

503

497

Sonderdruck aus

DIE MAKROMOLEKULARE CHEMIE

Band 79

1964

Seite 161—169

Crystalline Alternating Ethylene-Butadiene Copolymers

by

G. NATTA, A. ZAMBELLI, I. PASQUON, and F. CIAMPELLI

HÜTHIG & WEPF VERLAG · BASEL

From the Istituto di Chimica Industriale del Politecnico, Milano, Italy

Crystalline Alternating Ethylene-Butadiene Copolymers

By G. NATTA, A. ZAMBELLI, I. PASQUON, and F. CIAMPELLI

(Eingegangen am 2. März 1964)*

SUMMARY:

The copolymerization of ethylene with butadiene at -25°C . in the presence of co-ordinated anionic catalytic systems, prepared at -78°C . from a vanadium compound, organo-metallic compounds of aluminum and a weak LEWIS base, yields copolymers with particular crystalline structure.

By fractionation of crude products, crystalline ethylene-butadiene copolymers were obtained, the crystalline structure of which was attributed to a succession of ethylene units regularly alternating with *trans*-buta-1,4-dienic units.

ZUSAMMENFASSUNG:

Die Copolymerisation von Äthylen und Butadien bei -25°C ergibt Copolymere mit besonderer kristalliner Struktur; die koordinativ-anionischen Mischkatalysatoren für diese Reaktion wurden bei -78°C aus einer Vanadium-Verbindung, Al-organischen Komponenten und einer schwachen LEWIS-Base hergestellt.

Bei der Fraktionierung der Rohprodukte wurden kristalline Äthylen-Butadien-Copolymere erhalten, deren kristalline Struktur einer Folge von Äthyleneinheiten, die regelmäßig mit *trans*-Butadien-1,4-Einheiten abwechseln, zugeschrieben wird.

1. Introduction

Crystalline hydrocarbon copolymers consisting of a regularly alternating succession of two different monomeric units had already been obtained in this Institute by copolymerization of ethylene with a suitable olefin containing an internal double bond (e.g., *cis*-butene-2¹⁾, cyclopentene²⁾), in the presence of co-ordinated anionic catalysts.

The olefins used, having an internal double bond, do not homopolymerize in the presence of the catalysts mentioned above; as demonstrated, this is due to steric hindrances¹⁾. On the contrary, these olefins can copolymerize with ethylene that has limited steric hindrances; and, operating with high ratios of olefin to ethylene, alternating copolymers can be synthesized.

*) Revidiertes Manuskript vom 29. Mai 1964.

In these polymerizations, butadiene behaves different from the olefins with internal double bond. Actually, it is known that butadiene can homopolymerize very easily in the presence of co-ordinated anionic catalysts and, depending on the catalytic system used, it gives rise to different types of regular polymers³⁾.

Although butadiene homopolymerizes we also obtained ethylene-butadiene alternating crystalline copolymers by operating in the presence of suitable catalytic systems.

Other crystalline copolymers had already been obtained in this Institute by alternating copolymerization of monomers (such as dimethyl ketene and an aldehyde⁴⁾ or a ketene⁵⁾), which also homopolymerize with the catalytic systems used for the copolymerization. The results can be attributed to the particular values of the reactivity ratios corresponding to these copolymerizations.

2. Results

The catalysts are based on VCl_4 , AlR_3 , AlR_2Cl ($R = \text{alkyl}$) in the presence of a rather weak LEWIS base; among them anisol is particularly suitable. The best results have been obtained using these reagents in a 1:2:2:2 ratio. The catalyst was prepared in toluene at -78°C .; at this temperature the mixture yields an apparently homogeneous system; the polymerizations have been performed at temperatures of -20 to -30°C .

The catalytic system polymerizes butadiene slowly to a product rich in *trans*-1,4 monomeric units, but containing also 1,2 units.

Ethylene is polymerized rapidly to highly crystalline, high molecular weight polymers.

It was observed that polyethylene obtained at this temperature shows an X-ray diagram which differs from that of the usual polyethylene. Besides the two peaks corresponding to the usual orthorhombic modification (at $2\theta = 21^\circ30$ and 24°), the spectrum contains a further peak at $2\theta = 19^\circ30$ ($d = 4.55\text{--}4.56 \text{ \AA}$). This peak had already been observed on those polyethylenes that had undergone particular mechanical treatment⁶⁾.

By heating these polyethylenes to about 60°C ., the peak at $19^\circ30$ disappears and does not turn up if the polymer is cooled subsequently to -50°C . and maintained at that temperature for one week.

We have observed that this crystalline modification of polyethylene is obtained directly by synthesis whenever the polymerization of ethylene is effected at sufficiently low temperatures, independently of the catalytic system used⁷⁾.

Crystalline Alternating Ethylene-Butadiene Copolymers

In the case of copolymerization, the crude polymers separated by precipitation from the catalyst were fractionated by a series of extractions with solvents. The results obtained in one of these runs are reported in Table 1.

Table 1. Analysis of ethylene-butadiene copolymer fractions obtained by extractions with a series of solvents at their boiling temperature

Fraction	Solvent	% Extract	Mole-% of ethylene in the fraction ^{a)}	% <i>trans</i> -1,4 butadiene units, of polymerized butadiene in the fraction ^{b)}	$[\eta]$ 100 ml./g.
A	ethyl ether	75.60	28.3	80	not det.
B	ethyl ether	3.39	37.4	90	not det.
C	ethyl ether	0.44	42.2	91.5	not det.
D	<i>n</i> -pentane	1.20	50.6	93.5	0.25
E	<i>n</i> -pentane	0.35	44.7	95.5	0.28
F	<i>n</i> -hexane	8.53	45.0	94	not det.

a) Radiochemical analysis.

b) IR analysis; the balance to 100% consists of 1,2 units.

It has been observed that all fractions contain ethylene units. It must be noted that the polyethylene obtained in the presence of the catalytic systems described in this paper is insoluble in boiling *n*-hexane and *n*-heptane; hence, it can be concluded that ethylene units contained in soluble fractions are present in an ethylene-butadiene copolymer. Moreover, each fraction is crystalline, at least in part; the X-ray diagram (Fig. 1) shows the presence of peaks at angles $2\theta = 20^\circ 30'$ and 23° . These peaks cannot be attributed to any known modification of crystalline polybutadienes or polyethylene. Their intensity increases as the ethylene content in the copolymer approaches 50 mole-% (Fig. 1a, 1b, 1c, 1d). These peaks disappear when the polymer is heated to above 60–65°C., but they appear again by cooling.

In the *n*-hexane extractable fraction (F) reported in Table 1, crystalline *trans*-1,4 polybutadiene is present together with the crystalline ethylene-butadiene copolymers and with crystallized $-\text{CH}_2-$ sequences.

The residue of the hexane extraction essentially consists of a mixture of a small amount of *trans*-1,4 polybutadiene and of polyethylene.

The molecular weight of the crystalline copolymer obtained is too low to permit the preparation of fibers which can be oriented so as to obtain

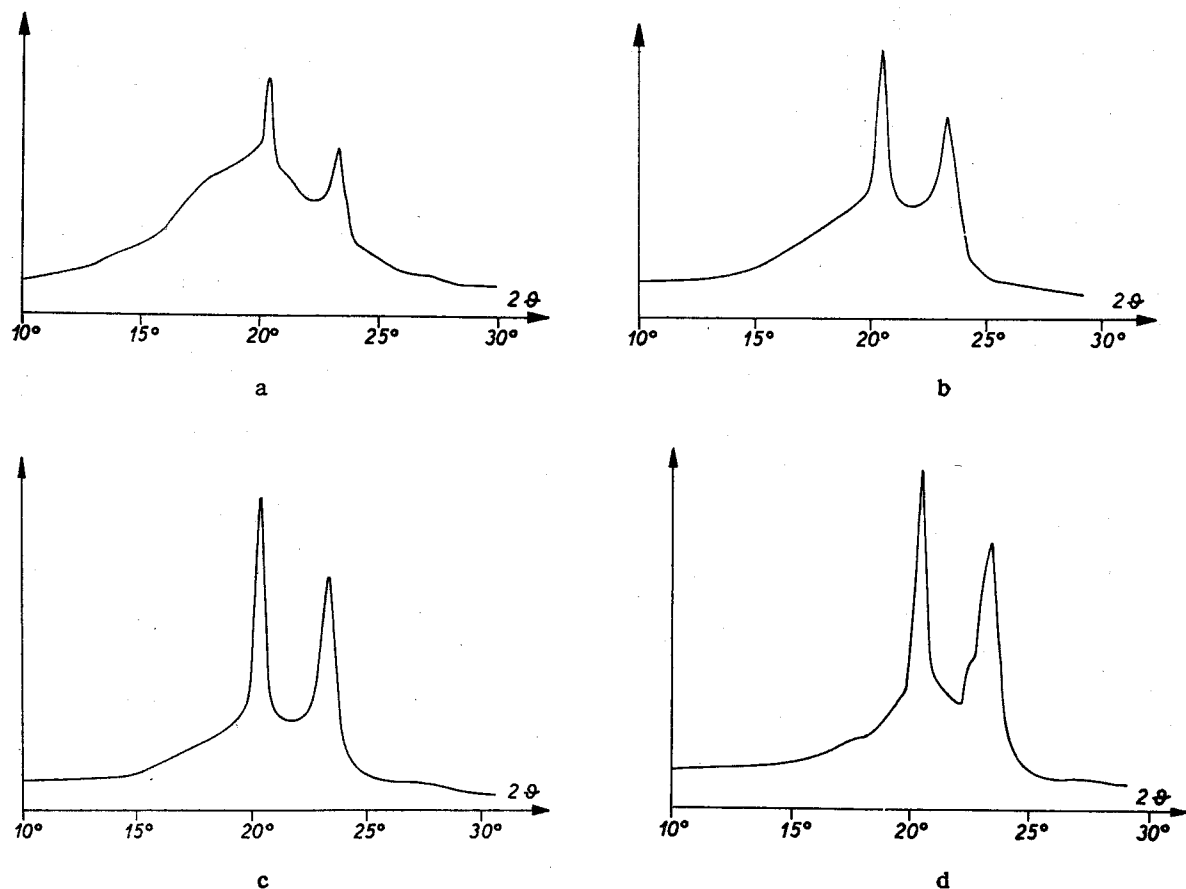


Fig. 1a. X-ray diagram (CuK_α) of butadiene-ethylene copolymer containing 28.3% C_2H_4 (sample A of Table 1)

Fig. 1b). X-ray diagram (CuK_α) of butadiene-ethylene copolymer containing 37.4% C_2H_4 (sample B of Table 1)

Fig. 1c. X-ray diagram (CuK_α) of butadiene-ethylene copolymer containing 42.2% C_2H_4 (sample C of Table 1)

Fig. 1d. X-ray diagram (CuK_α) of crystalline alternating *trans*-1,4 butadiene-ethylene copolymer containing 50.6% C_2H_4 (sample D of Table 1)

an X-ray fiber spectrum for evaluation of the identity period and for determination of the structure of the crystalline copolymer; therefore, further investigations were necessary to specify the nature of the product obtained.

The IR spectrum of a *n*-pentane soluble fraction containing about 50% of ethylene units is shown in Fig. 2. The spectrum reveals that the butadiene units are mostly *trans*-1,4 (band at 965 cm^{-1}). However, bands attributable to crystalline *trans*-1,4 polybutadiene are not detectable (at

Crystalline Alternating Ethylene-Butadiene Copolymers

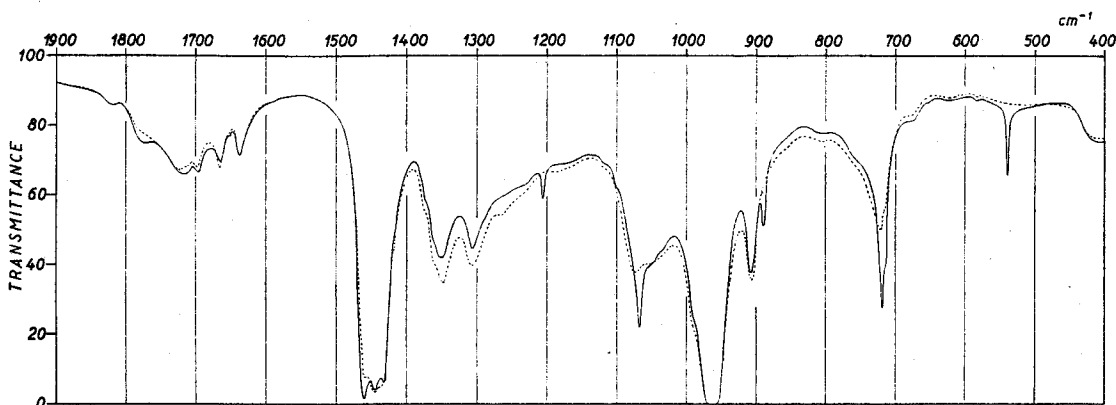


Fig. 2. IR spectrum of alternating *trans*-1,4 butadiene-ethylene copolymer containing about 50% ---: crystalline product; ---: product melted at 65°C.

1235, 1054, 773 cm^{-1})⁸). On the other hand, bands at 1206, 1070 and 889 cm^{-1} , which disappear in the molten state, are present in the spectrum of the copolymer in the solid state. These bands are characteristic of a new type of crystalline polymer; to a first approximation their intensity increases as the ethylene molar fraction in the copolymer approaches 50% (Fig. 3 a, 3 b, 3 c). Finally, in the spectra of fraction E can be observed the absence of the band at 722 cm^{-1} due to long methylene sequences and the presence of a band at 728 cm^{-1} which can be attributed to methylene sequences of 4 CH_2 groups⁹).

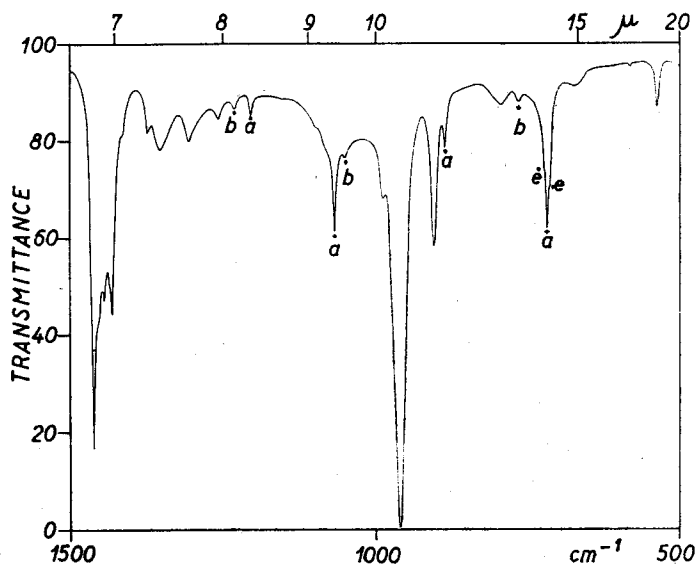


Fig. 3 a. IR spectrum of sample C of Table 1 (42.2% C_2H_4)

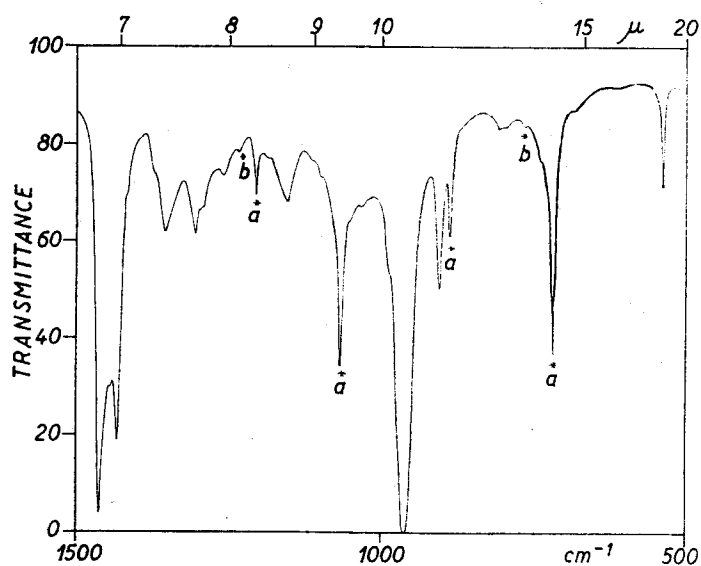


Fig. 3b. IR spectrum of sample D of Table 1 (50.6% C_2H_4)

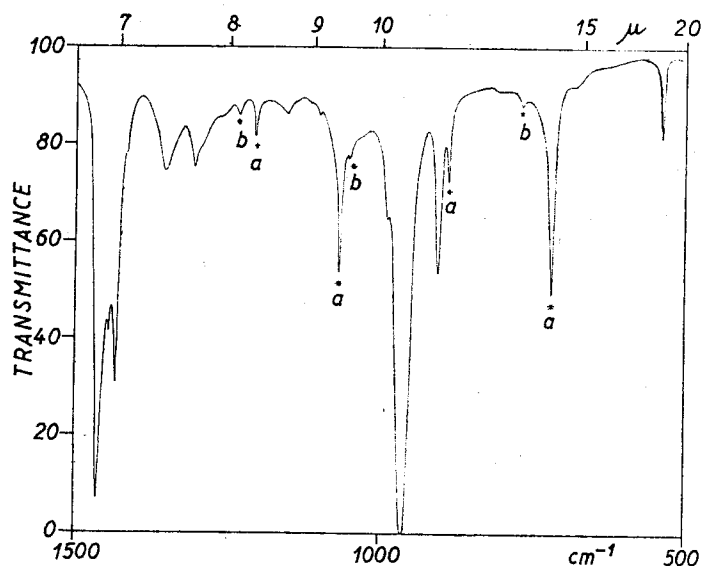
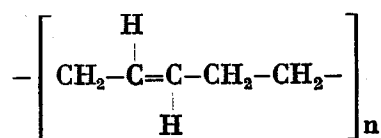


Fig. 3c. IR spectrum of sample E of Table 1 (44.7% C_2H_4)

a: bands due to alternating copolymer; b: bands due to *trans*-1,4 polybutadiene;
 c: bands due to crystallized $-CH_2-$ sequences

Therefore, these different results suggest that the crystallinity of this copolymer, shown by all fractions separated, must be attributed to an alternating *trans*-1,4 butadiene-ethylene copolymer. This hypothesis has been confirmed recently by comparing these spectra with those of completely linear stereoregular homopolymers, obtained by ring-opening homopolymerization of cyclopentene with the following formula¹⁰:

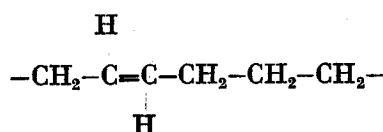
Crystalline Alternating Ethylene-Butadiene Copolymers



Conclusions

The use of catalytic systems prepared at -78°C . from $\text{VCl}_4\text{-AlR}_3\text{-AlR}_2\text{Cl}$ -anisol in suitable ratios, allowed to obtain crude polymers containing crystalline ethylene-butadiene copolymers when the copolymerizations were performed at -20° to -30°C .

The X-ray, IR and radiochemical analyses of the different fractions separated led to the conclusion that crystallinity of these new copolymers must be attributed to a regular, alternating succession of *trans*-1,4 butadiene and ethylene units corresponding to the formula:



In the polymers which have no very high molecular weight the crystallinity disappears by heating the more crystalline fraction to $60\text{--}65^\circ\text{C}$.; it re-appears by subsequent cooling.

It was also observed that the high molecular weight, highly crystalline polyethylene obtained by homopolymerization of ethylene at low temperature (*e.g.*, -25°C .), shows, independently of the catalyst used, a crystalline modification different from the usual orthorhombic, characterized by a lattice distance of $4.55\text{--}4.56\text{ \AA}$.

Experimental Part

Example of a Copolymerization Run

Anhydrous toluene (400 ml.) was introduced in a glass reactor having the capacity of 750 ml., under nitrogen atmosphere. After thermostating at -78°C ., the following compounds were introduced in this order: $4\cdot 10^{-3}$ moles VCl_4 ; $8\cdot 10^{-3}$ moles anisol; $8\cdot 10^{-3}$ moles $\text{Al}(i\text{-C}_4\text{H}_9)_3$; $8\cdot 10^{-3}$ moles $\text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$.

Butadiene (120 g.) was subsequently condensed in the reactor; then ^{14}C labelled ethylene was passed rapidly through the solution; simultaneously the reactor was transferred to a thermostated bath at -25°C . After 60 min. during which ethylene was kept bubbling the polymerization was stopped by coagulating the polymer with methanolic HCl. After a series of washings with methanol, the polymer was dried at room temperature. Thus, 15 g. of polymer were obtained.

Homopolymerization of ethylene and of butadiene were carried out in analogous manner. With $2 \cdot 10^{-3}$ moles of VCl_4 and 60 g. of butadiene 1.63 g. of polybutadiene were obtained after 1 hr.; this shows that the polymerization is rather slow.

Fractionation

The crude copolymer was fractionated in a KUMAGAWA extractor under nitrogen atmosphere with solvents of increasing boiling points. Ethyl ether, *n*-pentane, *n*-hexane were used. With ether and *n*-pentane, different fractions were obtained with each solvent by successive extractions. The fractions indicated in Table I, (e.g., A and B) are obtained from fractionation of the same polymer carried out at successive times with the same solvent. The last fraction indicated for each solvent, however, can be considered exhaustive for the polymer in that solvent.

Characterization

The intrinsic viscosities have been measured in tetraline at 100°C. IR measurements were carried out with a PERKIN ELMER apparatus, Mod. 125 with KBr optics and grating. The sample under examination had been prepared by melting between KBr windows.

The recorded X-ray powder spectra were obtained from a PHILIPS spectrogoniometer with a detector GEIGER tube (CuK_{α} -radiation).

The content of ^{14}C labelled ethylene in the different fractions was determined according to the methods described¹¹⁾.

Reagents

Toluene was a commercial product, dethiophenated with sulphuric acid and anhydriified by boiling on potassium and then by distillation. VCl_4 was supplied by Montecatini S.p.A. Before being used it was distilled under vacuum. Anisol was an RP (pure reagent) product supplied by Carlo Erba S.p.A. It was used after distillation. $Al(i-C_4H_9)_3$ had been supplied by Montecatini S.p.A. and was used after distillation. $Al(i-C_4H_9)_2Cl$ was prepared by reaction of $AlCl_3$ with $Al(i-C_4H_9)_3$ and subsequent distillation. The monomers used were ethylene supplied by Montecatini S.p.A., and Pure Grade butadiene supplied by Philips Co.

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, G. DALL'ASTA, G. MAZZANTI, I. PASQUON, A. VALVASSORI, and A. ZAMBELLI, Makromolekulare Chem. **54** (1962) 95.

³⁾ G. NATTA, Chim. e Ind. [Milano] **42** (1960) 1207.

⁴⁾ G. NATTA, G. MAZZANTI, G. F. PREGAGLIA, and G. POZZI, J. Polymer Sci. **58** (1962) 1201.

Crystalline Alternating Ethylene-Butadiene Copolymers

- 5) G. NATTA, G. MAZZANTI, G. F. PREGAGLIA, and M. BINAGHI, *J. Amer. chem. Soc.* **82** (1960) 5511.
- 6) R. H. PIERCE (jr.), J. P. TORDELLA, and W. M. D. BRYANT, *J. Amer. chem. Soc.* **74** (1952) 282; G. NATTA and P. CORRADINI, *Suppl. Ricerca sci.* **25** (1955); W. P. SLICHTER, *J. Polymer Sci.* **21** (1956) 141.
- 7) Unpublished data from this Institute.
- 8) D. MORERO, F. CIAMPELLI, and E. MANTICA, in *Advances in Molecular Spectroscopy*, ed. A. Mangini, Pergamon Press, London 1962.
- 9) H. L. MACMURRY and V. T. THORNTON, *Analytic. Chem.* **24** (1952) 318.
- 10) G. NATTA, G. DALL'ASTA, and G. MAZZANTI, *Angew. Chem.*, in press.
- 11) F. DANUSSO, G. PAJARO, and D. SIANESI, *J. Polymer Sci.* **22** (1956) 179.