$Cu(DMG)_2$ because the latter complex has a much greater tendency to hydrate as it dissolves.

INSTITUTE FOR ATOMIC RESEARCH AND
DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY
AMES, IOWA
CHARLES V. BANKS
SAMUEL ANDERSON

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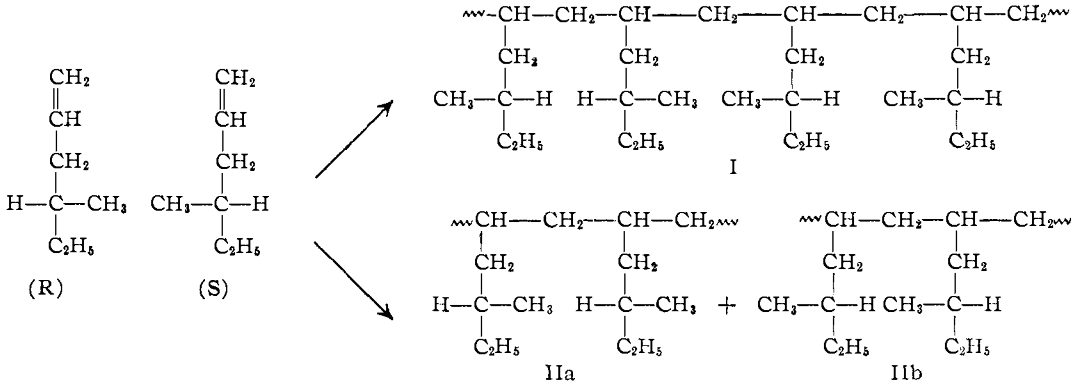
OPTICALLY ACTIVE VINYL POLYMERS. VI. CHROMATOGRAPHIC RESOLUTION OF LINEAR POLYMERS OF (R)(S)-4-METHYL-1-HEXENE

Sir:

Optically active polyhydrocarbons have been prepared up to now by polymerizing optically active[1,2] or racemic monomers,[3] or by polymerizing monomers which do not contain asymmetric carbon atoms in the presence of optically active catalysts.[4]

Recently we have interpreted[5] the fact that the crystalline structure of the polymers of (S)-4-methyl-1-hexene and of (R)(S)-4-methyl-1-hexene are identical, as indicating that the poly-4-methyl-1-hexene obtained from the racemic monomer is not a random copolymer of the two enantiomeric monomers [poly-(R)(S)-4-methyl-1-hexene, (I)], but it is actually a mixture of two types of macromolecules: the first originating predominantly from the (R) enantiomer and the second from the (S) enantiomer [(R)(S)-poly-4-methyl-1-hexene, (IIa) + (IIb)].



It should thus be possible, in principle, to resolve the polymer of the racemic 4-methyl-1-hexene into fractions having opposite signs of rotation; the resolution of the racemic polymer should provide a new method for preparing optically active polyhydrocarbons.

Separations of polymers having different steric structures (*e.g.*, isotactic and syndiotactic polypropylene) have been carried out successfully by chromatographic methods.[6] We have therefore tried to resolve some isotactic and block poly-α-olefins with asymmetric carbon atoms in the lateral chains using, as chromatographic support, an optically active isotactic poly-α-olefin which is insoluble in the eluting solvents.

TABLE I

CHROMATOGRAPHIC RESOLUTION OF RACEMIC POLY-4-METHYL-1-HEXENE.[a] SUPPORTING MEDIUM: CRYSTALLINE (+)POLY-(S)-3-METHYL-1-PENTENE[b,c]

Fraction	Eluent	T, °C.	Fraction weight, g.	$\alpha^{40}D$ (l = 2) in benzene solution	$[\alpha]^{40}D$
1	1:1 acetone diethyl ether mixture	25	0.0364	−0.175°	−23.0°
2	Diisopropyl	25	.0170	− .035°	−13.6°
3	ether	56.2	.0348	− .055°	− 6.7°
4	Diisopropyl	56.2	.0466	− .040°	− 4.1°
5	ether	56.2	.0154	+ .015°	+ 4.8°
6	Benzene	64.5	.0322	+ .185°	+25.0°
7	Benzene	77.1	.0162	+ .155°	+47.7°

[a] A diethyl ether insoluble, diisopropyl ether soluble fraction having [η] 0.92 at 120° in tetralin. [b] Boiling decalin insoluble fraction. [c] Weight of supporting polymer/weight of supported polymer = 30.4; supported polymer 0.22 g.; total polymer eluted 0.1986 g.

A partial resolution of a diethyl ether insoluble, diisopropyl ether soluble fraction of the polymer of the racemic 4-methyl-1-hexene[5,7] has been obtained by supporting the racemic polymer on a sample of highly crystalline poly-(S)-3-methyl-1-pentene, (III),[5] which is insoluble not only in the eluting solvents used, but also in boiling decalin. The supported polymer has been successively eluted with acetone and diethyl ether at room temperature, diisopropyl ether at room temperature and at 56.2°, benzene at 64.5° and benzene at 77.1° (Table I).

By the same method, acetone or diethyl ether soluble fractions of the racemic poly-3-methyl-1-pentene[5] have been resolved.

As shown in Table II, under comparable conditions the resolution increases with the stereoregularity (*i.e.*, melting point) of the fraction to be resolved.

In all the experiments the first fractions have negative optical rotation, while the last fractions have positive optical rotation. According to the relationship between optical rotation sign and the absolute configuration of the asymmetric carbon

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(1) P. Pino and G. P. Lorenzi, *J. Am. Chem. Soc.*, **82**, 4745 (1960).

(2) W. J. Bailey and E. T. Yates, *J. Org. Chem.*, **25**, 1800 (1960).

(3) G. Natta, P. Pino and G. P. Lorenzi, Italian Patent 605,786 (January 15, 1959).

(4) G. Natta, L. Porri, A. Carbonaro and G. Lugli, *Chimica e Industria*, **43**, 529 (1961).

(5) P. Pino, G. P. Lorenzi and L. Lardicci, *Chimica e Industria*, **42**, 712 (1960).

(6) G. Natta, I. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro, and A. Zambelli, *Rend. Acc. Naz. Lincei*, [VIII] **28**, 539 (1960).

(7) G. Natta, P. Pino, G. Mazzanti, P. Corradini and U. Giannini, *ibid.*, [VIII] **19**, 397 (1955).

TABLE II

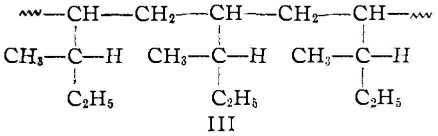
RESOLUTION OF RACEMIC POLY-4-METHYL-1-HEXENE SAMPLES HAVING DIFFERENT STEREOREGULARITY[a]

Sample			$[\alpha]_D$ in benzene[d]		$\Sigma_i\{[\alpha]_D\}_i\, w_i/W$[e]		
Solubility	$[\eta]$ 100 cm.³/g.[b]	Melting temp., °C.[c]	First fraction	Last fraction	Negative fractions	Positive fractions	R[g]
Acetone soluble	n.d.	...	−29.7°[f]	+10.8°[f]	−4.22°[f]	+2.94°[f]	26.5
Acetone in soluble, diethyl ether soluble	0.67	85–95	− 7.6°	+73.0°	−5.21°	+5.10°	25.6
Diisopropyl ether insoluble, isoöctane soluble	1.52	146–148	−21.0°	+97.5°	−8.46°	+8.02°	22.0

[a] Obtained by solvent extraction at the solvent boiling point. [b] At 120° in tetralin. [c] Determined using a Kofler melting point apparatus. [d] At 40°, if not otherwise indicated. [e] w_i = weight of the fraction having $\{[\alpha]_D\}_i$; W = total weight of the eluted polymer. [f] The optical activity measurements were carried out at 25°. [g] R = weight of supporting polymer/weight of supported polymer.

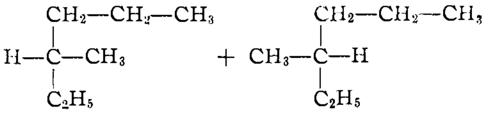
atoms of the lateral chains in optically active isotactic poly-3-methyl-1-pentene and poly-4-methyl-1-hexene,[8,9] we can now assume that the supporting polymer adsorbs more strongly the macromolecules in which most of the lateral chains possess asymmetric carbon atoms with the same absolute configuration of the corresponding asymmetric carbon atoms which are present in the lateral chains of the supporting polymer.

The remarkable difference between the affinity of the poly-(R)-4-methyl-1-hexene and poly-(S)-4-methyl-1-hexene for the poly-(S)-3-methyl-1-pentene used as chromatographic support, could depend mainly on the interactions between the lateral chains of the supported and the supporting polymers. Since our attempts to resolve low molecular weight hydrocarbons such as the 3-methylhexane (IV) at room temperature, by the same supporting medium, have failed, it appears, at least in the case of low molecular weight hydrocarbons having m.p. well below the fractionation temperature, that the different interactions of the *sec*-butyl groups having opposite absolute configurations of the racemic hydrocarbons, with the *sec*-butyl groups present as lateral chains in the optically active supporting polymer are not strong enough to allow resolution of a racemic hydrocarbon.



$$\sim\!\mathrm{CH{-}CH_2{-}CH{-}CH_2{-}CH}\!\sim \quad \text{each CH bearing } \mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}H} \text{ with } \mathrm{C_2H_5}$$

III



$$\mathrm{H{-}\overset{CH_2-CH_2-CH_3}{\underset{C_2H_5}{C}}{-}CH_3} + \mathrm{CH_3{-}\overset{CH_2-CH_2-CH_3}{\underset{C_2H_5}{C}}{-}H}$$

IV

The conformation of the principal chains of the polymer to be resolved should therefore play an important role in the resolution of the racemic poly-hydrocarbons. In other words macromolecules having the same conformation of the supporting polymer (*e.g.*, helical conformation of the same screw sense) are much more strongly adsorbed than macromolecules having different conformations.

From the point of view of the stereospecific polymerization mechanism these results nicely confirm that the highly stereospecific catalysts (*e.g.*, $TiCl_3$ + $Al(i\text{-}C_4H_9)_3$), are able to choose predominantly one or the other enantiomer from the racemic monomer in order to build up a single macromolecule.

INSTITUTE OF INDUSTRIAL ORGANIC CHEMISTRY, UNIVERSITY OF PISA, ITALY
PIERO PINO
FRANCESCO CIARDELLI
GIAN PAOLO LORENZI
INSTITUTE OF INDUSTRIAL CHEMISTRY POLYTECHNIC, MILAN, ITALY
GIULIO NATTA

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STEREOSPECIFIC CATALYSTS FOR THE HEAD-TO-TAIL POLYMERIZATION OF PROPYLENE TO A CRYSTALLINE SYNDIOTACTIC POLYMER

Sir:

Propylene can be polymerized stereospecifically to yield two types of crystalline polymers having monomeric units with a head-to-tail attachment: these polypropylenes are isotactic and syndiotactic. A polymer which may be considered as a third type of crystalline polypropylene having a head-to-head and tail-to-tail attachment and a di-syndiotactic structure can be obtained by the alternate copolymerization of ethylene with *cis*-butene-2.[1]

The catalytic systems described up to now and used for obtaining crystalline head-to-tail syndiotactic polymers of propylene consist predominantly of complexes which are specific for the polymerization of isotactic polypropylene. In fact, at the very best, the syndiotactic fraction has a low order of crystallinity, and is present only in small amounts in the crude polymer together with large amounts of isotactic polymer.[2] The syndiotactic fraction was separated from the isotactic one by adsorption chromatograph.[2]

We now have found some catalytic systems that permit the polymerization of propylene to polymers which crystallize without purification or fractionation, and whose crystallinity derives only from the presence of head-to-tail syndiotactic polypropylene.

Some of these catalytic systems, obtained from a vanadium compound and aluminum dialkylmonohalide are listed in Table I. Systems prepared from these compounds have been used previously for the copolymerization of α-olefins with ethylene, for obtaining amorphous polymers with elastomeric properties.[3] However we have

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[8] P. Pino, G. P. Lorenzi, L. Lardicci and F. Ciardelli, *Vysokomol. Soedineniya*, **3**, 1597 (1961).

[9] P. Pino, Lecture given at the Summer School of Macromolecular Chemistry, Varenna, Italy, 18–30 September, 1961.

[1] G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori and A. Zambelli, *J. Am. Chem. Soc.*, **83**, 3343 (1961).

[2] G. Natta, I. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro and A. Zambelli, *Rend. Acc. Naz. Lincei*, [8] **28**, 539 (1961).

[3] G. Natta, G. Mazzanti, A. Valvassori, G. Sartori and D. Fiumani, *J. Polymer Sci.*, **51**, 411 (1961).