TABLE I
THERMOELASTIC DATA OF ACRYLIC POLYMERS

Sample	$d \ln G/dT \times 10^3$, deg^{-1}	$\beta_L{}^0 \times 10^4$, deg^{-1}	f_e/f 60°	f_e/f 120°	$d \ln r_f{}^2/dT \times 10^3$, deg^{-1} 60°	$d \ln r_f{}^2/dT \times 10^3$, deg^{-1} 120°	$-\epsilon'$, cal/mol 60°	$-\epsilon'$, cal/mol 120°
Poly(2-hydroxypropyl acrylate)	3.6	2.8	−0.30	−0.53	−0.90	−1.35	200	420
Poly(isobutyl acrylate)	3.4	2.4	−0.20	−0.42	−0.60	−1.07	130	320
Poly(isobutyl methacrylate)	2.3	2.2		0.02		0.05		−20

the importance of intra- rather than intermolecular effects in rubber elasticity is again demonstrated. There is little reason to expect that values of f_e/f should be identical for PiBA and PHPA, since they are different in molecular constitution. In addition, the hydrogen bonds furnished by the -OH groups of PHPA probably also effect intramolecular interactions to some extent.

Table I also shows that d ln $r_f{}^2/dT$ for the polyacrylates are negative, while that for the polymethacrylate is positive. These are in general agreement with the results of Tobolsky.[5] Theoretically, Ptitsyn[9] has predicted the unperturbed chain dimensions to decrease with temperature for vinyl polymers, while Flory[6] arrived at the opposite conclusion. Present data indicate only that they are both possible, depending on the molecular structure of the polymer chains.

(9) O. B. Ptitsyn, *Vysokomol. Soedin.*, **4**, 1445 (1962).

Communications to the Editor

Quantitative Aspects of the Stereoselectivity in the Stereoregulated Polymerization of Racemic α-Olefins by Ziegler–Natta Catalysts

In previous papers[1-4] we reported the separation of polymers from racemic vinyl monomers into fractions having optical activity of opposite sign and containing macromolecules made up predominantly of *R* or *S* units.[3,5]

The degree of separation *F* was calculated[2] on the basis of the weight per cent and the optical rotation of the collected fractions by the empirical relationship between polymer rotatory power and optical purity[4,6] of polymerized monomer.

The presence of macromolecules made up predominantly of *R* or *S* units may be foreseen also in a statistical copolymer of the two antipodes; in this case the average prevalence of units of one type becomes vanishingly small at high DP.[7]

The polymerization of a racemic monomer will be considered stereoselective[8] if the actual separability *D* of the polymer obtained is higher than the theoretical separability D_0 of a statistical copolymer of the two antipodes with the same molecular weight; D_0 has been taken equal to the average prevalence[7] of *R* (or *S*) units in half-weight[9] of the statistical copolymer.

D is not in general equal to *F* as the *F*/*D* ratio or efficiency *E* of the method of separation[2] is expected to be lower than unity. Furthermore, under the present experimental conditions, the polymers of racemic α-olefins are separated not only with respect to prevalence of *R* or *S* units, as shown by the sign of optical activity of the fractions, but also with respect to molecular weight and stereoregularity.[2]

In the case of polymers from racemic α-olefins having the asymmetric carbon atom in the 3 position, like 3-methyl-1-pentene and 3,7-dimethyl-1-octene, the value of *F*, which is a minimum value of *D*, suffices[3] for a qualitative demonstration of the occurrence of stereoselectivity. By contrast a knowledge of *E* appeared to be necessary[3] for polymers of racemic 4-methyl-1-hexene, in which the asymmetric carbon atom is in the 4 position. Furthermore a quantitative evaluation of the stereoselectivity might give interesting information on the mechanism not only of the stereoselection, but also of the steroregulation by Ziegler–Natta catalysts.

In order to evaluate *E* we have synthesized polymers of *R* and *S* antipodes of the above α-olefins and we have investigated the separation of their mixture by elution chromatography on an optically active support.

(*S*)-3,7-Dimethyl-1-octene ($[\alpha]^{25}\text{D}$ +13.81 (neat),

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(1) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Amer. Chem. Soc.*, **84**, 1487 (1962).

(2) P. Pino, G. Montagnoli, F. Ciardelli, and E. Benedetti, *Makromol. Chem.*, **93**, 158 (1966).

(3) P. Pino, F. Ciardelli, and G. Montagnoli, *J. Polym. Sci., Part C*, **16**, 3265 (1968).

(4) E. Chiellini, G. Montagnoli, and P. Pino, *ibid., Part B*, **7**, 121 (1969).

(5) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, *Makromol. Chem.*, **61**, 207 (1963).

(6) P. Pino, F. Ciardelli, G. Montagnoli, and O. Pieroni, *J. Polym. Sci., Part B*, **5**, 307 (1967).

(7) P. L. Luisi, G. Montagnoli, and M. Zandomeneghi, *Gazz. Chim. Ital.*, **97**, 222 (1967).

(8) As is known a process is called stereoselective when produces one diastereoisomer of a given structure in considerable predominance over all the other possible diastereoisomers [E. L. Eliel, "Stereochemistry or Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 434]. Considering the units from a racemic monomer as *R* or *S*, independently of the main chain asymmetric carbon atom absolute configuration, we think that the above definition can be extended to an oligomerization or polymerization process which gives one type of copolymer of the two antipodes in larger amount over the other possible types.

(9) The half-weight to be considered is that containing all the macromolecules in which *R* (or *S*) units prevail and 50% of the macromolecules having the same content of *R* and *S* units. For the calculation of the prevalence the formulas reported in ref 7 have been used and the values averaged to give D_0.

TABLE I

PROPERTIES OF THE FRACTIONS COLLECTED IN THE CHROMATOGRAPHIC SEPARATION OF THE EQUIMOLAR[a] MIXTURE OF POLY-(*R*)- AND POLY-(*S*)-4-METHYL-1-HEXENE, EXTRACTED WITH ETHYL ACETATE, ON POLY-(*S*)-3-METHYL-1-PENTENE[b]

Fraction	Eluent at 25°		Fraction weight, %	$[\alpha]^{25}_{D}$ [c]	$\bar{M}_n \times 10^{-3}$ [d]	Ir stereoregularity index[e]
1	1:1	Acetone/*n*-pentane (v/v)	17.2	−57.7	2.6	0.62
2	1:1		12.5	−39.8	6.0	0.65
3	4:5		16.2	−43.7	8.4	0.63
4	2:3		13.6	−69.6	12.7	0.59
5	2:3		10.5	−74.5	7.1	0.76
6	1:3		11.5	+27.1	6.2	0.80
7	*n*-Pentane		12.9	+204	5.4	0.88
8	Cyclohexane[f]		5.6	+166	1.8[g]	0.73

[a] A 0.3874-g sample of a mixture was used having $[\alpha]^{25}_{589}$ −0.49, $[\alpha]^{25}_{436}$ −0.67, and $D_{B995}/D_{B964} = 0.69$ obtained by mixing 0.2396 g of poly-(*R*)-4-methyl-1-hexene ($[\alpha]^{25}_{589}$ −238, $[\alpha]^{25}_{436}$ −470, $\bar{M}_n = 10.6 \times 10^3$ and $D_{B995}/D_{B964} = 0.68$) with 0.2414 g of poly-(*S*)-4-methyl-1-hexene ($[\alpha]^{25}_{589}$ +240, $[\alpha]^{25}_{436}$ +484, $\bar{M}_n = 10.0 \times 10^3$ and $D_{B995}/D_{B964} = 0.70$); eluted polymer 0.3877 g. [b] Weight of supporting polymer/weight of supported polymer = 67.7. [c] In cyclohexane (c = 0.45–1.74 g/dl) with a Perkin-Elmer Model 141 polarimeter having sensitivity ±0.003°. [d] In benzene (c = 18.86–20.15 g/l.) with a Mechrolab 301 A osmometer; the data are not extrapolated to zero concentration. [e] Evaluated by the ratio of optical density of the band at 995 cm^{-1}, associated to stereoregularity, and at 964 cm^{-1}, independent of stereoregularity (base line points 1175 and 935 cm^{-1}), with a Perkin-Elmer Model 221 spectrophotometer. [f] In Kumagawa extractor at the solvent boiling point. [g] c = 11.34 g/l.

TABLE II

OPTICAL ROTATION OF THE FRACTIONS COLLECTED IN THE CHROMATOGRAPHIC SEPARATION OF THE EQUIMOLAR[a] MIXTURE OF POLY-(*R*)- AND POLY-(*S*)-3,7-DIMETHYL-1-OCTENE, EXTRACTED WITH ETHYL ACETATE, ON POLY-(*S*)-3-METHYL-1-PENTENE[b]

Fraction	Eluent at 25°		Fraction weight, %	$[\alpha]^{25}_{D}$ [c]
1	1:1	Acetone/*n*-pentane (v/v)	23.3	+25.0
2	1:1		11.0	+24.6
3	1:1		18.5	+14.4
4	4:5		15.9	+2.4
5	4:5		12.6	−10.7
6	2:3		6.3	−48.6
7	Cyclohexane		12.4	−69.7

[a] A 0.2572-g sample of a mixture having $[\alpha]^{25}_{589}$ − 1.8 and $[\alpha]^{25}_{436}$ − 4.1 obtained by mixing 0.1316 g of poly-(*R*)-3,7-dimethyl-1-octene ($[\alpha]^{25}_{589}$ −62.8, $[\alpha]^{25}_{436}$ −123, $\bar{M}_n = 6.6 \times 10^3$ and $D_{B1217}/D_{B1168} = 0.47$) with 0.1256 g of poly-(*S*)-3,7-dimethyl-1-octene ($[\alpha]^{25}_{589}$ +64.5, $[\alpha]^{25}_{436}$ +123, $\bar{M}_n = 6.1 \times 10^3$ and $D_{B1217}/D_{B1168} = 0.49$); eluted polymer 0.2564 g. [b] Weight of supporting polymer/weight of supported polymer = 77.6. [c] In cyclohexane (c = 0.68–1.95 g/dl) with a Perkin-Elmer Model 141 polarimeter having sensitivity ±0.003°.

optical purity[10] 84.7%) has been prepared from (*S*)-citronellol[11] and (*R*)-4-methyl-1-hexene ($[\alpha]^{25}_{D}$ +2.62 (neat), optical purity[12] 86.8%) from (*R*)-2-methylbutanoic acid obtained by resolution of the racemic acid with (*S*)-α-phenylethylamine;[13] (*R*)-3,7-dimethyl-1-octene and (*S*)-4-methyl-1-hexene with higher optical purity have been prepared as previously reported[10,12] and diluted with the racemic product to give samples with the same optical purity of the respective antipode.

The above olefins have been polymerized at room temperature with $TiCl_4$–$Al(i-C_4H_9)_3$ (1:3) catalyst, and the polymers fractionated by solvent extraction.[5]

Moderately crystalline fractions, having similar stereoregularity according to ir data and number average molecular weight, extracted with boiling ethyl acetate from the polymers insoluble in boiling acetone of the two antipodes of each olefin, have been mixed in suitable amount to give optically inactive polymer mixtures.

The two mixtures have been separated into fractions having optical activity of opposite sign by adsorption on crystalline isotactic poly-(*S*)-3-methyl-1-pentene and successive elution under the same conditions used for the polymers derived from the corresponding racemic monomers.[2] The average optical rotation of the polymer fractions having optical activity of the same sign is markedly lower, in absolute value, than that of the corresponding optically active polymer sample used to prepare the optically inactive mixtures (Tables I and II).

Although the monomers used have 85–86% optical purity and contain 92–93% of one enantiomer and 8–7% of the other one, it is reasonable to assume in first approximation[14] that *D* for the above optically inactive mixtures is 100%; therefore the evaluation of *F* gives *E* directly. From the optical rotation data of Tables I and II values of *F* (or *E*) equal to 0.32 and 0.37 have been obtained for the polymers of 4-methyl-1-hexene and 3,7-dimethyl-1-octene, respectively. The reasons of the low values of *E* are at least in part the same as those indicated for the polymers of racemic monomers. In fact, as Table I shows, the mixture of poly-(*R*)- and poly-(*S*)-4-methyl-1-hexene also has been fractionated according to molecular weight and stereoregularity.

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(10) F. Ciardelli and P. Pino, *Gazz. Chim. Ital.*, **95**, 1201 (1965).

(11) R. Rienäcker and G. Ohloff, *Angew. Chem.*, **73**, 240 (1961).

(12) P. Pino, L. Lardicci, and L. Centoni, *Gazz. Chim. Ital.*, **91**, 428 (1961).

(13) G. Odham, *Ark. Kemi*, **20**, 507 (1963).

(14) If the enantiomer present in smaller amount is not copolymerized it could yield some homopolymer which might be separated leading to a small increase of *F* and then to an apparent increase of *E*. However, considering the high optical purity of the olefins used this possible increase does not influence appreciably our conclusions.

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]

Acknowledgment. This work has been sponsored by the "Consiglio Nazionale delle Ricerche" through the "Instituto di Chimica delle Macromolecole, Milano."

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Received August 11, 1969

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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