Sonderdruck aus

DIE MAKROMOLEKULARE CHEMIE

Band 54 1962 Seite 95–101

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(Eingegangen am 19. März 1962)

SUMMARY:

The copolymerization of ethylene with cyclopentene and with cyclohexene in the presence of catalytic systems acting through an anionic co-ordinated polymerization mechanism is described. In the case of cyclopentene it was possible to obtain crystalline alternating copolymers with stereoregular structure using either catalytic systems acting in the heterogeneous phase or those acting in the homogeneous phase. The structure of the polymeric chains and the properties of these new polymers are described. The fact that the ethylene-cyclopentene copolymers are much more rich in cycloolefin units than the corresponding ethylene-cyclohexene copolymers is attributed to phenomena of steric hindrance.

ZUSAMMENFASSUNG:

Die Copolymerisation von Äthylen mit Cyclopenten oder Cyclohexen in Gegenwart von Katalysatorsystemen mit anionisch-koordiniertem Polymerisationsmechanismus wird beschrieben. Im Fall des Cyclopentens ist es möglich gewesen, kristalline alternierende Copolymere mit sterisch geordneter Struktur zu erhalten, und zwar sowohl mittels Katalysatorsystemen, die in heterogener, als auch mittels solcher, die in homogener Phase wirken. Die Struktur der Polymerketten und die Eigenschaften dieser kristallinen Polymeren werden beschrieben. Die Tatsache, daß die Äthylen-Cyclopenten-Copolymeren sehr viel reicher an Cycloolefin-Einheiten sind als diejenigen des Äthylens mit Cyclohexen, wird auf Phänomene sterischer Hinderung zurückgeführt.

Cycloolefins, such as cyclopentene and cyclohexene do not homopolymerize in the presence of catalysts acting through an anionic coordinated mechanism which, on the contrary, homopolymerize ethylene and alpha-olefins.

The impossibility of these cycloolefins to undergo polymerization with catalysts of this type primarily depends on steric factors. In fact, among the monomers of the $CH_2=CHR$ type, the polymerization rate is highest when R = H, and it decreases with the increase of the bulkiness of the

*) NATTA's co-workers are listed in alphabetical order.

R group, chiefly if the steric hindrance close to the double bond is remarkable (*e.g.* when R is an alkyl group branched near to the double bond). In the case of olefins with internal unsaturation, where both the carbon atoms of the double bond are substituted with organic groups, the steric hindrance is increased in such a measure that homopolymerization becomes practically impossible. However we observed that in similar cases the inability to homopolymerize does not necessarily exclude the possibility to copolymerize, when using very reactive comonomers, which are free from steric hindrances, and suitable catalysts[1]. We had already prepared copolymers of ethylene with olefins having an internal double bond (*e.g.* butene-2), which also do not homopolymerize in the presence of the above-mentioned catalysts[1-3].

We have already briefly described[2] that it is also possible to copolymerize cycloolefins with ethylene in the presence of catalysts acting through an anionic coordinated mechanism. This copolymerization involves the opening of the double bond of the cycloolefin *).

As observed in the other cases, also in this copolymerization of ethylene with monomers unable to homopolymerize, the addition of these monomers to the polymer chain most likely can take place only when an ethylene monomeric unit constitutes the end unit of the growing chain.

It follows that each cycloolefin monomeric unit is inserted between two ethylene monomeric units. On the other hand, the reactivity of cycloolefin is much lower than that of ethylene; thus only by operating with high cycloolefin to ethylene ratios in the liquid phase, it is possible to obtain copolymers with high contents of monomeric units derived from the cycloolefin. In this case the content of cyclo-olefin units in the crude copolymer may range between 0 to 50 mole-%.

These previsions are confirmed by the experimental data listed in Tables 1 and 2, which concern the copolymerization of ethylene with cyclopentene and with cyclohexene. It can be observed that no crude copolymer, nor any of its fractions, contains more than 50 mole-% of cycloolefin. This proves, in analogy with what had already been observed in the copolymerization of ethylene with butene-2, that the copolymer does not contain direct enchainments between the cycloolefin monomeric units.

*) Recently, H. SOUSA ELEUTERIO (DUPONT, U.S. Priority, June 20, 1957) succeeded in preparing high polymers of cycloolefins with the aid of catalysts based on molybdenum oxide at high temperature. These polymers, however, are formed by unsaturated linear chains, since they are originated by the opening of all the rings and not of the double bonds, as it happens in the case described here.

In the case of cyclopentene, by operating at sufficiently low partial pressures of ethylene, it was possible to obtain raw copolymers with a composition which is very near to the 1:1 molar ratio between the two olefins. As revealed by X-ray analysis, these copolymers show a high crystallinity of a type which is very different from the one of polyethylene.

By fractionation with boiling solvents, it was possible to separate a highly crystalline fraction, consisting of a copolymer containing 50 mole-% of the two monomers, whose X-ray spectrum (GEIGER-counter registration) is given in Fig. 1. According to the most intense reflections observed in this spectrum, main lattice distances of 5.83, 4.92 and 4.37 Å were calculated.

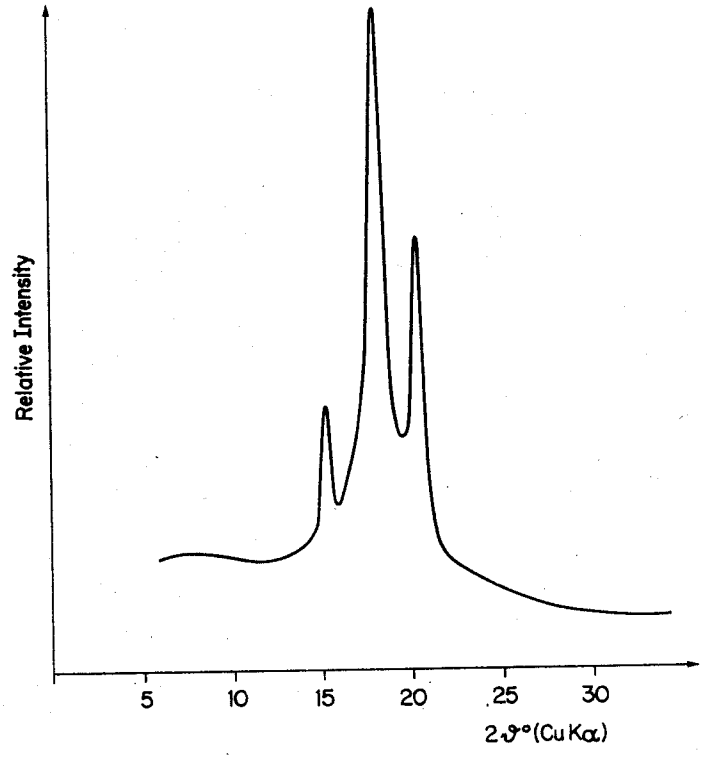
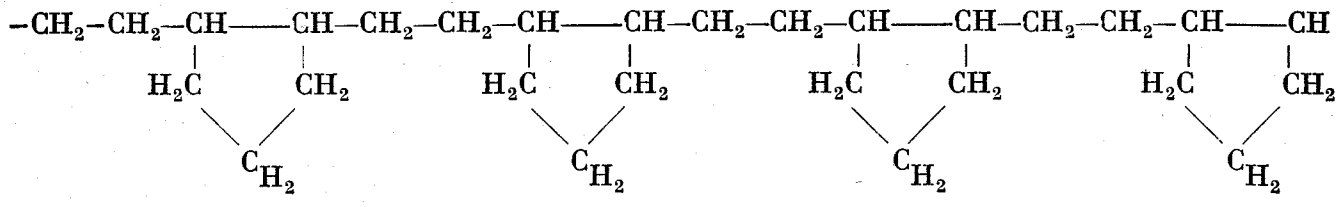


Fig. 1. GEIGER-counter registered X-ray diffraction spectrum (CuKα radiations) of the regularly alternating and sterically ordered ethylene-cyclopentene copolymer, prepared with the aid of anionic co-ordinated catalysts

This new product melts at 183–185 °C and has a density $d_4^{24} = 1.01$. By melt spinning, the high molecular weight copolymer can be drawn to crystalline fibers, having excellent mechanical properties.

The monomeric unit deriving from cyclopentene contains two tertiary carbon atoms (those enclosed in the main chain of the copolymer), which may originate stereoisomery phenomena; thus it must be assumed that these copolymers, which are highly crystalline by X-ray examination, possess a stereoregular structure of the tertiary carbon atoms.

From the X-ray analysis of stretched fibers, it resulted that this copolymer has a structure characterized by the regular and alternating succession of the ethylene and cyclopentene monomeric units. Its chain structure is probably of the erythro-isotactic type, with an identity period along the chain axis of 9.0 Å, analogously with what we observed in the case of crystalline alternating copolymers of ethylene with cis-butene-2:



The volume of the elementary unit cell, as calculated on the basis of the X-ray data, is of 617 $Å^3$; to it corresponds a calculated density of 1.03, which is in agreement with the experimental data.

The I.R. analysis of the copolymer in the molten state, confirms this structure, revealing the presence of sequences of two methylenic groups (absorption at 13.29 μ) and the absence of sequences higher than two methylenes (no absorption bands between 13.6 μ and13.9 μ). Moreover the I.R. analysis confirms the value of 1.5 for the ratio of the number of $-CH_2-$ in the ring to the number of $-CH_2-$ in the chain *).

It is interesting to point out that both the heterogeneous and the homogeneous catalytic systems used by us yield crystalline alternating ethylene-cyclopentene copolymers. This result differentiates the behaviour of cyclopentene from that of cis-butene-2 in the copolymerizations with ethylene. In fact, in the latter case, it was possible to obtain crystalline alternating copolymers only with the aid of heterogeneous catalytic systems (*e.g.* those prepared from VCl_4 + Al(alkyl)$_3$), which are stereospecific in the homopolymerization of alpha-olefins (even if to a limited extent). We wish to remind that the homogeneous systems (*e.g.* prepared from V(acetylacetonate)$_3$ + $AlCl(C_2H_5)_2$) quoted in Table 1 and 2, and used under the indicated conditions, homopolymerize alpha-olefins (for instance propylene), yielding atactic polymers. These catalytic systems, when used under particular conditions, polymerize propylene to polymers, which contain crystalline syndiotactic units.

As a stereoregular chain structure is obtained with the aid of all the types of catalysts employed, we can admit that the steric rather than the catalytic factors have a determining influence on the configuration of the tertiary carbon atoms of the cyclopentene monomeric units.

*) The number of $-CH_2-$ in the ring and in the chain is calculated on the basis of the absorption bands at 6.93 and 6.84 μ respectively.

Table 1. Ethylene-Cyclopentene Copolymerization (cyclopentene employed in each run, 10 g; reaction time, 7 hrs.; temp., −30 °C.)

Catalytic system	Solvent	$p_{C_2H_4}$ *) (Torr)	Co-polymer ob-tained (g)	Ethylene units **) contained in the raw copolymer (mole-%)	[η] (135°C in tetralin)	X-ray examination (GEIGER counter)	Boiling n-octane insoluble fraction: aliquod of total copolymer (wt.-%)	Boiling n-octane insoluble fraction: ethylene units **) content (mole-%)	Boiling n-octane insoluble fraction: [η] 135° C in tetralin
3.6 mmoles VCl_4 + 9.0 mmoles $Al(hexyl)_3$	37 ml n-heptane	100	4.29	61	1.7	crystalline alternating co-polymer showing also a low crystallinity of the polyethylene type	58	52	1.5
3.6 mmoles VCl_4 + 9 mmoles $Al(hexyl)_3$	37 ml n-heptane	50	1.97	55	1.0	only crystallinity due to the alternating copolymer	56	50	1.0
3.6 mmoles VCl_4 + 9 mmoles $Al(hexyl)_3$	37 ml n-heptane	25	0.97	53	0.9	only crystallinity due to the alternating copolymer	38	50	1.3
3.6 mmoles V(acetylacetonate)$_3$ + 18.0 mmoles $AlCl(C_2H_5)_2$	30 ml toluene	100	2.23	58	1.5	only crystallinity due to the alternating copolymer	47	53	1.3
3.6 mmoles V(acetylacetonate)$_3$ + 18.0 mmoles $AlCl(C_2H_5)_2$	30 ml toluene	50	1.13	55	0.9	only crystallinity due to the alternating copolymer	73	51	0.9
3.6 mmoles V(acetylacetonate)$_3$ + 18.0 mmoles $AlCl(C_2H_5)_2$	30 ml toluene	25	0.57	54	0.9	only crystallinity due to the alternating copolymer	45	51	1.0

*) Initial partial pressure (cyclopentene + solvent + nitrogen) = 750 Torr; (the indicated ethylene partial pressure is in addition to it).

**) The ethylene content in the copolymers was determined by radiochemical analysis using ^{14}C labelled ethylene.

Table 2. Ethylene-Cyclohexene Copolymerization (cyclohexene employed in each run, 10 g; reaction time, 7 hrs.; temp., −30 °C.)

Catalytic system	Solvent	$p_{C_2H_4}$ *) (Torr)	Copolymer obtained (g)	Ethylene units **) contained in the raw copolymer (mole-%)	$[\eta]$ (135 °C in tetralin)	X-ray examination (Geiger-counter)
3.6 mmoles VCl_4 + 9.0 mmoles Al(hexyl)$_3$	37 ml n-heptane	100	2.09	95	2.6	only crystallinity of the polyethylene type
3.6 mmoles VCl_4 + 9.0 mmoles Al(hexyl)$_3$	37 ml n-heptane	50	1.08	87	1.6	only crystallinity of the polyethylene type
3.6 mmoles VCl_4 + 9.0 mmoles Al(hexyl)$_3$	37 ml n-heptane	25	0.56	81	1.0	only crystallinity of the polyethylene type
3.6 mmoles V(acetylacetonate)$_3$ + 18.0 mmoles $AlCl(C_2H_5)_2$	30 ml toluene	100	1.60	97	2.6	only crystallinity of the polyethylene type
3.6 mmoles V(acetylacetonate)$_3$ + 18.0 mmoles $AlCl(C_2H_5)_2$	30 ml toluene	50	0.70	94	0.9	only crystallinity of the polyethylene type

*) Initial partial pressure (cyclohexene + solvent + nitrogen) = 750 Torr; (the indicated ethylene partial pressure is in addition to it).

**) The ethylene content in the copolymers was determined by radiochemical analysis using ^{14}C labelled ethylene.

In analogy with what already observed in the aliphatic olefins with internal unsaturation, the comparison between the results obtained from cyclopentene and cyclohexene respectively points out the importance of the steric factors also in the kinetics of the stereospecific polymerizations. Actually, it can be observed that the copolymerization rate of cyclohexene is much lower than that of cyclopentene. This is also demonstrated by the fact that many catalysts yielding alternating copolymers of cyclopentene have not yielded crystalline regularly alternating ethylene-cyclohexene copolymers.

[1] G. NATTA, G. DALL'ASTA, G. MAZZANTI, I. PASQUON, A. VALVASSORI, and A. ZAMBELLI, J. Amer. chem. Soc. **83** (1961) 3343.

[2] G. NATTA, Lecture delivered at the IUPAC Congress held in Montreal (Canada), July 1961.

[3] G. NATTA, G. DALL'ASTA, G. MAZZANTI, and F. CIAMPELLI, Lecture presented by G. Dall'Asta at the Deutsche Kolloid-Gesellschaft Congress at Bad Oeynhausen (Germany), October 1961, in press in Kolloid-Zeitschrift.