TABLE III
SEPARATION DEGREE (F) AND INTRINSIC SEPARABILITY (D) OF POLYMERS FROM RACEMIC α-OLEFINS AND OF EQUIMOLAR[a] MIXTURES OF HOMOPOLYMERS OF THE TWO ANTIPODES

Polymer submitted to chromatographic separation[b]	Fraction[c]	$\overline{DP}_n$ or ($\overline{DP}_v$)	Separation[d] deg, % (F)	Separability,[e] % (D)	Theoretical separability, %, of[f] a statistical copolymer of the two antipodes (D_0)		
Equimolar[a] mixture of poly-(R)- and poly-(S)-4-methyl-1-hexene	B	100	32.5	100			
Poly-(R)(S)-4-methyl-1-hexene	A	10	2.5	7.7		26	
	B	100	4.9	15		7	
	C	(2200)	5.1	16	2[g]		4.5[h]
	D	(950)	5.5	17	2.5[g]		7[h]
	E	(1800)	6.1	19	2.1[g]		6[h]
Equimolar[a] mixture of poly-(R)- and poly-(S)-3,7-dimethyl-1-octene	B	45	37.0	100			
Poly-(R)(S)-3,7-dimethyl-1-octene	A	7	12.3	33		30	
	C′	(250)	27.3	74	4.0[g]		14[h]
	C	(1300)	33.6	91	2.4[g]		6.5[h]

[a] Based on the monomeric units. [b] On poly-(S)-3-methyl-1-pentene. [c] Extracted successively with A acetone, B ethyl acetate, C ethyl ether, D isopropyl ether, E isoctane, C′ = B + C. [d] See ref 2 and A. Lucherini, Thesis, University of Pisa, Feb 1969. [e] $D = F/E$. [f] Having DP equal to $\overline{DP}$ of separated sample. [g] DP = $\overline{DP}_v$. [h] DP = 0.1$\overline{DP}_v$ (see ref 3).

The separability D for the polymers from racemic 4-methyl-1-hexene and 3,7-dimethyl-1-octene extractable with boiling ethyl acetate, calculated with the above values of E and with the F data previously obtained,[2] are much higher than the corresponding values of D_0 (Table III). This indicates that the polymerization leading to isotactic polymers is surely stereoselective for both monomers.

In the case of the fraction extracted with acetone which is less stereoregular than that extracted with ethyl acetate and of the fractions extracted with diethyl ether, diisopropyl ether, and isoctane which are more stereoregular,[5] the efficiency has not been evaluated up to now. Therefore an approximate evaluation of D for the above fractions has been made (Table III) using the values of E found in the present work considering that F does not change markedly with changing degree of stereoregularity.[2]

We can draw the following conclusions from a comparison of the D data with the corresponding D_0 values (Table III).

(i) Polymerization by heterogeneous Ziegler–Natta catalysts is stereoselective not only in the case of α-olefins having the asymmetric carbon atom in the 3 position, but also in the 4 position.

(ii) The efficiency is similar in both groups of polymers, but F decreases when the aysmmetric carbon atom is in the 4 instead of in the 3 position, indicating that the stereoselectivity decreases in the same direction.

(iii) The separability of polymers from racemic 3,7-dimethyl-1-octene is very similar to that of the corresponding mixture of the homopolymers from (S) and (R) antipodes.

(iiii) At least for the last monomer the process is stereoselective even when it leads to chains which, according to the absence of crystallinity at room temperature, should have very low degree of isotacticity.

These conclusions and particularly the last two suggest that the stereoselectivity is probably due to the intrinsic dissymmetry of the active sites rather than to the asymmetric induction by the growing chain end.[3] In fact the latter mechanism should yield block copolymers of the two antipodes which would not be separated by such a large extent.

It seems therefore that also the stereoregulation is mainly due to the dissymmetry of the sites as previously proposed.[3,15]

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Polymerization of Internal Olefins

Steric factors have been cited to explain the precedence of termination and alternate reactions over propagation[1] to linear polymer in internal olefins and in cyclic olefins larger than cyclobutene. Consideration of the effect of pressure on rates[2] suggests that propagation is favored more than other reactions[3] by pressures above a few kilobars. We have developed means of containing liquid monomers (about 0.2 ml per experiment) in a tetrahedral anvil device[4,5] where pres-

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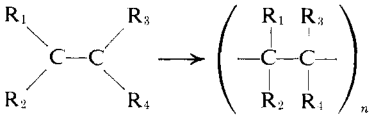
sures up to 65,000 atm (65 kbars) and temperatures up to 500° can be attained. It has been found that cyclic olefins, including cyclohexene, and internal olefins, including tetramethylethylene, give polymers by 1,2-addition polymerization at 300° and 65 kbars.



Cyclopentene (R^1 and R^3 = $-CH_2CH_2CH_2-$, R^2 = R^4 = H) has been chosen for discussion because comparison of our cyclopentene polymer with cyclopentene polymers formed by ring opening to *cis*- and *trans*-pentenamers[6] and other cationic polymerization to polymers[7] with both ring opened and cyclopentane units in the polymer chain is possible. When pure cyclopentene was sealed in a small platinum ampoule and heated 4 hr at 300° and 65 kbars in the tetrahedral anvil device, a waxy, polymeric solid was obtained in high conversion. This polymer was completely soluble in hydrocarbons, analyzed[8] for C_5H_8, showed no unsaturation according to infrared or nmr spectroscopy, and was different from previously reported cyclopentene polymers. Strong infrared absorption occurred as doublets at 3.4–3.5 and 6.8–7.0 μ; absorption in these regions is characteristic for all other cyclic olefin polymers obtained by our polymerization technique. Very thick polymer samples also showed weak absorptions at longer wavelengths. The proton magnetic resonance spectrum showed, even at high resolution (220 MHz), a poorly resolved peak at τ 8.5. Thermogravimetric analysis of polycyclopentene gave a 5% weight loss temperature of 275°, and maximum degradation occurred above 450°. The waxy polymer could be fractionated into a solid portion and a grease.

Other cyclic olefins when subjected to the reaction conditions also yielded saturated polymers. Those studied to date include cyclohexene, 3-methylcyclohexene, cycloheptene, cyclooctene, and cyclododecene. The polymer from cyclohexene is particularly noteworthy since it is the first reported addition polymer of cyclohexene.

cis- and *trans*-2-butenes have been studied as representative of polymerization of internal olefins. Each stereoisomer forms a saturated polymer; the infrared and nmr spectra of both polymers are indistinguishable from each other. Our 2-butene polymers are transparent in regions near 8 and 11 μ where polymers of 1-butene[9] absorb strongly. Previous attempts to prepare poly-2-butene using cationic initiators have given butene-1 polymers by rearrangement[10] prior to polymerization. Poly-2-butene also referred to in the literature as polyethylidene[11] has been obtained from diazoethane in stereoregular form and is high melting. Other authors[12] mentioned that most polyethylidene samples still contain nitrogen. In a manner similar to 2-butene polymerization, each of the isomers of *cis*- and *trans*-2-pentene formed a saturated polymer; these polymers like those of *cis*- and *trans*-butene are spectrally indistinguishable. 2-Hexene, the only other disubstituted olefin investigated, also polymerized. It should be noted that polymers from unsymmetrical olefins cannot be obtained by the diazoalkane route.

The polymerization is not limited to disubstituted olefins. Both 2-methyl-2-butene and 2,3-dimethyl-2-butene formed saturated polymers when heated at 300° at 65 kbars. According to nmr and ir spectra, no rearrangement occurred during polymerization.

High temperatues as well as high pressures were required to bring about the polymerizations of internal olefins. No polymerization was observed in several cases below 200°, a fact which may be related to the greatly increased melting points of monomers at these pressures but which also suggests a thermally initiated radical process for the polymerization. In spite of the heroic polymerization conditions, the reaction products remained colorless. We have not attempted to find optimum conditions for the polymerization of the individual monomers and molecular weights remained modest, as judged by inherent viscosities of 0.05–0.1 dl/g.

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