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CRYSTALLINE HIGH POLYMERS OF α -OLEFINS

Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained¹ by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

Using various heterogeneous solid catalysts which will be described elsewhere,² we have synthesized linear crystalline polymers of α -olefins and we are now reporting some properties of crystalline polypropylene, poly- α -butylene, and polystyrene. Depending on the structure of the catalyst, different amounts (ranging from 0 to 100%) of the polymerization products are crystallizable and can be separated easily from the much more soluble non-crystalline polymers by solvent extraction. In the case of polypropylene and polystyrene the X-ray diagrams of drawn fibers show reflections from about fifty different planes. Both equatorial and higher order X-ray reflections of polystyrene may be indexed on the basis of a hexagonal cell with $a = 21.9 \text{ \AA}$, and $c = 6.65 \text{ \AA}$. (space-group R 3c or R $\bar{3}c$). One of the two different crystal forms we observed for the poly- α -butylene seems to have a similar cell with $a = 17.3 \text{ \AA}$. and $c = 6.7 \text{ \AA}$. We have not yet collected sufficient data to establish the correct unit cell of polypropylene: the identity period along the fiber axis c is, in this case, 6.50 \AA .; the equatorial X-ray reflections may be indexed on the basis of an oblique cell with $a = 6.56 \text{ \AA}$, $b = 5.46 \text{ \AA}$. and $\gamma = 106^\circ 30'$.

In Table I the physical properties of the crystalline polypropylene and poly- α -butylene have been compared with those of the corresponding solid non-crystallizable substantially linear polymers obtained as by-products by the same polymerization processes.

The new crystalline polyhydrocarbons show higher melting point, higher density and lower

solubility in organic solvents, than the corresponding "amorphous" polyhydrocarbons having intrinsic viscosity of the same order of magnitude.

The infrared spectra³ of crystalline polypropylene, of melted samples of the same polymer and of the "amorphous" polypropylene show between 2 and 7.5μ the high adsorption regions characteristic of hydrocarbons. The wave lengths of the absorption bands between 7.5 and 15μ in normal and polarized light have been reported in the Table II. Most of the differences between the infrared spectrum of the crystalline and of the non-crystalline polypropylene⁴ disappear on melting the crystalline product and reappear after cooling the melted sample.

The large number and the cleanness of the X-ray reflections obtained from drawn fibers of the new polyhydrocarbons demonstrate the unusual regularity of their chain structure. By comparing X-ray and density data are seen that each stretch of principal chain, included in the elementary cell, corresponds to three monomeric units ($-\text{CH}_2-\text{CHR}-$ and therefore contains an odd number of asymmetric carbon atoms.

For these reasons we have excluded the presence of sequences of asymmetric carbon atoms having alternatively d and l configuration in the principal chain of the polymer, as was proposed for the crystalline poly-alkylvinyl ethers.⁵

Since the sequences of the type $d-l-l$ or $l-d-d$ do not seem probable, we attribute to the new crystalline polymers a structure in which at least for long portions of the principal chain, all the asymmetric carbon atoms have the same configuration.⁶ In this case, if the principal chain of a crystalline polymer of an α -olefin $\left[\begin{array}{c} -\text{CH}_2-\text{CH}- \\ | \\ \text{R} \end{array} \right]$, is represented

arbitrarily as a planar fully extended chain, all the

(3) A Beckmann IR 2, a Perkin-Elmer model 112, and a Perkin-Elmer model 21 spectrometer with NaCl prisms have been used.

(4) The infrared spectra of the crystalline and of the linear not crystallizable polypropylene are very different from infrared spectra of branched polypropylene produced using AlBr_3 as catalyst.

(5) C. E. Schildknecht, *et al.*, *Ind. Eng. Chem.*, **40**, 2104 (1948); C. E. Schildknecht, S. T. Gross and A. O. Zoss, *ibid.*, **41**, 1998 (1949); C. E. Schildknecht, A. O. Zoss and F. Grosser, *ibid.*, **41**, 2391 (1949).

(6) We propose to designate as "isotactical chains," from the Greek words *isos* = and *taxis* = to set up, the polymer chains having such exceptionally regular structure, containing series of asymmetric carbon atoms with the same steric configuration ("isotactical" asymmetric carbon atoms).

(1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 56.

(2) Details on the polymerization processes will be published in the *Journal of Polymer Science* and *Atti dell'Accademia Nazionale dei Lincei*.

TABLE I
PHYSICAL PROPERTIES OF "CRYSTALLINE" AND "AMORPHOUS" (NOT CRYSTALLIZABLE) POLYPROPYLENE, POLY- α -BUTYLENE AND POLYSTYRENE

	Intrinsic viscosity ^a cm. ³ /g. $\times 10^3$	Identity period along the chain, Å.	X-Ray density, g./cm. ³	Density d_{25}^{25}	X-Ray ^d or dilatometric ^e transition point, °C.	Melting point, °C.	Solubility/ ^f		
							Ether	n-Hep-tane	Toluene
Polypropylene									
(a) h.m.w. "crystalline"	2.40 ^b	6.50 \pm 0.05	0.94	0.92	158-160 ^d	..	i.	i.	s.
(b) l.m.w. "crystalline"	0.17 ^b	(6.50 \pm 0.05)	0.94	0.91	148-150 ^d	..	i.	sl.s.	s.
(c) "amorphous"	0.55 ^b	0.85	...	75	s.	s.	v.s.
Poly- α -butylene									
(a) "crystalline"	1.02 ^b	6.7 \pm 0.1	0.96	0.91	126-128 ^d	..	i.	s.	v.s.
(b) "amorphous"	0.35 ^b	0.87	...	65	s.	v.s.	v.s.
Polystyrene									
(a) "crystalline"	3.8 ^c	6.65 \pm 0.05	1.12	1.08	230 ^{d,e}	..	i.	i.	v.s.

^a Concentrations at 25°. ^b Tetralin as solvent at 135°. ^c Benzene as solvent at 25°. ^d Temperature at which all the X-ray reflections of crystals disappear. ^e First order transition point from dilatometric data. ^f i. = insoluble; sl.s. = slightly soluble; s. = soluble; v.s. = very soluble.

TABLE II
INFRARED SPECTRUM OF DIFFERENT TYPES OF POLYPROPYLENE BETWEEN 7.5 AND 15 μ

Crystalline product	Crystallizable polypropylene Crystalline cold drawn product		Melted product	Amorphous not crystalliz. polypropylene
	E-vector \updownarrow	\leftrightarrow		
7.53 w	...	7.53 w
7.67 m	7.67 m	7.67 w
7.71 sh	...	7.72 w
7.97 m	7.96 m	...	7.97 w	7.97 m
...	8.13 m
8.20	...	8.20 w
8.57 s	8.56 s	sh
8.66 sh	sh	8.67 m	8.70 s,b	8.66 s
9.06 w	9.06 w	9.06 w	9.06 w	9.06 sh
9.57 w	9.57 w
9.65 sh
10.02 s	10.02 s	10.02 w	10.02 w-m	10.02 w-m
10.28 s	10.28 s	10.28 m	10.28 s	10.28 s
10.64 w	...	10.63 w
11.12 m	11.12 vw	11.12 m	Wide absorption region between 11 μ and 12.7 μ with absorption maxima at 12.38 and 11.2 μ	Wide absorption region between 11 μ and 12.7 μ with absorption maxima at 12.3 μ and 11.90 μ and shoulder at 11.21 μ
11.89 s	11.89 s	11.89 w		
12.36 m	12.36 vw	12.36 m		

R groups must be placed on the same side of the plane of the principal chain. Such planar structure is impossible because of the steric impediments among the R groups and in order to reach the crystalline state a spiralization of the principal chains must take place.

This hypothesis agrees with the value found for the identity period (6.5-6.7 Å) of all these polymers, which is shorter than the length of a planar and fully extended paraffinic chain corresponding to three monomeric units (7.62 Å).

We suppose that a similar structure may be attributed to the crystalline polyalkylvinyl ethers having identity periods along the principal chain⁷

(7) C. E. Schildknecht, S. T. Gross, H. R. Davidson, I. M. Lambert and A. O. Zoss, *Ind. Eng. Chem.*, **40**, 2104 (1948).

roughly as long as those observed in the crystalline polyhydrocarbons we have prepared, and different properties from ordinary soft polymers.⁸

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- (8) S. H. Muthana and H. Mark, *J. Polymer Sci.*, **4**, 531 (1949).
(9) X-Ray structure determinations.
(10) Viscosity and density determinations.
(11) Infrared spectra determinations.
(12) Polymerization of α -olefins.