, the mixt. was decompd. by 200 mL. MeOH and 1.5 mL. concd. HCl. The solid polymer was washed with MeOH and dried at 80° and 20 mm. to give 9 g. white polymer with 50% crystallinity. Extractive fractionation with Et_2O and heptane gave 29.2% atactic rubbery head-to-tail polymer with an intrinsic viscosity of 0.08 in THF at 135°. The 2.8% heptane ext. was partially crystd. with 0.35 intrinsic viscosity, while the 68% insol. was a linear polymer, m. 290-300°.

Further examples comprise catalysts with Et_3Al and $TiCl_3$ or VCl_4 , and the monomers trimethylallyltin, 5-trimethylsilyl-1-pentene, trimethyl-5-pentenyltin, and allylsilane.

Bibliographic Information

Isotactic poly(vinyl ethers). Natta, Giulio; Dall'Asta, Gino; Oddo, Nino. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1960), DE 1091754 19601027 Patent language unavailable. CAN 55:134709 AN 1961:134709 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 206)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1091754		19601027	DE 1959-M41834	19590615
GB 906604			GB	
US 3133906		19640519	US 1959-819805	19590612

Abstract

Isotactic poly(vinyl ethers) (I) are obtained by the use of Friedel-Crafts catalysts of the type X_nMR_m at -30° to -100° in homogeneous or heterogeneous phase. In this formula, M is Al^{3+} , Ti^{4+} , V^{4+} , or V^{5+} , Cr^{3+} , Fe^{3+} , R an alkyl, aryl, alkoxy, or monocarboxylic residue, n and m = ≥ 1 , and X is halogen. These catalysts, e.g. $EtAlCl_2$ or Ac_2TiCl_2 have weak activity and give I with 10% amorphous portion. For example, into 50 ml. toluene and 0.28 ml. $EtAlCl_2$ under N at -80° , 33 ml. iso-Bu vinyl ether (distd. from Na) was added with stirring during 2-4 hrs. and cooled 4 hrs. at -80° . Finally, 100 ml. MeOH with 1 ml. 38% HCl and 0.1 g. N-(p-hydroxyphenyl)morpholine and further 500 ml. MeOH to ppt. the polymer were added. The dry polymer was dissolved in 100 ml. C_6H_6 , filtered, and pptd. with MeOH to give 19 g. I which was not tacky and could be stretched to highly cryst. threads with 85-90° softening temp. The intrinsic viscosity was 2.2 in toluene at 30° .

Bibliographic Information

Poly(vinyl ethers). Natta, Giulio; Mazzanti, Giorgio; Giannini, Umberto. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1960), DE 1084918 19600707 Patent language unavailable. CAN 55:128148 AN 1961:128148 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 195)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1084918		19600707	DE 1958-M39963	19581217

Abstract

Vinyl ethers $CH_2:CHOR$, in which R is alkyl, cycloalkyl, or aryl, give highly cryst. isotactic polymers, if the bimetallic complexes of Ti and Al are used in the presence of an aromatic solvent at -30 to -80° . Such complexes are $(C_5H_5)_2TiCl_2AlCl_2$ (I) or $(C_5H_5)_2TiCl_2EtAlCl_2$, in which (C_5H_5) is cyclopentadienyl. $(C_5H_5)_2TiCl_2$, obtained from C_5H_5Na and $TiCl_3$ in tetrahydrofuran, m. $279-81^\circ$ (from C_6H_6), is treated with $AlCl_3$ or $EtAlCl_2$ to give the catalyst, which resists O and active H. For example, 9.8×10^{-3} mole $(C_5H_5)_2TiCl_2$ in 60 ml. dry toluene reacted under N with 9.8×10^{-3} mole sublimed $AlCl_3$. After several hrs. heating, the soln. was filtered under N through a diaphragm. The solvent was removed and the residue treated with 80 ml. heptane to give 2 g. blue I, m. $155-60^\circ$. A soln. of 0.27 g. I in 40 ml. dry toluene and 7 g. iso-Bu vinyl ether were introduced simultaneously into a glass container with 10 ml. heptane and kept for 2 hrs. under N at 70° . The polymer was dissolved in 200 ml. C_6H_6 and pptd. by MeOH to give 6.2 g. polyether of high crystallinity with only 3% acetone-sol. portion.

Bibliographic Information

Copolymerization of acetylenes and α -olefins. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1960), Addn. to Ger. 1,052,689 (see Ital. 530,753, CA 52, 15128b). DE 1080778 19600428 Patent language unavailable. CAN 55:115302 AN 1961:115302 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 81/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1080778		19600428	DE 1956-M30745	19560609

Abstract

The catalyst from alkyl compds. of the Groups I-III and halides of Groups IVB-VIIIB is used in the

copolymerization of α -olefins and acetylenic hydrocarbons, esp. PhC.tplbond.CH, and 1-butene or 1-pentene. The mostly linear olefinic polymers can be vulcanized to give rubberlike materials. By discontinuous processing, the polymers are less homogeneous than in continuous operation as is shown by the I no. and extn. For example, under N, 32 g. PhC.tplbond.CH and a 50:50% mixt. of 1- and 2-butene were polymerized during 20 hrs. at 60-5° by 6.5 g. TiCl₃ and 11.4 g. Et₃Al in 500 cc. heptane. After pptn. with MeOH and purifying with HCl and Et₂O, the polymer was extd. with Me₂CO to give 53.9% polyphenyl-acetylene with I no. 136 and intrinsic viscosity 0.35 in tetrahydronaphthalene. Extn. with heptane gave 8.3% with I no. 84.5 and 1.46 intrinsic viscosity. C₆H₆ gave 23% ext. with 0.158 intrinsic viscosity.

Bibliographic Information

Polystyrene. Natta, Giulio; Beati, Enrico; Severini, Febo. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1960), DE 1074269 19600128 Patent language unavailable. CAN 55:90602 AN 1961:90602 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (D 104)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1074269		19600128	DE	

Abstract

To lower the brittleness of polystyrene and other vinylbenzene derivs., their monomers are copolymerized with 5-20% of the peroxides of a homo- or copolymer of CH₂:CHR, R is alkyl, or their copolymers with CH₂:CH₂. The best results are obtained with linear atactic poly(1-butene) or polypropylene with 2000-500,000 mol. wt. To improve the soly. of the peroxides in the vinyl monomer, aromatic solvents may be added. The polymerization is performed in block, suspension, or emulsion at 50-120°. The time is 5-100 hrs. and depends on the peroxide content and the desired mol. wt. At the end of the polymerization, the temp. is raised to obtain complete polymerization and to destroy HOO groups. For example, the Me₂O-insol. but Et₂O-sol. fraction of polypropylene, obtained with TiCl₄-Et₃Al catalyst, was peroxidized (Belg. 550,094). It had 3700 mol. wt., corresponding to mol. HOO group/88 monomer units. The peroxide (12 g.) was dissolved in 88 g. styrene and block-polymerized for 51 hrs. at 70°. The material obtained had 18 cm.-kg./sq. cm. notch impact strength.

Bibliographic Information

Stereospecific polypropylene. Natta, Giulio; Pasquon, Italo; Giachetti, Ettore; Sculari, Francesco. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1961), US 2971950 19610214 Patent language unavailable. CAN 55:84753 AN 1961:84753 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 172)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2971950		19610214	US 1958-751608	19580729
DE 1189715			DE	
GB 890913			GB	

Abstract

Isotactic polypropylene of regulated mol. wt. was prepd. by adding a small amt. of a polar compd. to the mixt. contg. the monomer and the stereospecific catalyst. In an example, a shaking autoclave. kept at 70° and under reduced pressure, was charged with anhyd. HCl or alkyl halide in heptane, with a suspension of TiCl₃ in anhyd. heptane, with AlEt₃ in heptane, and with 500 cc. heptane. The contents were stirred in vacuo for 20 min., and

then propylene was fed in at a rate which caused a partial pressure of 1000 mm. of Hg after a few min. The feeding rate throughout the expt. was regulated to keep the system at this pressure. After about 2 hrs., the feed was stopped, and the autoclave contents were discharged. Addnl. heptane 2000, H₂O 500, and HCl few cc. were added, and the mixt. was filtered. The polymer was recovered from the org. phase by evapn. The crude polymer contains at least 75% isotactic modification. The polar compd. can be an acid HX, where X is Cl, Br or F, or an alkyl halide contg. 1-5 C atoms. The polypropylene had a mol. wt. of 71,000-190,000, depending on the amt. and nature of catalyst system.

Bibliographic Information

High-molecular-weight polyethylene. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. (Karl Ziegler). (1959), Addn. to Ger. 1,046,319 (see Brit. 826,638, CA 54, 16019d). DE 1050547 19590212 Patent language unavailable. CAN 55:40712 AN 1961:40712 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (u 72)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1050547		19590212	DE	
US 3037972		19620605	US 1955-545511	19551107

Abstract

Gaseous C₂H₄ is polymerized by use of Fe compds. and, instead of R₂Al halide, in which R is a hydrocarbon residue, compds. of Group 1-III having the general formula R_nMX, in which R is a hydrocarbon residue, X is a halogen or hydrocarbon residue, M is the metal, and n is 1 less than the valence of the metal. Preferred are Li, Mg, Zn, and esp. Al, and R and X being alkyl groups. The catalyst is prepd. from a soln. of R_nMX and esp. FeCl₃ or mono- or dialkoxy Fe halides. The Fe salts used must not have an oxidizing anion. The polymerization is performed at 10-250 atm. and 50-80° in aliphatic or aromatic solvents. The temp. depends on the activity of the catalyst (Al trialkyl being the most reactive) and the desired mol. wt. The polyethylene obtained is completely linear (Me content 0.03-0.01%), of high crystallinity (80%), and m. 130°. No discoloration occurs on heating to 200-50°, and mol. wts. of 100,000-1,000,000 are obtained. Spun as superpolyamides, the stretched threads have tensile strengths up to 3000 kg./sq. cm. For example, an autoclave of 435-cc. content was filled with 2 steel balls and 5 g. FeCl₃ in a glass ampul. Into the air-free autoclave, 11 g. AlLi in 130 cc. n-heptane was introduced and at 80°, C₂H₄ was pressed up to 60 atm. With stirring, 80-90° and 40-50 atm. were maintained by addn. of further C₂H₄. When the pressure stopped dropping, the catalyst was killed with MeOH and the polymer washed with HCl. Similarly, from 10 g. FeCl₃ and 11.4 g. Et₃Al in 500 cc. C₆H₆ at 70° and 50 atm., a cryst. polyethylene was obtained, sintering at 123° and m. 200°. The mol. wt. was 1,000,000.

Bibliographic Information

Substituted and unsubstituted succinic acids. Natta, Giulio; Pino, Piero. (Lonza Elektrizitatswerke und Chemische Fabriken Akt.-Ges.). (1960), CH 345332 19600513 Patent language unavailable. CAN 55:13051 AN 1961:13051 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
CH 345332		19600513	CH	

Abstract

Succinic acid (I) and substituted I were prepd. by treating acetylene (II) or a substituted II with CO and H₂O at 80-250° and 100-500 atm. pressure in a neutral to acid medium in the presence of a catalyst comprising a salt of

a metal of Group VIII of the periodic table which will form a metal carbonyl of the formula $M_x(CO)_y$ in which x and y are both >1 . Thus, a mixt. of 7.13 g. Co succinate, 251 g. Me_2CO , 45 g. H_2O , and 0.27 mole II in an autoclave of 1710 cc. capacity was treated with a 4:1 mixt. of CO and H to a pressure of 250 atm. The mixt. was shaken and warmed to 170° for 5 hrs. The autoclave was cooled and opened to give a liquid contg. 45.5% I and 15% propionic and acrylic acids. Other similar examples were given, variations of the process were discussed, and a diagram for a suitable large-scale continuous reaction unit was included and described.

Bibliographic Information

Crystalline polystyrene. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica; Karl Ziegler). (1958), DE 1047435 19581224 Patent language unavailable. CAN 55:11272 AN 1961:11272 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (U 63/B)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1047435		19581224	DE 1956-M29937	19560312

Abstract

A high-mol.-wt. cryst. polystyrene is prepd. by polymerization of styrene with a catalyst obtained by reaction of compds. of Groups IV-VI, esp. $TiCl_4$, including Th and U, with metal alkyls, esp. Et_3Al in inert solvents, such as aromatic hydrocarbons, esp. $PhCl$ and $C_6H_4Cl_2$. Aromatic compds. contg. OH , NH_2 , or NO_2 are not suitable because of reaction with the catalyst. Besides pure styrene, mixts. (40% styrene) with ethylbenzene, such as obtained by catalytic dehydrogenation of ethylbenzene, can be used. For example, in a shaking autoclave, 640 cc. anhyd. C_6H_6 , 11.4 g. Et_3Al , and 250 g. freshly distd. styrene were heated in N to 69° , and 5.7 g. $TiCl_4$ in 30 cc. C_6H_6 was injected. Spontaneously, the temp. increased to 82° and decreased again to 75° . After 3 hrs., 3.8 g. $TiCl_4$ in 30 cc. C_6H_6 was injected, and the polymerization was continued for 15 hrs. at $70-5^\circ$ (82% conversion). The catalyst was decompd. and the polymer coagulated by addn. of $MeOH$. By treatment with acetone and HCl , the monomeric and amorphous polystyrenes were removed to obtain 105 g. polystyrene, still cryst. at 200° .

Bibliographic Information

α -Olefin polymerization. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1956), IT 545332 19560630 Patent language unavailable. CAN 54:136092 AN 1960:136092 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (U 73/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 545332		19560630	IT	

Abstract

The process of Ital. 526,101 is used for the production of highly cryst. or amorphous polymers by using the catalyst in a relatively less or more dispersed state, resp., in a solvent of the olefin. Catalysts obtained by reaction of V, Zr, or Cr compds. with an alkyl metal, esp. Et_3Al , are indicated. For example, 11.4 g. Et_3Al was dissolved in 70 ml. heptane and treated with 7.3 g. VCl_4 (dissolved in 20 ml. heptane). The reaction product was filtered under a N atm. The solid phase was washed 3 times with a 1% Et_3Al soln. in heptane, then suspended in 250 ml. n-heptane, introduced into an air-free flask, treated with 11.4 g. Et_3Al , warmed to 70° , treated with 150 g. styrene, shaken for 4 hrs. at $70-75^\circ$, cooled, and treated with $MeOH$ and HCl to give a highly cryst. polymer which was 68% insol. in acetone. If the filtrate (instead of the solid part) of the above catalyst

prepn. was used, a completely amorphous polymer was obtained.

Bibliographic Information

Olefinic polymerization catalysts from titanium compounds. Natta, Giulio; Mazzanti, Giorgio; Longi, Paolo. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1959), US 2905646 19590922 Patent language unavailable. CAN 54:106867 AN 1960:106867 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 87)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2905646		19590922	US 1956-597817	19560713
DE 1055243			DE	
GB 822926			GB	

Abstract

The title compds. are prepd. by the reaction of org. halides with Al-Ti alloys at 20-60°. The alloy should be finely divided and free from surface oxidn., as produced by grinding in an inert atm. or by spraying molten metal into such an atm. The org. halide may be with an alkyl radical of 2-18 C atoms or an aryl radical of 7-12 C atoms, the halide being Cl or Br. Thus, 10 g. of Al-Ti alloy (37.2% Ti), previously finely ground under N, was placed in a rotating autoclave ball mill of 2-1. capacity contg. 12 steel balls 1 in. in diam. EtCl (35 g.) was added, and the mixt. was ground overnight at 50°. The residual EtCl was removed under 20 mm. pressure. Heptane (600 ml.) was added, and C₂H₄ was introduced to raise the pressure to 30 atm. The temp. rose to 103°, and the pressure dropped to 20 atm. The pressure was raised to 30 atm. several times while the temp. remained at 100°. After 7 hrs., the vessel was cooled, the residual gas was vented, and the product was purified with MeOH acidified with HCl, filtered, and dried in vacuo. It weighed 570 g., was highly cryst. under x-rays, had an intrinsic viscosity of 0.80 in Tetralin at 135°, and a mol. wt. of 23,000.

Bibliographic Information

Chromium hexacarbonyl. Natta, Giulio; Ercoli, Raffaele; Calderazzo, Fausto. (1960), US 2940832 19600614 Patent language unavailable. CAN 54:94025 AN 1960:94025 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 146)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2940832		19600614	US 1958-711548	19580128

Abstract

See Ital. 578,731 (CA 53, 22784d).

Bibliographic Information

Rubberlike sulfochlorinated polypropylene. Natta, Giulio; Pino, Piero. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), DE 1015603 19570912 Patent language unavailable. CAN 54:71707 AN 1960:71707 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 64)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1015603		19570912	DE 1955-M27807	19550726

Abstract

Head-to-tail polypropylene with a mol. wt. of 10,000 obtained according to Ital. 535,712 (CA 53, 9728b) and Ital. 537,425 are sulfochlorinated with Cl and SO₂ or SO₂Cl₂ and pyridine in CCl₄ at 0-60° to a Cl content of <10%. The products are vulcanized and show high elongation and good elastic behavior. For example, in 400 cc. CCl₄, 10 g. linear polypropylene (I) with a mol. wt. of 40,000 was dissolved. At 70°, a mixt. of 3 parts SO₂ and 1 part Cl was introduced with a speed of 2.66 l./hr. during 1.25 hrs. The product was pptd. with MeOH and contained 5.94% Cl and 1.39% S. For the vulcanization, 7.5 g. of the polymer was mixed with 30% PbO and 3% mercaptobenzothiazole (II), whereby the temp. increased to 40°. The mixt. was held for 0.5 hr. at 150° to give a rubberlike material with an elongation of 500% and a strength of 5 kg./sq. mm. Similarly, 80 g. I with a mol. wt. of 13,500 was dissolved in 1500 cc. CCl₄ at 53°, and 1 cc. pyridine was added as the catalyst. During 1.5 hrs. 10 cc. SO₂Cl₂ was dropped in with simultaneous irradiation by using a 200-w. lamp. After 2 hrs., the reaction was stopped. The product obtained, contg. 4.6% Cl and 1.3% S, was vulcanized in a press with PbO 40, II 2, and rosin 5% for 60 min. at 150° to give a rupture load of 0.84 kg./sq. mm., a modulus at 200% of 0.36 kg./sq. mm., and an elongation of 500%.

Bibliographic Information

Elastomers from propylene. Natta, Giulio; Pino, Piero. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1955), IT 537429 19551228 Patent language unavailable. CAN 54:9347 AN 1960:9347 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 6 4)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 537429		19551228	IT	

Abstract

Polypropylene (mol. wt. > 20,000) is chlorinated or sulfochlorinated (max. of 20% Cl) and then vulcanized by warming in the presence of a bivalent metal. For example, 10 g. polypropylene (mol. wt. 40,000) was dissolved in 400 cc. CCl₄. Cl was bubbled at the rate of 1.3-1.5 l./hr. at 0° for 1.5-8.25 hrs. (fixed Cl, 1.38 to 17.43%, resp.). Vulcanization occurred when 7.5 g. of the product was mixed with 30% PbO and 3% mercaptobenzothiazole (temp. rose to 40°) and warmed to 150° for 0.5 hr.

Bibliographic Information

Hydroperoxides. Natta, Giulio; Beati, Enrico. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), DE 1000024 19570103 Patent language unavailable. CAN 54:7008 AN 1960:7008 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (F 8 1)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 1000024		19570103	DE 1954-M21468	19540111

Abstract

See U.S. 2,843,633 (C.A. 52, 20061h).

Bibliographic Information

Highly crystalline, linear polystyrene objects. Natta, Giulio; Crespi, Giovanni. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1959), US 2896264 19590728 Patent language unavailable. CAN 54:4422 AN 1960:4422 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 135)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2896264		19590728	US 1957-694488	19571105

Abstract

See Ital. 570,444 (C.A. 53, 15642d).

Bibliographic Information

Highly crystalline propylene polymers. Natta, Giulio; Pasquon, Italo; Giachetti, Ettore. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958), IT 580507 19580806 Patent language unavailable. CAN 53:128625 AN 1959:128625 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (U 153)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 580507		19580806	IT	

Abstract

Highly cryst. polypropylene is obtained by use of a catalyst consisting of a combination of a Ti4+ compd. sol. in the reaction system (also, after reaction with the Al alkyl), such as dihalodicyclopentadienyl derivs., alcoholates, haloalcoholates, or acylalcoholates, of a solid cryst. Ti halide, such as TiCl3 or TiCl3, and of an Al alkyl. For example, a suspension of 0.20 g. TiCl3 in heptane, a soln. of 0.1 ml. Ti isopropylate in heptane, and 1 ml. AlEt3 in heptane were introduced into a 2 l. autoclave. Heptane was added to 500 cc. After 10 min., propylene was introduced under a const. pressure of 3 atm. for 50 hrs. to yield 175 g. polypropylene (16% amorphous, 5% partially cryst., 79% cryst.). Without the alcoholate, an av. of 1.9 g. polymer/hr. was obtained.

Bibliographic Information

α -Olefin polymerization. Natta, Giulio; Pasquon, Italo; Giachetti, Ettore. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 567249 19571004 Patent language unavailable. CAN 53:128578 AN 1959:128578 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 147)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 567249		19571004	IT	

Abstract

Improvements of Ital. 526,101 and Ital. 545,332 (C.A. 53, 6686d) involve polymerization at 0-100°, preferably 20-80°, and the use of a catalyst obtained from very finely ground TiCl₃ (particles <1 μ in diam.) and alkyl Al or obtained by the repeated washing of TiCl₃ with liquid hydrocarbons. The grinding is in the presence of a hydrocarbon and in the absence of air and moisture. Such catalysts are shown to be more active and to give polymers of increasing intrinsic viscosity with decreasing concn. of the alkyl Al in the catalyst. In an example of the catalyst prepn., 30 g. TiCl₃ (obtained from TiCl₄ by reduction at 650° and washed with anhyd. heptane) and 100 cc. heptane are introduced into a ball mill in N atm. The mill is placed in rotation for 70 hrs., and an addnl. 200 cc. heptane added. The TiCl₃ suspension is decanted, washed 4-5 times with heptane, and stored in a N atm. In another example, the grinding is in the presence of 4% AlEt₃.

Bibliographic Information

Crystallizable catalysts for polymerization of unsaturated hydrocarbons. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958), IT 579112 19580708 Patent language unavailable. CAN 53:128577 AN 1959:128577 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)), (u 150)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 579112		19580708	IT	
DE 1061323			DE	

Abstract

Substances are claimed contg. (1) a transition metal of Groups IV-VI (2) Al, (3) 1 or more metal-C bonds able to react with compds. contg. mobile H, and (4) 1 or more halogen atoms, esp. those contg. cyclopentadienyl rings, e.g. (C₅H₅)₂TiAl(C₂H₅)₂Cl₂ (I). For example, 2.5 g. Ti dicyclopentadienyl chloride was introduced into a 150-ml. glass flask in a N atm. Then 50 ml. heptane and 2.85 g. AlEt₃ (96% active Al) were added. The mixt. was warmed at 70° for 1.5 hrs. to give an intense blue soln. The soln. was filtered in a N atm., cooled to -30°, and blue crystals were formed. The supernatant soln. was removed. Then the crystals were treated with 20 ml. heptane warmed to dissolve the crystals, and recrystd. (twice) to give I, blue-green needles, m. 121-2°, decompd. at 180° in the absence of air with formation of a red solid product. A soln. of 0.6 g. I in 40 cc. heptane was introduced into a 430-ml. stainless steel autoclave. Then 30 g. C₂H₄ was added. The mixt. was warmed at 90° for 20 hrs., cooled, and the catalyst decompd. with MeOH. The resulting polyethylene (8 g.) was linear and had a high mol. wt.

Bibliographic Information

Alkylstyrene linear polymers. Natta, Giulio; Sianesi, Dario; Serra, Renato. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 560712 19570410 Patent language unavailable. CAN 53:128574 AN 1959:128574 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)), (u 103)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 560712		19570410	IT	

Abstract

Isotactic polymers of o-, p-, and dimethylstyrene are claimed which are obtained by polymerizing the momomers in the presence of catalysts prepd. by reaction between organometallic compds. and transition metal compds. The p-methylstyrene polymer has the following properties: d. 1.03-1.04; n_D 1.577-1.578; insol. in acetone,

MeCOEt, or C₆H₆; sol. in Tetralin at 100°; mol. wt. 1,000,000-5,000,000; intrinsic viscosity 3-8; and amorphous. The o-methylstyrene polymer has the following properties: cryst.; m. 305-310°; d. 1.038; and insol. in all org. solvents. A copolymer of 2 parts p- and 1 part o-methylstyrene has the following properties: intrinsic viscosity 6-7; mol. wt. 4,000,000-5,000,000; transition temp. 87°; d. 1.038; insol. in acetone, MeCOEt, or C₆H₆; and amorphous. The dimethylstyrene polymer (chiefly from 2,4-dimethylstyrene) has the following properties: n_D15 1.5463, intrinsic viscosity 3.5; mol. wt. 2,000,000; in sol. in acetone or MeCOEt, less sol. in warm C₆H₆; x-ray m.p. >300°; cryst.; and d. 1.013. For example, a p-methylstyrene polymer was prepd. as follows: 1.1 g. Al-(C₂H₅)₃ dissolved in 10 cc. benzene was added slowly in N atm. to 0.70 g. TiCl₄ dissolved in 40 cc. C₆H₆ at 70°. Then 18 g. p-methylstyrene was poured into the mixt. This mixt. was let stand for 7 hrs. and treated with an excess of MeOH. The polymer formed is washed with HCl-contg. MeOH to yield 7.4 g. of an amorphous polymer (not contg. fractions sol. in acetone or MeCOEt and intrinsic viscosity 5.45.

Bibliographic Information

Styrene polymers with high impact strength. Natta, Giulio; Beati, Enrico; Severini, Febo. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958), IT 582006 19580915 Patent language unavailable. CAN 53:128569 AN 1959:128569 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (D 139)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 582006		19580915	IT	

Abstract

Resistant and rather transparent polymers are obtained from styrene or its derivs. by polymerization in the presence of a high polymer of a conjugated diolefin CH₂:CHC(R):CH₂, in which R is H or a C₁-3 alkyl group, in amts. of 1-20%, and of a peroxide initiator. For example, 4 g. amorphous polybutadiene was dissolved in 96 g. styrene. The soln. was mixed with 0.4% p-chlorobenzoyl peroxide and let stand at 80° for 22 hrs. The product (bright and transparent) could be worked like polystyrene and had an impact strength of 40 kg. cm./sq. cm. (as measured by the Charpy app.). Comparative products obtained without the peroxide were much less resistant. Polyisoprene (6 g.) (intrinsic viscosity 1.7) was dissolved in 94 g. styrene, the above peroxide added, and polymerized at 80° for 48 hrs. The product had similar properties to that of the 1st example.

Bibliographic Information

Crystalline butadiene 1,4-cis polymers. Natta, Giulio; Porri, Lido; Corradini, Paolo. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 566940 19570921 Patent language unavailable. CAN 53:128504 AN 1959:128504 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (U 121)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 566940		19570921	IT	

Abstract

Conditions are described for obtaining higher 1,4-cis polymer yields by the process described in previous patents (C.A. 53, 3756h). A transition metal of high valence and an AlEt₃/Ti compd. should be used. For example, 0.0075 mole TiCl₄ dissolved in 50 cc. heptane and 0.01 mole AlEt₃ dissolved in 50 cc. heptane were introduced into a 500-ml. autoclave (vacuum), stirred for 30 min., and mixed with 80 g. butadiene. The autoclave was shaken for 7-8 hrs., then 30 ml. MeOH was introduced. The product was coagulated with acid MeOH, washed with MeOH, and dried, yielding 40 g. solid polymer, from which the following successive exts. were

obtained: from acetone (20%), amorphous (1,4-trans 69, 1,4-cis 15 and 1,2 16%); from MeCOEt (28%), amorphous (1,4-trans 75, 1,4-cis 15, and 1,2 10%); from Et2O (35%), amorphous at room temp., 1,4-cis cryst. at -40° (1,4-cis 65, 1,4-trans 32 and 1,2 3%); residue (17%), cryst. (1,4-trans). The Et2O ext. was repeatedly pptd. by cooling at -50°: this fraction was 1,4-cis cryst. at room temp. Upon further extn. of the Et2O ext. with butane or pentane at -30°, the residue was 1,4-cis cryst. at room temp. In another example (catalyst: 0.0071 mole BuOTiCl3 and 0.0142 mole AlEt3), the Et2O ext. was 1,4-cis cryst. at -40°. Extn. with Et2O at -30° gave a residue of 1,4-cis cryst. at room temp.

Bibliographic Information

Vulcanized elastomers from α -olefin polymers and copolymers. Natta, Giulio; Crespi, Giovanni; Bruzzone, Mario. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958), IT 582002 19580915 Patent language unavailable. CAN 53:128338 AN 1959:128338 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 168)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 582002		19580915	IT	

Abstract

Optimum products are obtained from propylene or 1-butene polymers and their copolymers with C2H4, by mixing them with an initiator, e.g. an org. peroxide or hydroperoxide, and with an aromatic or aliphatic hydrocarbon contg. at least 1 double bond and able to react with the polymer, e.g. styrene, divinylbenzene, or butadiene, at 30-70°, and vulcanizing the mixt. at 100-250° under pressure. The elastomers obtained are of lower d. than H2O and transparent. Inert matter and (or) pigments may be added. For example, 100 parts C2H4-C3H6 copolymer (43% propylene, mol. wt. 200,000) was mixed with 20 parts of a mixt. of divinylbenzene 60.5, ethylvinylbenzene 15.4, and a satd. aryl alkyl hydrocarbon 24.1%; 2.4 parts di-tert-Bu peroxide was then added. The homogenized mixt. was then vulcanized at 200° for 20 min. under 70 atm. pressure. Also, an C2H4-C3H6 copolymer (57% propylene; mol. wt. 200,000) was mixed with styrene and dicumylperoxide was added. The homogenized mixt. was then vulcanized at 160° for 30 min. under 70 atm. pressure.

Bibliographic Information

Elastomers from α -olefin stereoisomeric block copolymers. Natta, Giulio; Crespi, Giovanni; Bruzzone, Mario. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958), IT 582004 19580915 Patent language unavailable. CAN 53:128335 AN 1959:128335 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 163)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 582004		19580915	IT	

Abstract

The production is described of elastomers with various properties by halogenation (esp. chlorination) of aliphatic α -olefin stereoisomeric block copolymers (esp. of 1-butene and propylene). Amts. of Cl from 2-12 to 12-30%, mol. wts. of 50,000-300,000, and chlorination temps. of 50-100° are indicated. For example, 50 g. polybutene (residue from extn. of crude linear polybutene with boiling CH2Cl2, mol. wt. 150,000) was dissolved in 1 l. CCl4. The soln. was warmed to 50° and Cl was bubbled at a rate of 5 l./hr. with exposure to ordinary light. The

chlorinated product was pptd. by coagulation with excess MeOH, then dried at 60° under reduced pressure. For reaction times of 45-150 min., Cl contents of 8.9-28.3%, resp., were detd. in the products. Their mech. resistance decreased with increasing amt. of Cl. The ultimate elongation reached a max. (730%) with 11.3% Cl, then decreased. The elasticity modulus upon 200% elongation was at a min. (15 kg./sq. cm.) for 19.7% Cl. By subjecting the most elongatable product to preliminary stretching of 600%, the mech. resistance was increased to 1100-1200 kg./sq. cm. and the ultimate elongation decreased to 120-30%. Cf. Natta, C.A. 51, 2319c.

Bibliographic Information

Polymerization of vinyl compounds by use of iron compounds as catalysts. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria Mineraria e Chimica). (1959), US 2882263 19590414 Patent language unavailable. CAN 53:128326 AN 1959:128326 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (u 63/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2882263		19590414	US 1955-552295	19551212

Abstract

By treating an Fe compd., esp. an ionizable one, with a catalytic metal alkyl compd., an agent is obtained which is capable of polymerizing hydrocarbons of the formula $\text{CH}_2\text{:CHR}$ (I), in which R is an aliphatic, alicyclic, or an aromatic radical, alone or in mixts. with each other or in mixts. with up to 5% of a monomer polymerizable therewith. The polymers obtained are mixts. of relatively high-mol., linear, head-to-tail amorphous and cryst. fractions. The amt. of the latter may be as much as 30-55% of the mixt. Esp. active catalysts are obtained by treating ionizable ferric compds. (II) in which the anion does not possess oxidizing properties with metal alkyls (III) contg. as a central atom an element of the 2nd or 3rd Group of the periodic table, e.g. Mg, Zn, or Al. The alkyl radicals may be the same or different and one may be replaced by a halogen or an alkoxy radical. The exchange reaction between II and III is always accompanied by a reduction of Fe^{+++} to Fe^{++} . This reaction is preferably carried out at 50-100° in an anhyd. inert paraffinic or aromatic solvent, the III:II mole ratio being <5:1, in the absence of O. Polymerization of carefully dried I takes place at 50-100° and, in the case of gaseous I, at 10-20 atm. Thus, 6 stainless-steel balls of 1 in. diam. were introduced with a glass vial contg. 10 g. anhyd FeCl_3 into a stainless steel autoclave. Anhyd. benzene (400 ml.) was then added and the autoclave closed and flushed with N. Then, 290 g. pure liquid propylene was admitted at 60° and a soln. of 11.4 g. Et_3Al in 90 ml. anhyd. benzene was injected under N. The autoclave was shaken, breaking the vial contg. the FeCl_3 , and agitated for 20 hrs. at 72-92°. The unreacted gases were then released and MeOH injected to destroy the catalyst. A liquid contg. a gummy, solid, brown-colored polymer in suspension was obtained. The solid was sep'd. by filtration and purified by treating with hot toluene and aq. HCl and coagulated with MeOH.

The polymer thus obtained contained 0.4% ash and weighed 15 g. By evapn. of the liquid, 21 g. of oily products was obtained. The solid polypropylene was fractionated by extn. with Me_2CO , Et_2O , and heptane in that order. The solid did not contain portions extractable by Me_2CO , but 62.6% could be extd. by warm Et_2O . The latter fraction was a solid with a softening point of 100° and a mol. wt. of about 30,000. It appeared to be entirely amorphous. The heptane ext. (36% of the solid) was also solid, had a softening point of 115°, a mol. wt. of about 50,000, and appeared to be about 50% cryst. The residue (1.3% of the solid) had a softening point of 160° and appeared to be cryst. polypropylene.

Bibliographic Information

Chromium hexacarbonyl. Natta, Giulio; Ercoli, Raffaele; Calderazzo, Fausto. ("Montecatini" Societa Generale per l'industria mineraria e chimica). (1958), IT 578731 19580701 Patent language unavailable. CAN 53:126882 AN 1959:126882 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 146)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 578731		19580701	IT	
DE 1076105			DE	
GB 877109			GB	

Abstract

A process is claimed which involves the use of CO or CO + H mixts.; metals more electropos. than Cr, e.g. Zn, Mg, Al, or their alloys or hydrides as reducing agents; electron donors contg. amine N, e.g. pyridine or pyridine bases; or halogens or org. or inorg. halogenated compds. having (or forming compds. with) an acid character. As starting Cr compds., the following are esp. reported: the acetate, ethylhexanoate, acetylacetonate, xanthate, and trichlorotripyridine; and Cr-Al alloys. The reducing agent should be used in an amt. sufficient to reduce Cr to metal. The activator (esp. a chlorinated compd.) should be 0.1-10% molar with reference to Cr. The reaction is performed in the presence of org. solvents, at 10-400 atm. and 80-200°. Example: A soln. contg. 0.054 mole trichlorotripyridine Cr per 100 g. pyridine was introduced into an autoclave with 10 g. Mg and subjected to the action of a 1:2 CO:H mixt. under 280 atm. at 160-70° during 7 hrs. The product was steam distd., giving a yield of 25%. In another example, the amts. of Cr(CO)₆ obtained from 17.5 g. Cr acetylacetonate under various conditions of pressure, temp., CO:H ratio, activator, reducing agent, etc., are tabulated. The max. yield was obtained in presence of pyridine 150, Mg 5.4, and I 0.5 g. at 150 atm. and 100° during 3 hrs.

Bibliographic Information

Catalysts for propylene polymerization. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958). IT 576203 19580430 Patent language unavailable. CAN 53:116904 AN 1959:116904 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (U154)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 576203		19580430	IT	

Abstract

The max. rate of polymerization is obtained by a Et₃Al:TiCl₄ ratio of 2:1 or by a AlEt₂Cl:TiCl₄ ratio between 15:1 and 17:1. The max. per cent of isotactic polymer is obtained by a Et₃Al:TiCl₄ ratio of 1:1 or >3:1. At the max. rate of polymerization, a polymer of min. mol. wt. resulted. By increasing age of the catalyst, the rate of polymerization is decreased (more rapidly during the 1st 30 min.).

Bibliographic Information

Products containing grafted polymers. Natta, Giulio; Beati, Enrico; Severini, Febo. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957). IT 564711 19570627 Patent language unavailable. CAN 53:86939 AN 1959:86939 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (D105)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 564711		19570627	IT	

Abstract

Films or yarns of polypropylene (cryst. or amorphous, mol. wt. 20,000) or of its copolymer are subjected to an almost superficial or deeper peroxidn. at 60-120° (or partially at 60-90°) by O or O-contg. gas mixts. at 1-10 atm. The O content of the peroxidized product is 0.01-0.05 g./sq. m. for superficial peroxidn. and more for those peroxidized to a greater depth. The products are subjected to further reaction and polymn. of the peroxidized surface at 50-80° with gaseous, liq., or dissolved monomers, e.g. vinyl or vinylidene compds., esp. Me methacrylate or acrylate, which are grafted on the linear polymer chains. The result of this treatment is the affinity of the film or yarn for solvents and dyes. For example, films of a highly isotactic propylene polymer (thickness of 0.16 mm.) were suspended (1) in a stainless steel autoclave warmed at 70° in the presence of air at 3 atm. for 5-7 h. (0.026-0.044 g. O per sq. m., fixed; mech. resistance unaffected), or (2) in a glass container contg. a mixt. of 10% O-90% N for 24 h. (0.017 g. O per sq. m., fixed). Then the films were plunged into liq. Me methacrylate at 70° for 4 h., washed with MeOH, and dried. No changes in the mech. properties occurred. In other examples of treatments allowing deeper penetration of O, the layer of grafted methacrylate (thickness of film increased) did not involve an increase of the mech. resistance. Similar examples are reported with yarns which were dyed satisfactorily.

Bibliographic Information

Catalysts for manufacturing highly linear α -olefin polymers. Natta, Giulio; Mazzanti, Giorgio; Capucci, Carlo M. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 564922 19570705 Patent language unavailable. CAN 53:86932 AN 1959:86932 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 110)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 564922		19570705	IT	

Abstract

Catalysts for polymerizing vinyl monomers are claimed which consist of a compd. (I) of a transition metal (such as Ti and V) of Groups IV-VI with org. groups (such as alcoholates, halo-alcoholates, and acetylacetonates) dispersed, e.g., by impregnation at 50-100° of the soln. in an org. solvent, on a high-surface carrier (such as SiO₂ and Al₂O₃), and of an alkyl compd. of the Groups II-III (such as alkyl Al). The ratio between the carrier and I (which influences the polymer yield and the percent of amorphous product), may range from 1:1 to 100:1. The use of the above catalysts results in the obtaining of amorphous linear α -olefin polymers with a higher mol. wt. than when using conventional catalysts. For example, 15 g. of silica and alumina (9:1) at 550° is introduced into a 2-l. autoclave, which is de.ovrddot.aerated, and a soln. of 6 g. Ti tetraisopropylate (II) in 100 cc. pentane is introduced. The autoclave is warmed at 55° for 30 min., and the solvent and iso-PrOH expelled under a 20-mm. vacuum. A soln. of 11.4 g. AlEt₃ in 1 l. heptane and 256 g. of propylene-propane mixt. (88:12) are introduced. The autoclave is warmed at 90° for 10 hrs. The unreacted gases are discharged. The metallo.ovrddot.org. compds. are removed by shaking with HCl-water mixt. The 2 phases are sepd. The heptane phase is coagulated with MeOH and acetone, and the obtained polymer sepd. by successive dissoln. in tetralin and coagulation with acetone and MeOH. Polypropylene (44 g.) is obtained with acetone, Et₂O and heptane exts. of 14.0% (oleous, low-mol. substances), 44.3% (amorphous, elastomerlike; intrinsic viscosity 1.47), and 12.5% (15% cryst.; intrinsic viscosity 3.6), resp. The residue is 29.2% (cryst.; intrinsic viscosity 5.2). Similar examples with Ti monochlorotributylate or VO(OC₃H₇)₃, instead of II, are given. In a further example, a separate prepn. of the catalyst is given. Carrier (100 g.) is refluxed in a N atm. with 3% II in a heptane soln. for 1 hr. Then the solvent is distd. off under a 20-mm. vacuum, and the product is washed several times with anhyd. heptane.

Bibliographic Information

Highly crystalline olefin polymers. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 566242 19570827 Patent language unavailable. CAN 53:86925 AN 1959:86925 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 73/E)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 566242		19570827	IT	

Abstract

Hydrocarbons of the formula $\text{CH}_2\text{:CHR}$ ($\text{R} = \text{H}$ or alkyl) are brought into contact, in the gaseous phase, in the absence of solvent, with a finely powd. solid catalyst. The catalyst is obtained from a solid compd. (e.g., halide) of a transition metal (e.g., Ti) of Groups IV-VI with a valence lower than the max. and an alkyl-metal (e.g. AlEt_3 and Al diethylmonochloride) of 1-3rd Group I-III. For example, 10 balls of stainless steel are introduced in a rotary 2.5-1. N-washed autoclave along with 3 g. TiCl_3 , 30 g. NaCl, and a soln. of 3.2 g. AlEt_3 in 150 cc. pentane. The mixt. is ground for several hrs. in a N atm. at room temp. The autoclave is warmed to 50° , and the pentane distd. off in a 20-mm. vacuum. Then the temp. is raised to 90° , and 1-butene introduced to 3 atm. (re-feed until 45 g. 1-butene is added). After 20 h. from the beginning of the reaction 50 cc. MeOH is introduced. The product is discharged, treated with warm Et_2O and HCl, coagulated with MeOH, filtered, and dried. Solid polybutylene (30 g.) is obtained, whose acetone, Et_2O and heptane exts. are resp. 5.1% (oleous low-mol. compds.), 13.9% (solid, amorphous; intrinsic viscosity 0.465) and 81% (solid, high cryst. polybutene; intrinsic viscosity 1.07). In a similar example, the use of Al diethylmonochloride in the catalyst formation and the use of propylene or ethylene as the olefin are considered.

Bibliographic Information

High-melting polymers of branched α -olefins. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 566243 19570827 Patent language unavailable. CAN 53:86924 AN 1959:86924 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) · (473)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 566243		19570827	IT	

Abstract

Highly linear polymer α -olefins are claimed with the general formula $\text{H}_2\text{C:CHCH(R)R}'$, in which $\text{R} = \text{H}$ or C1-3 alkyl; $\text{R}' = \text{C}1\text{-}3$ alkyl when R is alkyl, or $\text{R}' = \text{-(CH}_2\text{)}_n\text{CHR}''\text{R}'''$ with $n = 0$ or 1 and $\text{R}'' = \text{C}1\text{-}5$ linear alkyl and $\text{R}''' = \text{C}2\text{-}5$ alkyl, when R is H, such as 3-methyl-1-butene and 4-methyl-1-hexene. These polymers show a higher transition temp. than polymers of linear α -olefins with the same no. of C atoms. For example, to 3.6 g. TiCl_3 and a soln. of 5-7 g. AlEt_3 in 200 cc. heptane in a N atm., 92 g. of 3-methyl-1-butene is added. The mixt. is warmed to 70° and shaken for 15 hrs. MeOH is injected. The product is discharged and purified with HCl solvents. The polymer is coagulated with MeOH, filtered, washed with MeOH, and dried to give 43.7 g. white solid polymer. Successive exts. with Me_2CO , EtOAc, Et_2O , and heptane are 9.5% (oleous, low-mol. compds.), 6.7% (amorphous polymers), 1.1% (amorphous polymers), and 2.2% (partially cryst. polymers), resp. The residue is 80.4% (highly cryst. polymer with a transition temp. $>240^\circ$; d. 0.9). In another example similar to the preceding example but with VCl_3 instead of TiCl_3 , a yield of 45.5 g. is obtained whose Me_2CO , Et_2O , and heptane exts. are 5.5, 9.6, and 1.9%, resp.; residue 83%. In a further example with 27 g. 4-methyl-1-hexene, a yield of 5.25 g. polymer, and Me_2CO , EtOAc, Et_2O , and heptane exts. of 52.4, 19.7, 12.5, and 15.4% (high cryst.) resp., are reported.

Bibliographic Information

Highly crystalline, linear polystyrene objects. Natta, Giulio; Crespi, Giovanni. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 570444 19571210 Patent language unavailable. CAN 53:86920 AN 1959:86920 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 135)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 570444		19571210	IT	
DE 1200513			DE	

Abstract

Styrene polymers, obtained by polymerization with catalysts prepd. from metallo.ovrddot.org. compds. and transition metal derivs., are purified from atactic and block polymers by extrn. with a suitable solvent (e.g., ketones at <180°) and molded at 230°. Before the definitive molding, the polymer is obtained in the form of a sheet and annealed at 160-190° for several hrs. A mech. shaping at 160-230° is possible. For example, a powd. linear polystyrene, obtained by the process claimed in Ital. 545,332 (C.A. 53, 6686d) is boiled with Me Et ketone. The residue (mol. wt. 600,000) is molded at 260° and 30 atm. to disks, 1 mm. in thickness and 100 mm. in diam. These disks are annealed at 160-170° for 2-3 hrs. and finally used for molding objects at 190-200° and 10 kg./sq. cm. pressure.

Bibliographic Information

Acrylonitrile polymerization. Natta, Giulio; Dall'Asta, Gino. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 570434 19571210 Patent language unavailable. CAN 53:86911 AN 1959:86911 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 118)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 570434		19571210	IT	
DE 1068895			DE	
GB 858759			GB	

Abstract

High-linear acrylonitrile polymers are obtained by a conventional process and the use of a catalyst obtained from a metallo.ovrddot.org. compd. of Groups I-III (e.g., Al or Zn alkyls) and a compd. of a transition metal of Groups IV-VI (e.g., Ti, V, or Cr alcoholate or acetylacetonate) at 40-80° in the presence of a solvent of the monomer or of polyacrylonitrile, not reacting with the catalyst, such as dimethylformamide. For example, 10 stainless steel balls (diam. of 1 in.) are introduced into a 2-l. autoclave in a N atm. Then 0.03 mole Cr acetylacetonate and 50 cc. toluene are added. A soln. of 0.09 mole dibutyl zinc in 50 cc. toluene is added. The mixt. is warmed at 75° under a weak N pressure. The autoclave is put in rotation for 30 min. Then 3 moles acrylonitrile is introduced. The autoclave is shaken for 30 hrs. at 75°. The product is discharged, purified with HCl-alcs., filtered, washed with MeOH, and dried to give 150 g. of yellowish white polyacrylonitrile, which can be further purified by soln. in dimethylformamide and successive coagulation with acetone or MeOH. Other examples with catalysts obtained from Cr acetylacetonate and ZnEt₂ or AlEt₃, or with VOEt₃ and ZnEt₂, are reported.

Bibliographic Information

Catalysts for polymerization. Natta, Giulio; Danusso, F.; Sianesi, Dario. (Montecatini Societa generale per l'industria mineraria e chimica). (1958), IT 572660 19580201 Patent language unavailable. CAN 53:86900 AN 1959:86900 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u 112)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 572660		19580201	IT	

Abstract

Improved, active catalysts for the polymn. of olefins are obtained by allowing the metallo.ovrddot.org. compds. to act on more than one compd. of different transition metals, whose work of electron extn. (Lange's scale) is <5, esp. 4, eV, with extn. potentials <8, esp. 7, and 18 v., resp., for the 1st and 2nd electron. The enhancement of the catalytic activity is max. when the prepn. involves copptn., cogrinding or cocrystn., or when alloys or mixed salts (solid solns.) are used. Comparative graphs of the activity of catalysts prepd. from TiCl₄ and (or) VCl₄ reacting with AlEt₃ are reported. It was obsd. that the range of the ratio between the reacting substances is wider when the salt mixt. (instead of 1 salt) is used. For example, 0.23 g. TiCl₄ and 0.44 g. VCl₄, dissolved in 25 cc. benzene, are introduced into a 250-cc. flask in a N atm. and at 40°. Then 25 cc. benzene contg. 0.8 g. AlEt₃ and 18 g. styrene monomer are slowly added. After 7 h., an excess of MeOH is added. The formed polymer is washed with benzene, treated with HCl, and extd. with boiling acetone (no amorphous polystyrene in the acetone ext.). Isotactic polystyrene (5.10 g.) is obtained. In another example, 2.0 g. anhyd. FeCl₃ and 0.66 g. TiCl₄ in 25 cc. benzene are introduced into a 250-cc. flask, in a N atm. Then, 1.1 g. AlEt₃ dissolved in 25 cc. benzene and 18 g. styrene monomer are dropped in at 40°. After 7 h., an excess of MeOH is added, and the pptd. polymer is extd. with boiling acetone (the acetone ext. contg. 1.2 g. amorphous polystyrene) to obtain 4.4 g. isotactic polystyrene. In addnl. examples, the use is reported of mixts., such as CoCl₂ and TiCl₄, VOCl₃ and TiCl₄, TiCl₃ and FeCl₃ (or CoCl₂), for polystyrene, polypropylene and polyisoprene prodn.

Bibliographic Information

Vulcanizable elastomers from α -olefin amorphous polymers and copolymers. Natta, Giulio; Crespi, Giovanni; Borsini, Giancarlo. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958), IT 574913 19580329 Patent language unavailable. CAN 53:86833 AN 1959:86833 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 141 + U 141/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 574913		19580329	IT	

Abstract

Vulcanizable elastomers are obtained by combining amorphous polymers (or copolymers) from compds. of the formula CH₂:CHR (R = lower alkyl), such as propylene or 1-butene (or copolymers with 35-70% ethylene, 0.5-10% C₂H₂, or 0.5-20% of a conjugated diolefin with at least a vinyl bond, such as isoprene or buadiene), with a compd. contg. ≥ 1 double bond in the mol. and 1 or more acid groups (which can react with the polymer in the presence of an activator, such as an org. peroxide or hydroperoxide), such as maleic anhydride or acid, fumaric, acrylic, or methacrylic acids. At least 10% of the C of the main chain of the polymer or copolymer should be tertiary, with Me as optional substituent. The mixts. may contain also basic substances, such as ZnO, MgO, PbO, org. multivalent compds., a diamine, or a glycol, and are prepd. at 30-70° in presence of an optional solvent and vulcanized at 120-80°. For example, 100 parts of an ethylene-propylene copolymer (I) contg. 60% propylene is introduced into a cylinder mixer at 60° and mixed for 20 min. to a homogeneous sheet. Then 3 parts Bz₂O₂ is added. The mixing is continued for 10 min. more. Then, 8-10 parts maleic anhydride and, after 15 min., 2 parts ZnO, are again mixed. Finally the mixt. is vulcanized at 160° for 10-20 min. Sheets with satisfactory elastic properties are obtained.

Bibliographic Information

Unsaturated linear elastomeric high polymers. Natta, Giulio; Mazzanti, Giorgio; Boschi, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 565323 19570716 Patent language unavailable. CAN 53:86815 AN 1959:86815 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 174)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 565323		19570716	IT	

Abstract

High polymers contg. double bonds in the main chain are obtained by polyimg. a mixt. of 3 hydrocarbons (C₂H₄, C₂H₂ hydrocarbons, such as C₂H₂ or phenylacetylene, and α -olefins, such as propylene or 1-butene) in presence of a hydrocarbon solvent and a catalyst, obtained from a compd. of a transition metal of the Groups IV-VI (e.g., VOCI₃) and from a metallo-org. compd. (Groups I-III) (e.g., trihexylaluminum), at 50° and 1-20 atm. The above copolymers are vulcanizable elastomers. For example, a mixt. of C₂H₄ 10, propylene 80, C₂H₂ 2.7, and propane 7.3 parts by vol. are put into a 1-l. autoclave (contg. 0.018 mol. trihexylaluminum in 250 cc. heptane) and warmed, while shaking, to 160°. The reactor is fed continuously with the monomer mixt. at a const. pressure of 6 atm. and an output of 80 l./h. The temp. is kept at 25-30°. After 3 h. the product is discharged and washed with aq. HCl in N atm. The 2 phases are sepd. The heptane phase is washed with H₂O. The polymer is coagulated by an excess of acetone and MeOH to give 22 g. of a blackish product. This is extd. successively with acetone, Et₂O, and CCl₄. The exts. are, resp., 10% (red-yellowish semisolid contg. (IR spectrum) C₂H₄ 44, propylene 40, and C₂H₂ 16%), 63% (solid yellow; propylene 70, C₂H₄ 24, and C₂H₂ 6%; intrinsic viscosity 1.1), 14.4% (purple solid, intrinsic viscosity 2.7, IR spectrum same as the preceding fraction). The residue (12.5%) is solid, black, amorphous, and C₂H₂-rich. Both the total product and its fractions are vulcanizable.

Bibliographic Information

Unsaturated high-molecular linear copolymers. Natta, Giulio; Mazzanti, Giorgio; Boschi, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 566913 19570921 Patent language unavailable. CAN 53:75554 AN 1959:75554 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 117)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 566913		19570921	IT	

Abstract

High-linear copolymers, without homopolymers, of 1 or more CH₂:CHR olefins (R = H or alkyl), such as propylene, with conjugated diolefins having at least 1 vinyl bond, such as isoprene, are obtained from the monomer mixt. in the presence of an inert solvent and of a catalyst obtained from a transition metal of Groups IV-VI (e.g., VOCI₃) and a metallo-ovrddot.org. compd. of Groups II-III (e.g., n-C₆H₁₃)₃ Al at 20-80°. For example, 0.024 mole n-(C₆H₁₃)₃ Al in 350 cc. heptane is introduced into a 2-1. autoclave in a N atm., and 0.4 mol. isoprene added. A mixt. of 5.8 moles propylene and 0.7 mole propane is injected. The mixt. is warmed to 50°, stirred, treated with 0.004 mole VOCI₃ dissolved in 50 cc. heptane under a N atm., left for 1.5 hrs., injected with 0.3 mole isoprene, and left for 3 hrs. The product is discharged, and the inorg. substances are removed by aq. HCl. The heptane phase is treated again with HCl and then several times with H₂O. The product is

coagulated with acetone and MeOH and dried to give 30 g. product. The acetone, Et₂O, and heptane exts. are 6.4%, 53.6% (isoprene content 15%), and 40% (isoprene content 10%), resp. Other examples with propylene, ethylene, and propane mixts. are reported.

Bibliographic Information

Polymerizing ethylene to highly-crystalline linear polymers. Natta, Giulio; Farina, Mario; Ragazzini, Mario. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 566630 19570913 Patent language unavailable. CAN 53:75516 AN 1959:75516 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 119)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 566630		19570913	IT	
GB 853229			GB	

Abstract

The use is claimed of catalysts prepd. from an alcoholate of a transition metal of Groups IV-VI (e.g. Ti tetraalcoholate) and a metallo. ovrddot.org. compd. of the Groups II-III (e.g. AlEt₃) in a molar ratio between 1:20 and 1:250. For example, the catalyst is prepd. in a N atm. by dissolving AlEt₃ and Ti isopropylate in anhyd. heptane. The soln. is pumped into an autoclave at the reaction temp., and after 15 min., C₂H₄ is admitted continuously. In 3 expts. (pressure of 25 atm. for 4 hrs.; total heptane, 1000 cc.) with the AlEt₃/Ti isopropylate ratio increasing from 10 to 50, the polyethylene yield nearly doubled, and the butene per cent dropped from 67 to 15%.

Bibliographic Information

Elastomers with improved elastic properties obtained from linear amorphous polymers of α -olefins containing more than three carbon atoms. Natta, Giulio; Bruzzone, Mario; Borsini, Giancarlo. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 564806 19570702 Patent language unavailable. CAN 53:75409 AN 1959:75409 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) - (U 104)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 564806		19570702	IT	
US 3050503		19620821	US 1957-651785	19570409

Abstract

Amorphous high polymers of α -olefins above propylene, particularly with 4-10 C atoms, after chlorosulfonation and vulcanization, give elastomers with better elastic properties than chlorosulfonated and vulcanized polypropylene (Ital. 537,429). For example, 10 g. amorphous poly(α -butene) (intrinsic viscosity in Tetralin at 135°, of 1.5×10^2 cc./g.) is dissolved in 200 cc. CCl₄. The temp. is kept at 50°, and 1.3 cc. SO₂Cl₂ added dropwise in the presence of 0.08 cc. pyridine and light (200-w. lamp). After 2 hrs. the polymer is pptd. by an excess of MeOH and dried at 65°. The product 100 is mixed with PbO 40, 2-mercaptothiazole 2, rosin 5, and antioxidant 1 part at 30° for 10-20 min. and vulcanized for 30 min. at 150° and 50 kg./sq. cm. Other examples with poly(α -hexene) are reported.

Bibliographic Information

Elastomers with highly elastic properties from copolymers of ethylene with α -olefins. Natta, Giulio; Mazzanti, Giorgio; Bruzzone, Mario. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 563508 19570601 Patent language unavailable. CAN 53:75401 AN 1959:75401 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 108)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 563508		19570601	IT	
GB 861542			GB	

Abstract

Vulcanizable elastomers are obtained from linear, amorphous copolymers, free from double bonds along the polymeric chain, from ethylene with aliphatic α -olefins of 3-6 C atoms, such as propylene, by modifying the copolymers by adding macromols. of substituents, such as Cl or SO₂R, where R = Cl or OH, or radicals suitable to form transverse bonds. The various conditions of influencing the structure of the copolymers are examd. in detail. For example, 10 g. ethylene-propylene copolymer (45% propylene; mol. wt. 165,000) are dissolved in 200 cc. CCl₄ and subjected to chlorosulfonation by pouring into the soln. at 50° within 90 min. a soln. of 1.8 cc. SO₂Cl₂ in 50 cc. CCl₄ in the presence of 0.16 cc. pyridine. The reaction is stopped after 2 hrs. with an excess of MeOH. The coagulated polymer, contg. 4.4% Cl and 1.0% S, is dried at 65°. The product 100 is mixed with Pb oxide 40, rosin 5, 2-mercaptobenzothiazole 2, and stearic acid 3 parts (or with thiourea 10.5 and rosin 2.5 parts) and vulcanized at 163° (or 150°) for 40 (or 30) min. at a pressure of 50 kg./cc. The satisfactory elastic properties of the obtained sheets are reported.

Bibliographic Information

Propylene polymers of high molecular weight. Natta, Giulio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1955), IT 535712 19551117 Patent language unavailable. CAN 53:54109 AN 1959:54109 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (u 59)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 535712		19551117	IT	
DE 1094985			DE	

Abstract

The use of Ziegler-type catalysts for the low temp. production of cryst. and amorphous polypropylenes and C₃H₆C₂H₄ copolymers is described. The materials obtained have mol. wts. of 20,000 to >100,000, specific viscosities of 0.12-0.38, m. ps. of 120-170°, and ds. of 0.90-0.97. The materials can be formed and shaped easily and the cryst. materials are claimed to be useful for textiles. For example, 335 g. C₃H₆ and 15 g. C₂H₄ were pumped, in 2 batches, into an autoclave contg. 1.8 g. TiCl₄ plus 11.8 g. AlEt₃ in 500 ml. C₆H₆ and made to react at 60°. The 180 g. of white solid produced was extd. successively with MeOH, (iso-Pr)₂O, acetone, Et₂O, and heptane yielding cryst. material of specific viscosity 0.374 as a 1% soln. in Tetralin. The material had a d. of 0.92, sintered at 120°, lost its crystallinity at 150°, and fused to an oil at 170°. It could be stretched to 700% of its original length, a 0.3-mm. diam. filament thus stretched having a breaking strength of 32 kg./sq. mm. and an elastic limit of 40%. The structure appeared to be that of a spiral hydrocarbon chain with a repeating distance of 6.4 Å. The extd. products were amorphous and could be recovered as plastics of lower mol. wt.

Bibliographic Information

Polymerization of α -olefins. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1956), Addn. to Ital. 526,101. IT 545332 19560630 Patent language unavailable. CAN 53:37492 AN 1959:37492 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u73/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 545332		19560630	IT	
US 3261820		19660719	US 1958-753624	19580807

Abstract

The use of catalysts based on metals of the 4th-6th group, instead of Ti, is claimed, and further details are given. For example, introduce 2 steel pellets and a vial contg. 4.3 g. VCl_4 into a 435-cc. autoclave, evacuate, introduce N and then 5.7 g. AlEt_3 dissolved in 100 cc. heptane, warm to 81° , introduce 118 g. liquid propylene, shake to break the vial, and keep the temp. at $81\text{-}3^\circ$ until the pressure drops. When the pressure stops decreasing, decomp. the catalyst with MeOH, discharge the product (solid green mass), free it from inorg. compds. by treatment with Et_2O and HCl, coagulate with MeOH, filter, and wash with MeOH. The dry white product obtained (72 g.) contains an Et_2O -extractable aliquot (37.5 g., amorphous) and a highly cryst. residue (48% polymer).

Bibliographic Information

High-molecular-weight olefin copolymers. Natta, Giulio; Mazzanti, G.; Boschi, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 554803 19570116 Patent language unavailable. CAN 53:20603 AN 1959:20603 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u96)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 554803		19570116	IT	

Abstract

Linear, high-mol., homopolymer-free copolymers of $\text{CH}_2\text{:CHR}$ (R .dbd. alkyl), such as propylene, 1-butene, 1-pentene, and 1-hexene, with each other or with C_2H_4 , are obtained by causing them to react in the presence of an org. solvent and a catalyst formed by the reaction product of a sol. compd. of a transition metal (Groups IV-VI), with a metalloalkyl compd. (a metal of Groups II-III, alkyl with $>4\text{C}$), at $<50^\circ$ or 100° (according to the desired mol. wt.). For example, to a soln. of 0.025 moles AlEt_3 in 300 cc. heptane in an N atm. 185 g. propylene (88.5%) + propane and 12 g. C_2H_4 are added, and the mixt. is warmed to 45° . On the addn. of a soln. of 0.008 moles VOCl_3 in 50 cc. heptane, the temp. is increased to 65° , and the pressure dropped to 23 atm. Then 150 cc. MeOH is injected to stop the reaction. The product is discharged, purified with acid, e.g. HCl solvents, and coagulated with MeOH to give 43 g. product (I). Me₂CO extd. from I 14% oily, low-mol. copolymers, whose infrared spectrum showed bands of Me and H_2C groups; Et_2O extd. from I 66.4% amorphous solid, intrinsic viscosity 0.89, mol. wt. 27,000, contg. 85% propylene (infrared detn.); and heptane extd. 19.6% amorphous solid, intrinsic viscosity 2.44, contg. 48% propylene.

Bibliographic Information

High-molecular-weight linear polymers of α -olefins. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1956), IT 545337 19560630 Patent language unavailable. CAN 53:20569 AN 1959:20569 CAPLUS (Copyright (C) 2007 ACS on SciFinder

(R). (u 73/c)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 545337		19560630	IT	

Abstract

The temp. limits claimed in Ital. 526,101 are increased from -70° to 200° , thus the av. mol. wt. of the polymer is influenced. For crystallizable polymers, the most active catalysts, i.e., Group IV-VI metals, with a valence less than max., such as $TiCl_3$, are used. Data on yield and degree of polymerization of polymers obtained from C_3H_6 or C_4H_8 or C_5H_{10} with the above mentioned catalysts, at various temps., are tabulated. For example, 5.7 g. $AlEt_3$ dissolved in 60 cc. heptane is placed in a 500-cc. flask (N atm.) and cooled to -25° . Then, 60 g. of a 1:1 mixt. of 1-butene and 2-butene, is added at -25° . $TiCl_4$ (3.8 g.) dissolved in 30 cc. heptane is dropped in and left for 6 hrs. at -25° . MeOH is introduced slowly, and the temp. allowed to increase to 20° (20 l. gases collected). The resulting product is treated with Et_2O and HCl and coagulated with MeOH to give 11 g. polybutene with an intrinsic viscosity (in Tetralin at 135°) of 1.72. In another example, 7 g. $TiCl_3$ and a soln. of 6.4 g. $AlEt_3$ in 500 cc. heptane are placed in a 2080-cc. autoclave, warmed to 170° , and 190 g. of propylene (80%)-propane mixt. (temp. increased) is added. The autoclave is shaken for 20 hrs., and 100 cc. MeOH added. The product is discharged, treated with HCl, coagulated with MeOH, filtered, and washed to give 137 g. white solid polypropylene. The oily impurities are removed with warm acetone. The extrn. residue has an intrinsic viscosity of 0.27 and is cryst. (x-ray). The residue of a heptane extrn. has a viscosity of 0.63 (mol. wt. 16,000) and is highly cryst.

Bibliographic Information

Crystalline linear high polymers of diolefins. Natta, Giulio; Porri, Lido; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1955), IT 536631 19551207 Patent language unavailable. CAN 53:20463 AN 1959:20463 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)), (u 78)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 536631		19551207	IT	

Abstract

Conjugated diolefins with at least 1 double vinyl bond can be transformed to regular linear and cryst. polymers by performing the conventional reaction (even at room temp.) in the presence of a solid catalyst (e.g., the reaction product of $TiCl_3$ with $AlEt_3$) contg. chiefly a solid Ti (valence <4) halide and, at least superficially, metalloalkyl (I) bonds, or metallo-H bonds capable of giving I by reaction with a double vinyl bond. For example, 3 steel beads and a vial contg. 6.1 g. $TiCl_3$ are placed in a stainless autoclave (2150 cc.) in N atm. Then, a soln. of 11.4 g. $AlEt_3$ in 500 cc. heptane is added, warmed to 65° , and 310 g. butadiene introduced. The autoclave is shaken to break the vial and shaking is continued for 20 hrs. at $60-5^{\circ}$. The unreacted gases are discharged, and MeOH is pumped into the autoclave to decomp. metallo.ovrddot.org. compds. A brown-violet semisolid mass is poured from the autoclave, purified with Et_2O and HCl under a N atm., and further coagulated with MeOH, filtered, washed with MeOH to obtain a solid polymer whose Et_2O -insol. (but heptane-sol.) fractions are highly cryst. (by x-ray). The infrared absorption spectrum shows the double bonds of the product not to be vinyl, but over 90% are of the trans type. In a similar example, an isoprene polymer is obtained which is partially Et_2O -sol. The insol. portion is sol. in warm benzene, highly cryst. on x-ray examn., and has the same spectrum as natural purified gutta-percha (α - and β -forms). In another example, a pentadiene polymer is reported, which gave on extrusion, flexible yarn whose x-ray examn. showed polymer micromols. placed parallel to the yarn axis.

Bibliographic Information

Succinic acids. Natta, Giulio; Pino, Piero. (Lonza Elektrizitatswerke und Chemische Fabriken A.-G.). (1958). US 2851486 19580909 Patent language unavailable. CAN 53:17106 AN 1959:17106 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2851486		19580909	US 1956-573444	19560323
GB 828441			GB	

Abstract

Succinic acid (I) compds. are prepd. by treating monoacetylene compds. with CO and H₂O in the presence of group 8 metal carbonyl catalyst in a solvent by dissolving the monoacetylene compds., H₂O, and the catalyst at 80-250°/150-500 atm. in an acid medium. Thus, 216 g. acetone, 72 g. H₂O, and 10 g. [Co(CO)₄]₂ was placed in a 1710 cc. autoclave, 14 l. C₂H₂ introduced, CO gradually forced into the autoclave to 200 atm., the autoclave heated at 110° 3 hrs., cooled to room temp., the gases released, the liquid product withdrawn, filtered, the acetone and part of the liquid distd., H₂O, cyclopentanone, and 3.8 g. mixt. of acrylic and propionic acids distd., the residue dissolved, and recrystd. to yield 60 g. I, also prepd. using dioxane solvent and Co succinate catalyst. Similarly prepd. was di-Ph deriv. of I, m. 166°. A continuous process and an app. were described.

Bibliographic Information

Block polymers from α -olefins. Natta, Giulio; Crespi, G. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957). IT 557911 19570221 Patent language unavailable. CAN 53:9848 AN 1959:9848 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) , (U 85)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 557911		19570221	IT	

Abstract

Block polymers of α -olefins CH₂.dbd.CHR (R = alkyl or aryl), such as propylene, 1-butene, and 1-pentene, are obtained by selective extn. with solvents, such as Et₂O and iso-Pr ester from mixts. with isotactic and nonisotactic polymers.

Bibliographic Information

Hydroperoxides of α -olefin polymers. Natta, G.; Beati, E.; Severini, F. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957). IT 556509 19570206 Patent language unavailable. CAN 53:9847 AN 1959:9847 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) , (T 150)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 556509		19570206	IT	

Abstract

Polymers (mol. wt. >1000) of α -olefins of the formula $\text{CH}_2=\text{CHR}$ (R is an alkyl, aryl, or alkylaryl group), such as polymers of styrene, methylstyrene, propylene, and butylene, are transformed to hydroperoxides by soln. in an aromatic solvent (e.g., cumene) and by action of O-contg. gases in the presence of 1-3% MeOH at 60-80° and at a pressure > 1 atm. For example, 28 g. amorphous polystyrene (mol. wt. 10,000) is dissolved in 43 g. cumene, warmed to 70°, pressurized with air to 25 atm., reduced to 24 atm., and shaken for 7 hrs. The polymer is pptd. with MeOH, and the solvent removed to give the product (intrinsic viscosity corresponding to a mol. wt. of 8000) having a hydroperoxide group for every 18 monomer units. Cumene has 0.25% fixed O. By adding 1.9 g. MeOH to the above treatment, leaving the reaction until the pressure drops to 22 atm., and shaking for 8 hrs., the ratio of hydroperoxide is doubled. Cumene has 0.4% fixed O, and the polymer has a mol. wt. of 8000.

Bibliographic Information

High-molecular-weight linear diolefin polymers. Natta, G.; Porri, L. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), IT 553904 19570104 Patent language unavailable. CAN 53:9843 AN 1959:9843 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (478/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 553904		19570104	IT	
GB 835752			GB	

Abstract

Diolefins, such as butadiene, isoprene, and 1,3-pentadiene are polymd. in presence of solid catalysts, insol. in the polymn. liq. phase. These catalysts are obtained by reaction between Al or Zn alkyls with halides (or oxyhalides) of metals with an at. no. >22 (Groups IV-VI) at their max. valence, such as VCl_3 and V or Cr oxychlorides. For example, 0.0285 mols. AlEt_3 and 50 cc. heptane are placed in a 250-cc. 3-neck flask under a N atm., and to this is added 0.01 mol VOCl_3 dissolved in 35 cc. heptane (black ppt.). Gaseous butadiene (at 20-5°) is introduced for 2.5 h. The reaction is stopped by adding 50 cc. MeOH. The product is treated with dild. HCl, coagulated with MeOH, filtered, washed with MeOH, and dried to give 16 g. of a polymer (x-ray cryst.). The acetone, Et_2O , and heptane exts. were 20, 10, and 21%, resp.; amorphous, amorphous, and cryst., resp.; and had 71, 75, and 95%, resp., of monomeric units with 1-4 linkage. The residue of the heptane extrn. (47%) was cryst.

Bibliographic Information

High-molecular-weight linear polyethylenes of high melting point. Natta, Giulio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1956), IT 547314 19560825 Patent language unavailable. CAN 53:9841 AN 1959:9841 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (494)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 547314		19560825	IT	

Abstract

C_2H_4 polymers, having a mol. wt. >50,000, without side branches, m. 130-40°, and d. of 0.95-0.98, are produced by performing the polymerization in presence of catalysts having a microcryst. structure. These

catalysts are obtained by surface reaction of solid microcryst. transition metals (Groups IV-VI), having lower-than-max. valence and insol. in the olefin solvent, with metallocene compds. (e.g. Ti, V, Zr halides, especially $TiCl_3$, with $AlEt_3$). For example, 0.83 g. $TiCl_3$ and 200 cc. heptane are put in a 1100-cc. autoclave having a N atm. and a pressure of 50 mm. Hg, warmed to 95°, injected with a soln. of 2.4 g. $AlEt_3$ in 30 cc. heptane, treated with C_2H_4 up to 4 atm., and shaken for 45 min. at 95-104°, (fed with C_2H_4 to a const. 4 atm.). The product is discharged, washed with BuOH and MeOH, and dried to give 24 g. polyethylene (highly cryst.) with a mol. wt. of 380,000, and Vicat no. of 133°.

Bibliographic Information

α -Olefin polymers with high melting points. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1956), IT 545342 19560630 Patent language unavailable. CAN 53:9840 AN 1959:9840 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u73/D)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 545342		19560630	IT	

Abstract

By polymerizing (cf. Ital. 526,101) $CH_2:CHR$ (where R is $(CH_2)_nCHMe_2$ and n is >1), particularly 4-methyl-1-pentene (I) and 5-methyl-1-hexene, products are obtained with a m.p. much higher than those obtained from linear α -olefins. For example, 3.2 g. $TiCl_3$ and 36 g. I are treated with 5.7 g. $AlEt_3$, and stirred for 8 hrs. at the b.p. (54-70° with increasing polymerization). The catalyst is decompd. with MeOH or HCl. MeOH is added to sep. a white waxy polymer which is washed and dried. Its acetone ext. (44%) is oily (low-mol. wt.). The EtOAc ext. (17.5%) is solid and partially cryst. (intrinsic viscosity 0.24). The Et₂O ext. (14%) is poly(4-methyl-1-pentene), partially cryst. with an intrinsic viscosity of 0.54. The residue of the last ext. (24.5%) is a poly(4-methyl-1-pentene), highly cryst. with a transition temp. of 200-5° (intrinsic viscosity 1.37).

Bibliographic Information

Copolymers of α -olefins with diolefins. Natta, Giulio; Pino, Piero; Porri, Lido. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1956), IT 545333 19560630 Patent language unavailable. CAN 53:9839 AN 1959:9839 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (u73/B)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 545333		19560630	IT	
GB 836790			GB	

Abstract

Diolefins with at least 1 vinyl bond (such as 1,3-butadiene, isoprene, and 1,3-pentadiene) and aliph. α -olefins $CH_2:CHR$ (R = alkyl) with at least 3 C atoms (such as 1,5-hexadiene) are copolymd. at 20-80° in the presence of a suitable catalyst for the prepn. of amorphous polymer (cf. Ital. 526,101). Solid, amorphous, linear, and high-mol. polymers are obtained. For example, 9 g. $AlEt_3$ dissolved in 400 cc. heptane and a mixt. of α - and β -butene (55% of α) are placed in a 2-1. autoclave, shaken, and warmed to 50°. A little cylinder contg. 8.5 g. $TiCl_2(BuO)_2$ dissolved in 50 cc. n-heptane is introduced. Then 79 g. tech. butadiene is added within 1 h., and allowed to stand for 4 h. The reaction is stopped with 50 cc. MeOH. The unreacted gases are recovered. The remaining mixt. in the autoclave is cooled, coagulated with acidic (HCl) MeOH, and filtered (washed with MeOH).

to sep. 50 g. of solid polymer (amorphous; I no. 350) and, from the filtrate, 3 g. of viscous liq. polymer.

Bibliographic Information

Acetylene-olefin copolymers of high molecular weight. Natta, Giulio; Piero, Pino; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1955). IT 536899 19551212 Patent language unavailable. CAN 53:9837 AN 1959:9837 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

(U 81/A)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 536899		19551212	IT	

Abstract

The catalysts of Ital. 530,753 (C.A. 52, 15128b) can polymerize C₂H₂ in the presence of olefin hydrocarbons to form linear high-mol. copolymers, if the olefin contains vinyl double bonds CH₂.dbd.CHR (where R can be linear, have side branches, or on aryl group). With phenylacetylene (I) and α -olefins, copolymers are obtained with high intrinsic viscosity. For example, 6.5 g. TiCl₃, 11.4 g. AlEt₃ (in 500 cc. heptane), 32 g. I, and 205 g. butylene mixt. (1- and 2-butene, 1:1 are placed in an autoclave (2080 cc.), shaken, and warmed to 60-5° for 20 hrs. The unreacted gases are discharged. MeOH is pumped into the autoclave. A yellow copolymer is discharged, treated with Et₂O and HCl, coagulated with MeOH, filtered, washed with MeOH, and dried. The acetone, Et₂O, heptane, and benzene exts. were 53.9, 12.45, 8.3, and 23%, resp., of the polymer, and were orange-red (chiefly I polymer), yellow (iodine no. = 146), clear yellow (iodine no. = 84.5), and orange-yellow, resp. Further examples with I and 1-pentene, C₂H₂ and styrene, and I and propylene as starting materials are reported.

Bibliographic Information

Crystalline polystyrene. Natta, Giulio; Danusso, Ferdinando; Sianesi, D. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957). IT 558314 19570207 Patent language unavailable. CAN 53:9828 AN 1959:9828 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)), (U 63/D)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 558314		19570207	IT	
GB 847102			GB	
GB 847102			GB	
US 3161624		19641215	US 1957-640523	19570215

Abstract

A description is given of styrene polymerization in the presence of halides (I) of transition metals of Groups IV-VI at their max. valence and of metallo.ovrddot.org. compds. (II) (Groups II-III), particularly in presence of TiCl₄ and AlEt₃ (3.5:2). This process is improved by allowing the reagents to be brought into contact in the following order: I in a soln. of a hydrocarbon, II in the same solvent, and styrene at a temp. of 70-100°. An isotactic, cryst. polymer is formed.

Bibliographic Information

Styrene-derivative polymers. Natta, G.; Beati, E.; Severini, F. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957). IT 553905 19570104 Patent language unavailable. CAN 53:9827 AN 1959:9827 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)), (D 104)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 553905		19570104	IT	

Abstract

Styrene-deriv. polymers, obtained at 50-120° in the presence of a high-mol. amorphous linear polymer (mol. wt. 2000-500,000) of α -olefins especially of propylene and 1-butene, are dissolved in the amt. of 5-20% in the styrene monomer or their peroxide derivs. (O content 0.1-1%). For an example of prepn., styrene is polymerized in the presence of a linear polymer consisting of the acetoneinsol., ether-sol. fraction of the polymerization product of propylene with $TiCl_4$ and $AlEt_3$.

Bibliographic Information

Hydroperoxides. Natta, Giulio; Beati, Enrico. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1958), US 2843633 19580715 Patent language unavailable. CAN 52:113514 AN 1958:113514 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (F & 1)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2843633		19580715	US 1954-402129	19540104

Abstract

This process describes the production of cumene hydroperoxide from cumene by heating a mixt. of MeOH (2.5 to 6.25% by vol.) with cumene in an enclosed stainless-steel vessel with air enriched with O at 8-15 atm. and at 90-120°.

Bibliographic Information

High-molecular-weight polymers of acetylene hydrocarbons. Natta, Giulio; Pino, Piero; Mazzanti, Giorgio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1955), IT 530753 19550715 Patent language unavailable. CAN 52:85716 AN 1958:85716 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U & 1)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 530753		19550715	IT	
DE 1052689			DE	
GB 826674			GB	
US 3119799		19640128	US 1956-570962	19560312

Abstract

Sol. high polymers from C_2H_2 hydrocarbons are obtained at 0-150° and 20-80 atm. by use of catalysts formed from compds. of transition metals of the 4-8th group contg. alkyl groups attached to the metal. Such catalysts are obtained by reaction between the transition metal and a metallorganic compd., e.g., Al-, Zn- or Li-alkyls, e.g.,

TiCl₃ with Et₃Al. The hydrocarbons are conveniently dild. with inert or nonreacting gases, e.g., H or CH₄. For example: (1) put 7.5 g. TiCl₃ and 5.7 g. of a soln. of Et₃Al in 425 cc. C₆H₆ into a stainless-steel autoclave in a N atm. Introduce C₂H₂, warm to 40°, and continue to introduce C₂H₂ up to 40 l. After 30 hrs., discharge unreacted gases, introduce MeOH, discharge the reaction product as a black powder, filter, and purify from inorg. products by repeated suspension in MeOH and HCl. Finally, filter, wash with MeOH, and dry, to get 17 g. polymer. (2) Introduce a soln. of 11.4 g. Et₃Al in 200 cc. heptane into a flask with a stirrer, bubble in C₂H₂ at 20°, drop in slowly a soln. of 1.9 g. TiCl₄ in 50 cc. heptane, continue to bubble in C₂H₂ at 3 l./hr. for 17 hrs. at 50°. Introduce 100 cc. MeOH, treat the (black) reaction product with HCl, filter, wash repeatedly with MeOH, and dry, to get 12.5 g. polymer. The polyacetylene obtained is said to be formed by linear chains of methine groups with a series of double conjugated bonds of high reactivity, and to have a mol. wt. above 1000. Phenylacetylene gave a red polymer, ethylacetylene a dark-brown one.

Bibliographic Information

Esters from cyclohexene, carbon monoxide, and alcohols. Natta, Giulio; Pino, Piero; Ercoli, Raffaele. ("Montecatini," Societa generale per l'industria mineraria e chimica). (1957), US 2805245 19570903 Patent language unavailable. CAN 52:35434 AN 1958:35434 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4 50)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2805245		19570903	US	

Abstract

Esters of mono- and polycarboxylic acids are produced by treating cyclohexene with CO and an alc. using a special alc. sol. catalyst and lower temp. and pressure than previously used. An oscillating autoclave of 435 cc. capacity is charged with 4.5 g. [Co(CO)₄]₂ (l), 100 cc. soln. of 44.4 g. cyclohexene in 34.7 g. MeOH, and 140 atm. CO, heated to 165°/240 atm. 7.5 hrs., and the product distd. yielding 25.1 g. unchanged cyclohexene, 26.2 g. Me hexahydrobenzoate, and 4 g. other products (mainly hexahydrobenzaldehyde di-Me acetal). Similarly prepd. was 45% Bu hexahydrobenzoate. I (4 g.), 144 g. MeOH, 32 g. propylene, and 250 atm. CO heated to 135° 12 hrs. gave 198 g. mixt. contg. 85% Me butyrates. Me hexahydrobenzoate (25 g.) in 39 g. of BuOH contg. 5% Na butylate refluxed 1 hr. and slowly rectified with strong reflux in a 90 cm. Fenske packing column gave 7 g. MeOH and 23 g. BuOH; distg. the residue in vacuo gave 77% Bu hexahydrobenzoate, b₂₀ 115-9°. Cf. C.A. 46, 5615e.

Bibliographic Information

Crystalline butadiene polymers. Natta, Giulio; Porri, Lido. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1956), IT 538453 19560125 Patent language unavailable. CAN 52:27895 AN 1958:27895 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (4 89)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 538453		19560125	IT	

Abstract

Cryst. linear butadiene polymers, chiefly with 1-2 linkage, are obtained by performing the polymerization at -80° to 150° in the presence of a catalyst formed by the reaction of a metal-org. compd. (1st-3rd group metal) with an O-contg. compd. of a transition metal of the 4th-6th group. Highly cryst. products are obtained by extg. the

amorphous part of the raw polymer with suitable solvents. Thus: shake 2.5 g. AlEt₃ in 50 cc. heptane and 100 g. tech. 95% butadiene in vacuo, add 2.5 g. Ti(OBu)₄ in 50 cc. heptane, shake for 10 hrs. at 15°, introduce 20 cc. MeOH, recover unreacted butadiene, treat the reaction product repeatedly with HCl, wash with water, coagulate with MeOH, filter, dry the solid residue (11.5 g. white polymer) at 50° in vacuo, and evap. the filtrate to get 2.5 g. oily polymer. The acetone ext. of the solid polymer is amorphous (x-ray examn.), and 60% of its unsatd. bonds are vinyl groups; the same is true for the ether ext., while the heptane ext. (40%) is sharply cryst. and with nearly 100% of vinyl groups. The mol. wts. of the 3 exts. are 8700, 33,000, and 13,000, resp. Instead of Ti(OBu)₄ the Cr or V compds. with acetylacetone are also used. Cf. C.A. 51, 10171e.

Bibliographic Information

Furfural and acetic acid from pentosan-containing materials. Natta, Giulio. (Oronzio De Nora Impianti Elettrochimici). (1957), US 2818413 19571231 Patent language unavailable. CAN 52:22813 AN 1958:22813 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2818413		19571231	US 1954-444859	19540721

Abstract

See Ital. 502,590 (C.A. 51, 18503a).

Bibliographic Information

Oxygenated compounds, particularly aldehydes from olefins, carbon monoxide, and hydrogen. Natta, Giulio; Ercoli, Raffaele; Castellano, Salvatore. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1955), IT 516716 19550224 Patent language unavailable. CAN 52:6604 AN 1958:6604 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (U 51)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 516716		19550224	IT	

Abstract

The oxo synthesis is allowed to take place at 50-130°, in a homogeneous phase, in the presence of Co₂(CO)₈ (l) (or other sol. Co compd. suitable for the catalysis), under a partial CO pressure of 5-35 atm. and a molar ratio H-CO of 4:60. To obtain a max. conversion velocity at 110°, the CO pressure should be 7-10 atm. I (1.2 g.) and 11.6 g. cyclohexene in n-heptane under 20 atm. CO and 100 atm. H in a 435-cc. autoclave warmed to 115°, stirred 35 min., and cooled rapidly gave 10.3 g. hexahydrobenzaldehyde. I. (1.4 g.) and 45.5 g. 2-ethyl-1-hexene in toluene in a 435-cc. autoclave warmed to 110° under 45 atm. H, treated with 20 atm. 1:1 CO-H, the pressure kept const. 68 min., and the mixt. cooled rapidly gave 13.5 g. aldehydes. I (2.8 g.), 70 g. toluene, and 25 g. propylene similarly treated gave 11.2 g. aldehydes.

Bibliographic Information

Furfural and acetic acid from pentosan-containing materials. Natta, Giulio. (Oronzio De Nora Impianti Elettrochimici). (1957), GB 774809 19570515 Patent language unavailable. CAN 52:3529 AN 1958:3529 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
GB 774809		19570515	GB 1954-22192	19540729

Abstract

See Ital. 502,590 (C.A. 51, 18503a).

Bibliographic Information

Furfural and acetic acid from pentosan-containing materials. Natta, Giulio. (1954), IT 502590 19541130 Patent language unavailable. CAN 51:102550 AN 1957:102550 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 502590		19541130	IT	

Abstract

The material is treated with HCl contg. recycled AcOH in a continuous, countercurrent app. at atm. pressure. As HCl is continuously refluxed down by the newly fed material, no HCl is consumed except for a small amt. required to neutralize natural basic substances in the material. The furfural vapor leaving the app. is HCl-free. The countercurrent operation permits higher yields. The treated material leaves the app. completely dry and acid-free. Upon entering the app., the material is moistened to 25% H₂O. Cf. C.A. 49, 14810b.

Bibliographic Information

Esters of mono- and polycarboxylic acids. Natta, Giulio; Pino, Piero; Ercoli, Raffaele. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1955), IT 512307 19550131 Patent language unavailable. CAN 51:66751 AN 1957:66751 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (U 50)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 512307		19550131	IT	

Abstract

A synthetic method from olefins, CO, and alcs. is given which involves (1), for the Me esters, a reaction of olefin or polyolefin compds. with CO (10-150 atm.) and excess MeOH at 130-180° in the presence of Co catalysts contg. Co carbonyl and (2), for the higher esters, the previous synthesis of the Me ester, as above, and transesterification with the higher alc. [Co(CO)₄]₂ (4.5 g.), 100 cc. of a soln. contg. 44.4 g. cyclohexene and 34.7 g. MeOH, and CO (at 140 atm.) heated in a 435-cc. autoclave 7.5 hrs. at 165° and the product distd. give 25.1 g. unreacted cyclohexene, 26.2 g. Me hexahydrobenzoate, and 4 g. other products.

Bibliographic Information

Continuous separation of gas mixtures having at least three components by solvent extraction.

Natta, Giulio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1957), US 2791290 19570507 Patent language unavailable. CAN 51:49970 AN 1957:49970 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (F 85)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2791290		19570507	US 1953-353715	19530508

Abstract

See Ital. 489,556 (C.A. 50, 11733i).

Bibliographic Information

Production of acetic acid and methyl acetate from methanol and carbon monoxide. Natta, G.; Pino, P. (Lonza Elektrizitatswerke und Chemische Fabriken A.-G.). (1955), CH 306638 19550430 Patent language unavailable. CAN 51:9477 AN 1957:9477 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
CH 306638		19550430	CH	19520131

Abstract

On addn. of 0.25-4 moles Me₂O/mole MeOH and 0.15-0.2 moles MeBr to a mixt. of MeOH and CO in the absence of H₂O, the reaction readily proceeds at 230-350° and 400-600 atm. in the presence of Ni carbonyl catalysts. The AcOH yield/mole of MeOH converted are considerably higher (as high as 66.5%) than in previously patented processes, since secondary reactions involving the loss of MeOH are minimized. The Me₂O is recovered and re-used.

Bibliographic Information

Separation of gas mixtures. Natta, Giulio. ("Montecatini," Societa generale per l'industria mineraria e chimica). (1956), US 2757754 19560807 Patent language unavailable. CAN 50:80159 AN 1956:80159 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (F 84)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2757754		19560807	US 1953-353714	19530508

Abstract

See Brit. 747,411 (C.A. 50, 11066e).

Bibliographic Information

Continuous isothermal separation of gases with boiling points close to each other. Natta, Giulio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1954), IT 489557 19540123 Patent

language unavailable. CAN 50:62812 AN 1956:62812 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (F 84)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 489557		19540123	IT	

Abstract

Continuous sepn. with practically complete recovery is accomplished by fractional absorption as a gas. The solvent is then completely freed of the component more sol. in the solvent and the residual gas mixt. then is put back into circulation. For example, a gas mixt. of 70% butylene and 30% butadiene was dissolved in anthracene oil and fractionated at 28° and 2 atm. For every 100 vols. of gas mixt., 2 vols. of solvent are used. The butadiene so obtained is 96-8% pure. The soly. at 28° in anthracene oil is 51 parts for butylene and 25 parts for butadiene.

Author Name task started on Wed May 9, 2007 at 10:15 AM

Explored by Author in CAPLUS and MEDLINE.

Natta, Giulio

Selected 2 of 3 candidates

NATTA G (325 references)

NATTA GIULIO (410 references)

Refine by Document Type started

Note: Refine by Document Type "Patent" is not supported by MEDLINE.

239 references were found when refined by Document Type "Patent"

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Bibliographic Information

Continuous separation of gas mixtures having at least three components by solvent extraction.

Natta, Giulio. ("Montecatini" Societa generale per l'industria mineraria e chimica). (1954), IT 489556 19540123 Patent language unavailable. CAN 50:62811 AN 1956:62811 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (F 8 5)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 489556		19540123	IT	

Abstract

Component A of a gas mixt. (A + B + C) is obtained practically pure with high yields by use of a special solvent Q. B can be miscible with A and also sol. in Q, but the soly. of B in Q must be less than that of A in Q. The soln. of A in Q is obtained by absorption at a pressure higher than atm. This soln. is then treated countercurrently in a fractional-distn. app. with the mixt. A + C. C should be almost insol. in Q. For example, a mixt. contg. 9% C₂H₂ A, 4% CO₂ B, and 87% other gases, principally CO and H, was compressed at 35-40 atm. and washed in countercurrent with 0.31 vol. of ethylene glycol diacetate per 100 vols. of fresh mixt.

Bibliographic Information

Hydrogenation of starch and similar carbohydrates. Natta, Giulio; Beati, Enrico. (Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler). (1953), DE 892590 19531008 Patent language unavailable. CAN 50:34328 AN 1956:34328 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 892590		19531008	DE 1941-D6087	19410507

Abstract

Starch and similar polyoses are hydrogenated in an aq. soln. contg. a small amt. of H₃PO₄ in the presence of a usual hydrogenation catalyst, such as a Ni-on-kieselguhr catalyst, at elevated temp. and possibly under pressure. For example, a suspension of potato starch in water (vol. ratio 1:4) is treated with H at 200 atm. and 170° in the presence of the catalyst. After 3 hrs. 99.6% of the starch is converted to sorbitol.

Bibliographic Information

Esters of 4-oxopimelic acid. Natta, Giulio; Pino, Piero. (1955), US 2699445 19550111 Patent language unavailable. CAN 50:1694 AN 1956:1694 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2699445		19550111	US 1952-296758	19520701

Abstract

CO and C₂H₂ in an alc. (Me or Bu) under 80-220 atm. pressure at 130-70° give mixts. contg. mainly dicarboxylic acids of 4 C atoms and their esters. However, at 200-400 atm. and 80-100°, esters of CO(CH₂CH₂CO₂H)₂ (I) are also formed. The yield of I can be increased by increasing the ratio of C₂H₂ to alc. (50 l. C₂H₂ to 100 g. MeOH). Esters formed in the reaction, such as Me and Et succinates, that have lower b.ps. than the oxopimelates, are desirable solvents. Metals of the Fe group or their halides, especially Raney Co, are suitable catalysts. Specifically, 80 g. of MeOH contg. 5 g. Raney Co in suspension in a 300-cc. autoclave, was charged with 7 l. C₂H₂ and CO to a pressure of 250 atm., the autoclave shaken and heated at 85° until no further absorption was observed at pressures greater than 200 atm., cooled, the gaseous components were removed, 10 more l. C₂H₂ and CO to 200 atm. pressure were introduced, this procedure was repeated 5 times, then the products were removed and fractionated; the Me ester of I was found in the fraction b15 150-70°.

Bibliographic Information

Furfural and acetic acid from pentosan-containing material. Natta, Giulio. (Oronzio De Nora Impianti Elettrochimici). (1954), US 2689250 19540914 Patent language unavailable. CAN 49:78067 AN 1955:78067 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2689250		19540914	US 1951-223032	19510426

Abstract

A mixt. of pentosan-contg. material (corn cobs, rice hulls, etc.), 15% water, and 3% HCl is fed continuously into a column, into the bottom of which superheated steam is introduced. The upward flow of steam causes vaporization of the HCl near the bottom of the column. This HCl condenses partially nearer the top of the column, thereby increasing the HCl concn. in this zone and causing reaction to occur. Gaseous products contg. furfural and HOAc are drawn off through the top of the column while the exhausted material, free of acid and water, at the bottom of the column is removed continuously.

Bibliographic Information

Ketones. Natta, Giulio; Ercoli, Raffaele. ("Montecatini" Societa Generale per l'Industria Mineraria e Chimica). (1952), IT 475040 19521009 Patent language unavailable. CAN 49:56835 AN 1955:56835 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)), (u 28)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 475040		19521009	IT	

Abstract

The process involves a reaction of olefins (including mixts. with paraffins) with CO (contg. up to 10% H as an impurity) and primary or secondary alcs., at 150-250° and 150-500 atm. pressure, in the presence of Co-contg. catalysts (fine Co, Raney Co, Co on an inert carrier, Co carbonyl or hydrocarbonyl, or other Co compds. which decomp. to the ones mentioned). Examples are: (1) secondary BuOH (I) 87 g., ethylene (II) 41.5 g., Raney Co (III) 4 g., and CO 140 l. in a 1-l. autoclave are shaken and warmed to 200-10° for 5 hrs., and cooled. Gas analysis shows that 25% of II did not react, while the liquid phase was shown to contain ketones 42.5, II 43.5, and propionaldehyde (IV) 3%. The yield of Et₂CO (V) was 65% based on the wt. of II reacted; (2) MeOH 75 g., II 25 g., III 3 g., and CO 180 l. were treated in the autoclave at 190-95° for 85 hrs. to give: unreacted II 19%, and

V 53%, Me propionate 20, and IV 7%, (based on the wt. of II reacted; (3) MeOH 220 g., propylene (VI) 84 g., III 16 g., and CO 105 l. at 200-10°, and 150-300 atm. yielded unreacted VI 49% and C7-ketones 27.5, Me butyrate and isobutyrate 33% based on the wt. of VI reacted.

Bibliographic Information

Dicarboxylic esters. Natta, G.; Pino, P. (Lonza Elektrizitatswerke und chemische Fabriken A.-G.). (1953), Addn. to Swiss 285,125 (C.A. 47, 11806c). CH 291730 19531001 Patent language unavailable. CAN 49:8419 AN 1955:8419 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
CH 291730		19531001	CH	

Abstract

A mixt. of Me oxalate (I), maleate (II), and fumarate (III) is obtained in good yield from C₂H₂, CO, and MeOH in the presence of certain catalysts. C₂H₂ (13.5 l. at standard temp. and pressure) in 100 cc. MeOH is treated with CO (80 to 150 atm.) at 105-5° in the presence of 1 g. Co deposited on 4 g. kieselguhr; the products are: CH₂:CHCO₂Me 7, I and II 21, III 3.5, and polymers 21 g.

Bibliographic Information

Separation of cashew-shell oil from kernel oil. Natta, Giulio; Rigamonti, Rolando. (1952), IT 476540 19521215 Patent language unavailable. CAN 48:74954 AN 1954:74954 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 476540		19521215	IT	

Abstract

The seeds are scraped in a rotatory app. with sand or steel wool, heated at 100-300° for up to 1 hr. in an inert atm. to avoid oxidation of the oil. They are then washed with an oil solvent, roasted at 400-700° in an inert atm., and cracked, possibly at freezing temps. to solidify traces of shell oil. The kernels are sepd. from the shells by a cold salt soln. and shell-oil traces removed by MeOH or EtOH.

Bibliographic Information

Methyl acrylate. Natta, G.; Pino, P. (Lonza Elektrizitatswerke und chemische Fabriken A.-G.). (1952), CH 285125 19521216 Patent language unavailable. CAN 47:69944 AN 1953:69944 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
CH 285125		19521216	CH	

Abstract

Acetylene, 4.8 l., in 210 ml. methanol and 11 l. CO is heated 2 hrs. at 150° and 150 atm. pressure with 2 g. finely pulverized Co and 1 g. NiCl₂. The reaction mixt. contains 4.8 g. methyl acrylate monomer, 1.5 g. dimethyl fumarate, and 3.5 g. other carboxylic acid esters.

Bibliographic Information

Furfural. Parodi-Delfino, Bombrini; Natta, Giulio. (1947), Addn. to Ital. 414,795. IT 423904 19470730 Patent language unavailable. CAN 46:14699 AN 1952:14699 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 423904		19470730	IT	

Abstract

A process is described for the manuf. of furfural which comprises introducing a counter current of gaseous or vaporized aq. HCl into a reactor fed with an aq. pentosan soln. The AcOH formed in 6-7% yield as a by-product and taken off in mixt. with HCl is converted to the Ca salt or sepd. from the HCl by passing the vapors consecutively through an absorbent having a high pH (absorption of HCl) and then through an absorbent with a low pH (absorption of AcOH).

Bibliographic Information

Esters. Natta, Giulio; Pino, Piero. (1950), IT 454922 19500208 Patent language unavailable. CAN 45:44387 AN 1951:44387 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 454922		19500208	IT	

Abstract

Olefin or polyolefin compds. (which must have a vapor pressure of less than 1 atm. at 150° and must not have 2 quaternary C atoms directly bound to the double bond, as the esters of oleic and linoleic acids) are allowed to react with CO and alcs. (in excess) in the presence of a solid catalyst contg. metallic Co at 100-200° and a pressure of 10-100 atm. with vigorous stirring. No practical examples are given.

Bibliographic Information

Production of aldehydes. Natta, Giulio; Beati, Enrico. (1950), GB 646424 19501122 Patent language unavailable. CAN 45:32814 AN 1951:32814 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
GB 646424		19501122	GB 1946-23404	19460807

Abstract

Aliphatic and cyclo-aliphatic aldehydes are obtained from olefins and cyclo-alkenes (having a b.p. not below the reaction temp.), H, and CO at a temp. above 80° and at a pressure of 10-50 atm. in the presence of a Co-contg. catalyst. Alkenoic acids with the double bond not adjacent to the CO₂H group and their esters react similarly. A preferred catalyst is partially reduced CoO activated with up to 2% Fe₂O₃ and supported on a carrier. Thus, to Me(CH₂)₁₅CH:CH₂ 1 and catalyst 0.1 kg. (obtained by partial reduction of basic carbonates of Co 98% and Fe 2% with H at 350°) in a 3-1. tank are added CO and H at a pressure of 12 atm., the mixt. heated at 100-10°, and the addn. of CO and H continued until the absorption ceases, to yield mainly Me(CH₂)₁₆CHMeCHO and Me(CH₂)₁₈CHO contg. small quantities of the corresponding alcs. One example each for the similar reaction with Me oleate, olive oil, and grape-stone oil is given.

Bibliographic Information

Continuous production of furfural. Parodi-Delfino, Bombrini; Natta, Giulio. (1948), FR 939810 19481125 Patent language unavailable. CAN 45:29782 AN 1951:29782 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 939810		19481125	FR	19470118

Abstract

In treating materials contg. pentosans, e.g. cornhusks, to obtain first pentoses and then, by elimination of water, furfural, the material is treated with HCl and passed into the top of a tower to be met with superheated steam coming in from the bottom. Condensation and fractionation of the vapors yield the acid, which can be reused to treat the pentoses; 80-90% of the theoretical yield of furfural is obtained. Cf. C.A. 44, 2032f.

Bibliographic Information

Preparation of formaldehyde with recovery of the hydrogen by dehydrogenation of methanol. Natta, Giulio; Baccaredda, Mario. (1948), IT 433280 19480405 Patent language unavailable. CAN 44:10167 AN 1950:10167 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 433280		19480405	IT	

Abstract

MeOH is dehydrogenated with a catalyst of Ag-wire mesh, activated with Pt, with an admixt. of less than 10% O, the quantity of the latter being kept below the limit of forming an explosive mixt. If the O content is high, no heating is necessary after the initial induction of the process; at low concns. heat is required. The O also prevents poisoning of the catalyst. The admixt. of 1 vol. H/vol. MeOH vapor decreases the dehydrogenation process only insignificantly but has a considerable retarding effect on the decompn. of the HCHO formed. The added H also permits the recovery of the H liberated in the process which otherwise would be too dil. to be recovered. The addn. of H to the mixt. furthermore reduces the danger of explosion.

Bibliographic Information

Purification of olefins from diolefins by selective hydrogenization. Natta, Giulio. (1948), IT 433554 19480410 Patent language unavailable. CAN 44:10136 AN 1950:10136 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 433554		19480410	IT	

Abstract

The selective hydrogenation of diolefins to olefins is possible by the use of catalysts of the Fe group, reduction of the oxides being avoided by working at low temp. (isothermally) and by dilg. the reducing gas with N or H₂O vapor. The catalyst was prepd. by reducing a mixt. of NiCrO₄ 3 with ZnCrO₄ 1 part on kaolin. A mixt. of 4.450 l. piperylene and 10.050 l. pentene was passed with an excess of H at 150° at the rate of 130 vols./hr. over 1 vol. catalyst; pentene 14.030 and piperylene 0.770 l. were recovered, and no trace of pentane was formed. A mixt. of butylene and butadiene at 170° gave pure butylene.

Bibliographic Information

Unsaturated alcohols. Natta, Giulio. (1948), IT 420794 19480220 Patent language unavailable. CAN 44:5596 AN 1950:5596 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 420794		19480220	IT	

Abstract

A process for the hydrogenation of unsatd. acids (without solvents) at 240-280° and 100-300 atm. in the presence of catalysts contg. metals with a H overvoltage between 0.3 and 0.6 v. and no tri- or higher-valent metal oxide or its hydrolyzable compds. is described. The catalyst may contain also metals with a H overvoltage lower than 0.3 v. The most suitable is said to be a mixt. of Cu and Cd oxides, or Cu and Sn oxides, prepd. by pptn. from mixed solns. of suitable salts. No detailed examples are given.

Bibliographic Information

Aliphatic alcohols. Natta, Giulio. (1948), IT 430809 19480220 Patent language unavailable. CAN 44:5595 AN 1950:5595 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 430809		19480220	IT	

Abstract

In the hydrogenation of free aliphatic acids of high mol. wt. to alcs., along with the catalyst CuO, promoters are

used which (1) have no activity on the esterification of the acids with the alcs. formed, (2) are not oxides or hydroxides or hydrolyzable compds. of tri- or highervalent metals, and (3) are preferably oxides of bivalent metals with atomic diam. between 1.50 and 1.8×10^{-7} mm., e.g., ZnO. The mixt., e.g., CuO-ZnO (resp. 95 and 5%), is obtained by pptn. of Cu and Zn basic carbonates from their salt solns.

Bibliographic Information

Petrolatum substitute. Natta, Giulio; Russo, Francesco. (Istituto per Lo studio della gomma sintetica). (1948), IT 429446 19480127 Patent language unavailable. CAN 43:48691 AN 1949:48691 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (443)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
IT 429446		19480127	IT	

Abstract

A dry mixt. (free from oxygenated compds.) of butylenes (which may contain pentene) with 20-30% butadiene is copolymerized in an autoclave at 50° in the presence of 1-3% AlCl₃, BF₃, or SnCl₄. The heat of reaction must be removed; the temp. may be raised at the end of the reaction especially when a higher percentage of butadiene is employed. The reaction product is then treated with bleaching earths and distd. in vacuo to remove the small quantity of light products formed. The purified product has 20-50° Engler viscosity at 100°, and can be easily emulsified with solns. It can be substituted entirely or in part for petrolatum.

Bibliographic Information

Keto alcohols. Natta, Giulio. (Alien Property Custodian). (1945), US 2378573 19450619 Patent language unavailable. CAN 39:25524 AN 1945:25524 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (22)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2378573		19450619	US 1940-340225	19400612

Abstract

A ketone such as Me₂CO is treated with CH₂O in dil. aq. soln. of pH 8-9. With approx. equimol. quantities of Me₂CO and CH₂O and a temp. of 25-32° 3-keto-1-butanol is the chief product. With 2 mols. of CH₂O to 1 mol. of Me₂CO and temp. of 30-40° 2-methylene-3-keto-1-butanol is the chief product. Without further purification the neutral or acidified soln. of the above may be hydrogenated to 1,3-butanediol and 2-methyl-1,3-butanediol, resp.

Bibliographic Information

Styrene. Natta, Giulio. (Alien Property Custodian). (1943), US 2308229 19430112 Patent language unavailable. CAN 37:21284 AN 1943:21284 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (24)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2308229		19430112	US 1940-340226	19400612

Abstract

Ethylbenzene is dehydrogenated with the formation of azeotropes of ethylbenzene and styrene; such mixt. is rectified with sufficient water to maintain a control temp. at which the azeotropes will sep., and the styrene is sepd. from the ethylbenzene.

Bibliographic Information

Catalytic process for alcohols. Natta, Giulio. (1940), AT 158416 19400410 Patent language unavailable. CAN 36:14804 AN 1942:14804 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (M6)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
AT 158416		19400410	AT	

Abstract

See Fr. 822,818 (C. A. 32, 5166.9).

Bibliographic Information

Catalyst suitable for use in producing methanol from carbon oxides and hydrogen, etc. Natta, Giulio. (1940), US 2193464 19400312 Patent language unavailable. CAN 34:31060 AN 1940:31060 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (M6)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2193464		19400312	US 1937-147253	19370609

Abstract

A ZnO catalyst is prepd. by decomp., by heat, a molten anhyd. org. Zn salt having a decomp. temp. above its m. p., such as Zn acetate.

Bibliographic Information

Catalysts. Natta, Giulio. (1938), GB 492073 19380914 Patent language unavailable. CAN 33:9640 AN 1939:9640 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (M6)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
GB 492073		19380914	GB 1937-16111	19370610

Abstract

See Fr. 822,818 (C. A. 32, 5166.9). Other oxides that are not reduced in the conditions of use may be incorporated in the ZnO, preferably by addn. of org. salts of the kind mentioned.

Bibliographic Information

Catalysts. Natta, Giulio. (1938), FR 822818 19380108 Patent language unavailable. CAN 32:37007 AN 1938:37007 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (16)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 822818		19380108	FR	19370609

Abstract

A catalyst for chem. reactions in which oxides of C participate contain ZnO prepd. by heating to decompn. org. salts of Zn, the f. p. of which are below decompn. pt. Thus, the ZnO may be prepd. by decompn. of Zn(OAc)₂ and may be used for the prepn. of MeOH.

Bibliographic Information

Hydrogen from water gas. Natta, Giulio. (1936), US 2038440 19360421 Patent language unavailable. CAN 30:29980 AN 1936:29980 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 2038440 IT 314985		19360421	US 1934-729477	19340607

Abstract

A heated mixt. contg. CO and steam is brought into contact with smithsonite (suitably at a temp. of about 300-500°) to effect H production from the steam.

Bibliographic Information

Gas. Natta, Giulio. (1935), DE 614928 19350625 Patent language unavailable. CAN 29:63194 AN 1935:63194 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)). (11)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 614928		19350625	DE 1928-N29477	19281031

Abstract

Solid fuel is gasified by O, water vapor and heat to give a mixt. of CO, H and CO₂ suitable for the synthesis of aics., especially MeOH. The temp. of the gas producer is kept below 750° and the proportions of O and steam are not more than 1 vol. of O to 2 vols of steam.

Bibliographic Information

Oxygenated organic compounds from carbon monoxide and hydrogen. Natta, Giulio. (1935), DE 612267 19350418 Patent language unavailable. CAN 29:36712 AN 1935:36712 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (M 2)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
DE 612267		19350418	DE 1928-N29478	19281101

Abstract

This corresponds to Fr. 670,763 (C. A. 24, 1869), but gives addnl. details.

Bibliographic Information

Hydrogen. Natta, Giulio. (1934), GB 420652 19341205 Patent language unavailable. CAN 29:26692 AN 1935:26692 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
GB 420652		19341205	GB 1934-16722	19340605
IT 314985				

Abstract

See Fr. 774,308 (C. A. 29, 2318.4).

Bibliographic Information

Hydrogen. Natta, Giulio. (1934), FR 774308 19341205 Patent language unavailable. CAN 29:18022 AN 1935:18022 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 774308		19341205	FR	
IT 314985				

Abstract

H is obtained by passing water gas over a mineral Zn carbonate (smithsonite) calcined at least in part and impregnated with alkali hydrates or carbonates.

Bibliographic Information

Alcohols. Natta, Giulio. (1929), CH 147151 19291015 Patent language unavailable. CAN 26:20862 AN 1932:20862 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) (M 3)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
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CH 147151
IT 273579

19291015 CH

Abstract

Alcs. contg. more than 1 C atom are prepd. by the reaction of CO with H under raised temp. and pressure, with intermediate formation of MeOH. A catalyzer for the synthesis of MeOH is present together with an alkali salt of a fatty acid. Thus, the CO and H form CH₃OH, which then with KOH forms CH₃OK. This, with more CO forms CH₃COOK and this, finally with H forms C₂H₅OH and KOH. The process is continuous.

Bibliographic Information

Methanol synthesis. Natta, Giulio. (1931), US 1815677 19310721 Patent language unavailable. CAN 25:48080 AN 1931:48080 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (11)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
US 1815677		19310721	US 1929-345236	19290307

Abstract

MeOH and other oxygenated org. compds. are formed by subjecting a mixt. of CO and H to the catalytic action of mineral smithsonite.

Bibliographic Information

Ethanol and other alcohols produced synthetically. Natta, G.. (1929), GB 340656 19291016 Patent language unavailable. CAN 25:43212 AN 1931:43212 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (13)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
GB 340656		19310108	GB 1929-31470	19291016

Abstract

In the synthesis of EtOH and higher alcs. from CO and H mixts. under pressure, with or without addn. of MeOH, there are employed as catalysts alkali salts of aliphatic acids such as formates, acetates or propionates of K, Rb or Cs mixed with porous supports such as ZnO, pumice, magnesite, silica or methanol-synthesis catalysts such as calcined Smithsonite. A temp. of 400-20° and pressure of 250-300 atm. are suitable. Synthetic MeOH may be used for washing the reaction gases to remove CO₂.

Bibliographic Information

Gas mixtures. Natta, Giulio. (1929), CH 141827 19290307 Patent language unavailable. CAN 25:20349 AN 1931:20349 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (11)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
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CH 141827

19300831

CH

19290307

Abstract

A gas mixt. of CO, H and CO₂ contg. at least twice as much H as oxide of C, is obtained by passing an O and steam current (contg. at least twice as much steam as O) over C at about 700° and not over 750°. Cf. C. A. 24, 5765.

Bibliographic Information

Methanol. Natta, Giulio. (1929), CH 140093 19290309 Patent language unavailable. CAN 25:6272 AN 1931:6272 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (1 2)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
CH 140093		19290309	CH	

Abstract

See Fr. 670,763 (C. A. 24, 1869).

Bibliographic Information

Methanol synthesis. Natta, G.. (1929), GB 330919 19290311 Patent language unavailable. CAN 24:53258 AN 1930:53258 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (1 2)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
GB 330919		19300611	GB 1929-7966	19290311

Abstract

See Fr. 670,763 (C. A. 24, 1869)

Bibliographic Information

Hydrogen and carbon monoxide mixtures for synthesis of organic compounds. Natta, G.. (1929), GB 330918 19290311 Patent language unavailable. CAN 24:53218 AN 1930:53218 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (1 1)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
GB 330918		19300611	GB 1929-7965	19290311

Abstract

A mixt. of O and water vapor (not more than 1 vol. of O to 2 vols. of water vapor) is passed over C at a temp. not exceeding 750° and CO₂ is removed, to obtain a mixt. contg. H 2 and CO 1 vol. By preheating the O and water vapor and using a temp. below 700°, a mixt. of H 3 and CO 1 vol. is obtained. Pressures up to 20 atm. may be used, and the gas mixts. obtained may be used for the synthesis of hydrocarbons, MeOH and other O-contg org. compds.

Bibliographic Information

Alcohols. Natta, Giulio. (1929), FR 683320 19291015 Patent language unavailable. CAN 24:41703
AN 1930:41703 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (13)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 683320		19300611	FR	19291015

Abstract

Alcs. higher than MeOH are prepd. from mixts. of CO and H using alkali salts of fatty acids on porous supports as catalysts, e. g., HCOOK or AcOK, MeOH may be added to the CO and H, or a catalyst favoring the production of MeOH from CO and H may be added to the other catalyst.

Bibliographic Information

Methanol. Natta, Giulio. (1929), FR 681147 19290207 Patent language unavailable. CAN 24:39534
AN 1930:39534 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (11)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 681147		19300509	FR	19290207

Abstract

Hydrocarbons, alcs. and other compds., particularly MeOH, are made from gaseous mixts. of CO, H and CO₂, which contain at least 2 vols. of H for 1 vol. of CO, obtained by passing a mixt. of 1 vol. of O with at least 2 vols. of steam over charcoal heated to about 700°. Cf. C. A. 24, 1809.

Bibliographic Information

Methanol. Natta, Giulio. (1929), FR 670763 19290304 Patent language unavailable. CAN 24:17011
AN 1930:17011 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R)) . (12)

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 670763		19291204	FR	19290304

Abstract

The mineral smithsonite, previously heated to 400-500°, is used as catalyst in the production of MeOH from CO

and H. Cf. C. A. 23, 5196.

Bibliographic Information

Methanol. Natta, Giulio; Faldini, Mario. (1928), FR 658788 19280718 Patent language unavailable.
CAN 23:45165 AN 1929:45165 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
FR 658788		19290619	FR	19280718
IT 360492				

Abstract

MeOH is obtained by passing a mixt. of CO and H at high pressure over a mixt. of FeO or CoO and oxides of other bivalent metals such as Mg, Mn, Cr, Zn, Be with or without small amts. of oxides of trivalent metals.