

### ETHYLENE-BUTENE-2 ALTERNATING CRYSTALLINE COPOLYMERS

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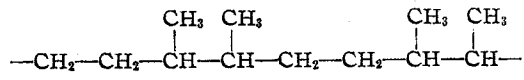
The aliphatic olefins containing an internal double bond do not yield high molecular weight homopolymers with the catalytic systems acting by an anionic coordinated mechanism, active for the  $\alpha$ -olefins polymerization.

However, using many homogeneous or heterogeneous catalysts, able to polymerize ethylene through an anionic coordinated mechanism, we succeeded in preparing linear high-molecular weight copolymers of these monomers with ethylene.

As appears in Table I, the over-all copolymerization rate and the composition of the copolymers obtained, depend on the type of catalysts employed. This is in agreement with the ionic

could be expected that in the copolymerization two butene-2 monomeric units never can be bound directly one to the other, as has been confirmed by the results reported here.

When employing sufficiently low ethylene concentrations, we prepared ethylene-butene-2 alternating copolymers, or at least copolymers containing long sequences with the chemical structure



The structure of these alternating copolymers was demonstrated by the experimental results: (1) Even decreasing as much as possible the concentration of ethylene present in the liquid phase in which the copolymerization occurs, neither crude copolymers nor their fractions having a butene-2 molar content higher than 50% have ever been obtained. (2) The analysis of the infrared absorption spectrum of copolymers containing about 50 mole % of butene-2 shows an intense absorption band at 13.2  $\mu$ , which is to be attributed to sequences of two methylenic groups. Absorption bands between 13.6 and 13.9  $\mu$ , from longer sequences of methylenic groups, are practically absent. (3) By fractionating the crude products, prepared with suitable catalytic systems, such as those prepared from vanadium tetrachloride and aluminum trialkyls, we isolated ethylene-*cis*-butene-2 alternating crystalline copolymers having a density of 0.90. They show a characteristic X-ray spectrum (see Table II and Fig. 1). The identity period along the chain axis, determined on oriented fibers, is about 9.15  $\text{\AA}$ , and the melting temperature is 130-135° (as determined by X-rays).

The high crystallinity of some alternating ethylene-butene-2 copolymers confirms the regularity of the chemical structure, and also demonstrates a high regularity of steric structure. In fact, in each monomeric unit of butene-2 two tertiary carbon atoms are present, and therefore stereoregular structures of the di-isotactic or di-syndiotactic type can be foreseen. Accurate investigations on the configurations of these crystalline polymers are in progress and will be described in other communications.

A great number of catalytic systems, and also some systems that are stereospecific only to a limited extent in the homopolymerization of  $\alpha$ -olefins, may promote, when employed under suitable conditions, the formation of ethylene-*cis*-butene-2 alternating copolymers rich in crystallizable fractions.

Catalytic systems, which are not stereospecific in the polymerization of  $\alpha$ -olefins, e.g., systems yielding, under the same operating conditions, completely atactic polymers of propylene (e.g., vanadium-triacetylacetonate/aluminum-diethylmonochloride) are not stereospecific in the ethylene-*cis*-butene-2 copolymerization. In fact, they promote the formation of alternating copolymers that

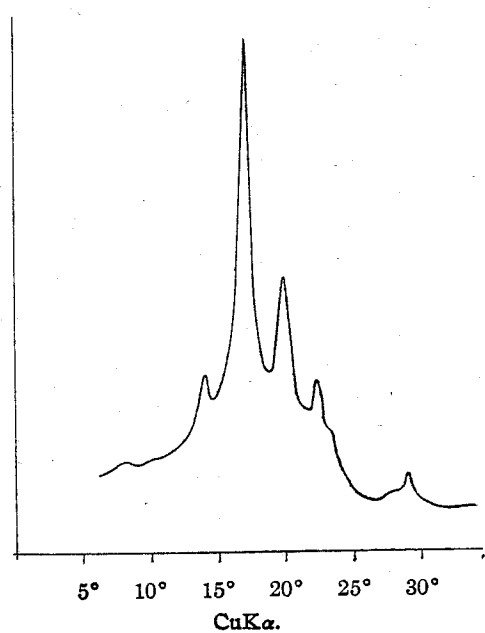


Fig. 1.—Geiger-counter registration of the X-ray spectrum of ethylene-*cis*-butene-2 alternating copolymer.

mechanism of these copolymerizations.<sup>1</sup> Copolymers having a high content of monomeric units deriving from a monomer containing an internal double bond are obtained only when operating with high concentrations of the latter and with very low ethylene concentrations. On the contrary, when operating under high ethylene pressure, the polymer obtained practically consists only of polyethylene. When comparing the copolymerization of ethylene with *cis*-butene-2 or, respectively, with *trans*-butene-2, a higher copolymerization rate with the *cis* isomer is observed.

Taking into account that with all the catalysts of the anionic coordinated type used by us no homopolymerization of butene-2 occurs, it also

(1) G. Natta, G. Mazzanti, A. Valvassori and G. Sartori, *La Chimica e l'Industria*, 40, 717 (1958).

TABLE I  
 ETHYLENE-BUTENE-2 COPOLYMERIZATION

Experimental conditions: ethylene partial pressure maintained constant during the copolymerization = 100 mm.; initial partial pressure (nitrogen + butene-2 + solvent) = 750 mm.; butene-2 employed, 10 g.

Butene-2 employed	Catalyst employed		Moles butene-2/ moles transition metal	Solvent, cc.	T, °C.	Time, min.	Co-polymer obtained, g.	[ $\eta$ ] at 135° in tetralin	Molar content butene % <sup>a</sup>
	Type	Moles transition metal/moles aluminum							
<i>cis</i>	VCl <sub>4</sub> /Al(hexyl) <sub>3</sub>	1:2.5	50	<i>n</i> -Heptane, 35	-30	500	3.83	1.44	38
<i>trans</i>	VCl <sub>4</sub> /Al(hexyl) <sub>3</sub>	1:2.5	50	<i>n</i> -Heptane, 35	-30	500	2.44	2.04	16
<i>cis</i>	V(acetylacetonate) <sub>3</sub> / Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl	1:5	64	Toluene, 30	-30	500	2.91	1.27	20
<i>trans</i>	V(acetylacetonate) <sub>3</sub> / Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl	1:5	64	Toluene, 30	-30	500	1.74	1.92	6
<i>cis</i>	$\delta$ -TiCl <sub>3</sub> /Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1:1	29	Toluene, 18	0	1200	0.4	n.d.	4

<sup>a</sup> Mean values of radiochemical and infrared spectrophotometric analyses.

 TABLE II  
 FRACTIONATION OF A RAW ETHYLENE-*cis*-BUTENE-2 COPOLYMER BY BOILING SOLVENTS EXTRACTION  
 Molar content of *cis*-butene-2 in the raw copolymer, 41%; [ $\eta$ ] at 135° in tetralin 1.68

	Diethyl ether extract (37.8 weight %)	<i>n</i> -Hexane extract (45.3 weight %)	<i>n</i> -Heptane extract (8.6 weight %)	Extraction residue (10.3 weight %)
Butene-2 content % per moles	50	49	12	2.5
[ $\eta$ ] at 135° in tetralin	0.21	0.41	1.2	3.3
Crystallinity by X-rays	Low of the alternating type	High of the alternating type	Low of the polyethylene type	High of the polyethylene type

are either completely amorphous ( $d = 0.87$ ) or exhibit a very low crystallinity by X-rays.

The ethylene-*trans*-butene-2 alternating copolymers, produced up to now with all the catalysts examined, are not crystalline when examined by X-rays at room temperature. This proves that steric factors may exert a remarkable influence not only on the rate of this copolymerization, but also

on the steric structure of the polymer.

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