Stereochemical Aspects of the Copolymerization of Asymmetric α-Olefins by Stereospecific Catalysts

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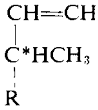
ABSTRACT: Racemic 3,7-dimethyl-1-octene and 3-methyl-1-pentene have been copolymerized, respectively, with (*S*)-3-methyl-1-pentene and (*R*)-3,7-dimethyl-1-octene in the presence of $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ or $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalyst. Optical activity measurements on the recovered nonpolymerized monomers showed that the antipode of the racemic monomer B having chirality opposite to that of the optically active monomer A was polymerized with a lower rate than the other antipode. Solvents extraction of copolymerization product yielded fractions having different chemical composition. Optical activity and infrared absorption of the fractions demonstrated that copolymerization takes place predominantly between A and the antipode of B having the same chirality as A. The other antipode of B gives the homopolymer. These results are discussed with reference to stereoelective and stereoselective polymerization of racemic α-olefins.

Polymerization of racemic α-olefins in the presence of Ziegler–Natta-type catalysts was demonstrated to be stereoselective[1] when the asymmetric carbon atom in the monomer was in the α or β position with respect to the double bond. In fact, the polymers were separated in fractions having optical activity of opposite sign[2] and the separation degree obtained was larger than that calculated[3] for a statistical copolymer of the two antipodes.[1]

The stereoselectivity of the polymerization process should exist also in the copolymerization of monomers of the above type, particularly with the asymmetric α-olefins (I) having substantially the same structure in the vicinity of the double bond.



$$\begin{array}{l} CH{=}CH_2 \\ | \\ C^{*}HCH_3 \\ | \\ R \end{array}$$

I

If the stereoselectivity is high enough, the copolymerization of an optically active monomer A with a racemic one B should yield copolymer of A with the antipode of B having the same chirality as A and homopolymer of the other antipode of B. The occurrence of this process can be easily detected as homopolymers and copolymers can be separated by solvents extraction.[4,5]

Following a preliminary communication[6] on this subject we describe in the present paper the copolymerization of racemic 3,7-dimethyl-1-octene [I, R = $-(CH_2)_3CH(CH_3)_2$] or racemic 3-methyl-1-pentene [I, R = $-C_2H_5$] with (*S*)-3-methyl-1-pentene or (*R*)-3,7-dimethyl-1-octene, respectively, using $TiCl_4$ in combination with $Zn(i\text{-}C_4H_9)_2$ or $Al(i\text{-}C_4H_9)_3$ as catalysts. The results are discussed with reference to stereoelectivity and stereoselectivity of the polymerization process.

Experimental Section

1. Materials. Racemic 3,7-dimethyl-1-octene, 3-methyl-1-pentene, and (*S*)-3-methyl-1-pentene (optical purity 89%) were prepared and purified as reported in previous papers.[7,8] (*R*)-3,7-Dimethyl-1-octene having n^{25}D 1.4143, $[\alpha]^{25}$D −15.5 (neat), and then optical purity 95% was prepared by pyrolysis at 490-500° of (*R*)-3,7-dimethyl-1-octyl acetate obtained from (+)-pulegone.[9]

$TiCl_4$, $Al(i\text{-}C_4H_9)_3$, and $Zn(i\text{-}C_4H_9)_2$ were purified by distillation under reduced pressure and handled under nitrogen.

2. Copolymerization Experiments. Copolymerization experiments (Table I) were carried out operating as described in the following example.

To 0.601 g (3.35 mmol) of $Zn(i\text{-}C_4H_9)_2$, cooled in a glass vial by an ice–salt mixture, 2.01 g (1.06 mmol) of $TiCl_4$ was added dropwise under nitrogen. The comonomers mixture containing 2.91 g (20.8 mmol) of racemic 3,7-dimethyl-1-octene and 0.51 g (6.1 mmol) of (*S*)-3-methyl-1-pentene (optical purity 89%) was then introduced. The vial was sealed and kept at room temperature (20–25°) under occasional shaking for several days. The catalyst was destroyed by adding 100 ml of pure methanol and the nonpolymerized monomers were distilled as azeotropic mixture with methanol; the distillation was stopped when the distilling methanol did not contain detectable amount of olefins, as tested by gas chromatography using a Perkin-Elmer Model F 11 gas chromatograph and a 2-m column packed with polypropylene glycol on Chromosorb W.

The hydrocarbons mixture, separated from methanol by washing with cold water, was dried on $CaCl_2$ and treated with bromine in chloroform at 0° in the dark. The brominated product was accurately fractionated by distillation under vacuum. A fraction having n^{25}D 1.4923 gave, by treatment with zinc powder in methanol, 3,7-dimethyl-1-

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(2) (a) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Amer. Chem. Soc.*, **84**, 1487 (1962); (b) P. Pino, G. Montagnoli, F. Ciardelli, and E. Benedetti, *Makromol. Chem.*, **93**, 158 (1966).

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(7) P. Pino, F. Ciardelli, and G. P. Lorenzi, *Makromol. Chem.*, **71**, 184 (1964).

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TABLE I

COPOLYMERIZATION OF RACEMIC AND OPTICALLY ACTIVE 3,7-DIMETHYL-1-OCTENE WITH OPTICALLY ACTIVE AND RACEMIC 3-METHYL-1-PENTENE, RESPECTIVELY, IN THE PRESENCE OF CATALYSTS OBTAINED BY REACTION OF $TiCl_4$ WITH DIFFERENT ORGANOMETALLIC COMPOUNDS (MeR_n)

Run	Comonomers Type	Comonomers Amt, g	Catalyst $TiCl_4$ +	Mol of A + mol of B/mol of $TiCl_4$	Mol of MeR_n/mol of $TiCl_4$	Nonpolymerized monomer (B),[c] deg g^{-1} cm^2 α^{25}D[d]	Nonpolymerized monomer (B),[c] deg g^{-1} cm^2 $[\alpha]^{25}$D	Polymer, g Methanol soluble	Polymer, g Methanol insoluble
C_1	B (*R*)(*S*)-3,7-Dimethyl-1-octene A (*S*)-3-Methyl-1-pentene[a]	2.910 0.510	$Zn(i\text{-}C_4H_9)_2$	25.4	3.2	−0.07[e]	−0.19	0.3067	0.4232
C_2	B (*R*)(*S*)-3,7-Dimethyl-1-octene A (*S*)-3-Methyl-1-pentene[a]	2.910 0.067	$Zn(i\text{-}C_4H_9)_2$	18.0	2.8	−0.055[e,g]	−0.15	0.4010	0.6194
C_3	B (*R*)(*S*)-3,7-Dimethyl-1-octene A (*S*)-Methyl-1-pentene[a]	5.810 1.040	$Al(i\text{-}C_4H_9)_3$	65.0	3.0	−0.10[f]	−0.14	0.2903	1.7702
C_4	B (*R*)(*S*)-3-Methyl-1-pentene A (*R*)-3,7-Dimethyl-1-octene[b]	3.500 1.740	$Zn(i\text{-}C_4H_9)_2$	22.5	2.8	+0.22[e]	+0.60	0.2470	1.0329

[a] Optical purity 89%. [b] Optical purity 95%. [c] The monomer which was initially racemic was isolated as reported in Section 2 of the Experimental Section. [d] Neat. [e] l = 0.5 dm. [f] l = 1.0 dm. [g] The optical rotation of this sample has been checked by a Perkin-Elmer Model 141 polarimeter (sensitivity ±0.003°) obtaining α^{25}D (l = 0.5) −0.059° and α^{25}_{436} (l = 0.5) −0.12°, the corresponding specific rotatory power being −0.15 and −0.29, respectively.

octene still containing about 2–3% of 3-methyl-1-pentene; by successive fractional distillation at room pressure 3,7-dimethyl-1-octene (bp 155–155.5°) was obtained which contained less than 0.1% 3-methyl-1-pentene (bp 54–54.5°) as shown by gas chromatographic analysis under the above-mentioned conditions. The 3,7-dimethyl-1-octene thus purified had[9] n^{25}D 1.4146 and α^{25}D (l = 0.5) −0.07° (neat) measured by a Schmidt–Haensch Lippich polarimeter with sensitivity ±0.005° (see also Table I).

After removal of the nonpolymerized monomers by distillation the methanolic suspension of the polymer was filtered. The solid methanol insoluble polymer was purified by treatment under nitrogen with boiling methanol and with diethyl ether saturated with gaseous HCl. By successive coagulation with methanol and drying under reduced pressure of 0.4232 g of polymer was obtained.

The methanolic solution was concentrated and extracted with *n*-pentane; by evaporation of the pentane under vacuum at room temperature 0.3067 g of liquid methanol soluble polymer was obtained.

3. Polymer Characterization. The solid methanol insoluble polymer was extracted with boiling solvents, under nitrogen, in Kumagawa[2b] extractors. Extraction with each solvent was stopped when 10–20 ml of percolating liquid did not leave a ponderable residue after solvent evaporation. Intrinsic viscosity was determined in tetralin at 120° by a Desreux–Bischoff dilution viscometer. Optical rotation measurements were carried out by a Schmidt–Haensch Lippich polarimeter with sensitivity ±0.005°. Hydrocarbon solutions having concentrations in the range 0.5–5.0 g/dl were used.

Ir examination of polymer fractions was carried out by a Perkin-Elmer Model 221 spectrophotometer on thin films, prepared by evaporating polymer solutions, and on solutions in carbon disulfide. X-Ray diffraction patterns were obtained at room temperature with a Philips diffractometer, Model PW 1010/25.

Results

Racemic 3,7-dimethyl-1-octene was copolymerized with (*S*)-3-methyl-1-pentene in the presence of $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ or $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalyst with molar ratio (R_m) racemic monomer to optically active monomer 3.4 and 26. The sole experiment in which racemic 3-methyl-1-pentene and (*R*)-3,7-dimethyl-1-octene were used was carried out in the presence of $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ catalyst with R_m = 3.4.

In all above experiments the recovered nonpolymerized monomer B, racemic at the starting, resulted to be optically active (Table I), the optical purity being always lower than 2% for a conversion[10,11] between 20 and 35%. The optical purity of the polymerized B was comprised between 1.8 and 5.4% (Table II).

The solid polymeric products, separated from the liquid oligomers soluble in methanol, were fractionated by boiling solvents extraction.[12] In the experiments C_1, C_2, and C_3, in which racemic 3,7-dimethyl-1-octene was used, the same series of solvents (Table III) was employed as for the homopolymer of the same monomer.[13] In run C_4, carried out with racemic 3-methyl-1-pentene, the series of solvents reported in Table IV was used. The properties of the fractions obtained in the experiments with racemic 3,7-dimethyl-

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(10) F. Ciardelli, C. Carlini, G. Montagnoli, L. Lardicci, and P. Pino, *Chim. Ind.* (Milan), **50**, 860 (1968).

(11) In calculating the optical purity (P_0) of the polymerized monomer B we used the values of the total conversion as conversion of monomer B, under the assumption that the two comonomers A and B polymerize with the same rate. This is at least partially justified by the fact that polymerization rate of branched α-olefins depends mainly on the type and position of branching with respect to the double bond [see for instance ref 8 and T. W. Campbell and A. C. Haven, Jr., *J. Appl. Polym. Sci.*, **1**, 73 (1959)] and that both A and B have a methyl group in 3 position. An experimental test was till now impossible owing to the much higher volatility of 3-methyl-1-pentene with respect to 3,7-dimethyl-1-octene and mainly to the small quantity of compounds which should be used.

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

(13) P. Pino, F. Ciardelli, G. Montagnoli, and O. Pieroni, *Polym. Lett.*, **5**, 307 (1967).

TABLE II

RELATIVE POLYMERIZATION RATE OF THE TWO ANTIPODES OF SOME RACEMIC α-OLEFINS (B) IN THE PRESENCE OF OPTICALLY ACTIVE α-OLEFINS (A)

Run	Comonomers	R_m = mol of B/ mol of A	Catalyst	Conversion (C),[a] %	Optical purity of B: Nonpolymerized[b] (P_m)	Optical purity of B: Polymerized[c] (P_p)	Relative polymerizn rate[d] (R_p)
C_1	B (R)(S)-3,7-Dimethyl-1-octene A (S)-3-Methyl-1-pentene[e]	3.41	$TiCl_4$-$Zn(i\text{-}C_4H_9)_2$	21.2	1.2	4.46	1.09
C_2	B (R)(S)-3,7-Dimethyl-1-octene A (S)-3-Methyl-1-pentene[e]	26.0	$TiCl_4$-$Zn(i\text{-}C_4H_9)_2$	34.3	0.93	1.77	1.04
C_3	B (R)(S)-3,7-Dimethyl-1-octene A (S)-3-Methyl-1-pentene[e]	3.36	$TiCl_4$-$Al(i\text{-}C_4H_9)_3$	30.1	0.85	1.97	1.04
C_4	B (R)(S)-3-Methyl-1-pentene A (R)-3,7-Dimethyl-1-octene[f]	3.36	$TiCl_4$-$Zn(i\text{-}C_4H_9)_2$	24.4	1.75	5.45	1.12

[a] C = (weight of methanol-soluble polymer + weight of methanol-insoluble polymer) × 100/[starting weight of A + starting weight of B]. [b] Calculated assuming $[\alpha]^{25}\text{D}$ −16.3 and +38.1 for optically pure neat (R)-3,7-dimethyl-1-octene and (S)-3-methyl-1-pentene, respectively. [c] $P_p = P_m\,[(100 - C)/C]$. [d] $R_p = (100 + P_p)/(100 - P_p)$. [e] Optical purity, 89%. [f] Optical purity, 95%.

TABLE III

PHYSICAL PROPERTIES OF FRACTIONS OBTAINED BY EXTRACTING WITH BOILING SOLVENTS THE POLYMERIC PRODUCTS PREPARED BY COPOLYMERIZING (R)(S)-3,7-DIMETHYL-1-OCTENE WITH (S)-3-METHYL-1-PENTENE (OPTICAL PURITY 89%)

Fractions extracted successively with	C_1[a]			C_2[b]			C_3[c]		
	Wt %	$[\alpha]^{25}\text{D}$[d]	D_B 763/ D_B 732[e,f]	Wt %	$[\alpha]^{25}\text{D}$[d]	D_B 763/ D_B 732[e,g]	Wt %	$[\alpha]^{25}\text{D}$[d]	D_B 763/ D_B 732[e,g]
1 Methanol	42.0	+3.0	N.d.[h]	39.3	+0.6	N.d.[h]	14.1	+1.2	N.d.[h]
2 Acetone	16.9	+26.1	N.d.[h]	21.1	+4.2	(0.35)	8.8	+5.0	(0.53)
3 Ethyl acetate	29.7	+64.9	0.56	17.2	+14.5	0.18	11.6	+49.5	0.43
4 Diethyl ether	8.5	+38.0	0.50	10.1	+20.9	0.17	37.2	+76.0	0.55
5 Diisopropyl ether	2.9	−51.6	0.20	4.2	+21.6	0.20	2.7	+28.6	0.44
6 Cyclohexane	0			8.1	−25.2	0.12	25.6	−19.6	0.18

[a] Intrinsic viscosity in tetralin at 120° of fractions 4 and 5 was 0.93 and 0.52 dl/g, respectively. [b] Intrinsic viscosity in tetralin at 120° of fractions 4, 5, and 6 was 0.35, 0.40, and 0.70 dl/g, respectively. [c] Intrinsic viscosity in tetralin at 120° of fractions 4, 5, and 6 was 3.40, 4.20, and 6.90 dl/g, respectively. [d] In cyclohexane (c = 0.4–1.0 g/dl). [e] Base line points 670 and 892 cm^{-1}. [f] In CS_2, for the homopolymer of 3,7-dimethyl-1-octene this ratio was 0.11. [g] Film, for the homopolymer of 3,7-dimethyl-1-octene this ratio was 0.11. [h] Not determined.

TABLE IV

PHYSICAL PROPERTIES OF FRACTIONS OBTAINED BY EXTRACTING WITH BOILING SOLVENTS THE PRODUCT OF THE COPOLYMERIZATION OF (R)(S)-3-METHYL-1-PENTENE WITH (R)-3,7-DIMETHYL-1-OCTENE (OPTICAL PURITY 95%) IN THE PRESENCE OF THE $TiCl_4$-$Zn(i\text{-}C_4H_9)_2$ CATALYTIC SYSTEM

	Fractions[a]						
	1	2	3	4	5	6[b]	7[c]
Wt %	19.3	23.2	25.5	6.8	18.2	2.9	4.1
$[\alpha]^{25}\text{D}$[d]	−1.1	−43.3	−73.5	−87.7	−48.4	+27.0	N.d.[f]
$D_{B\,763}/D_{B\,732}$[e]	N.d.	1.5	1.8	2.1	2.7	4.5	N.d.

[a] Fractions 1–5 obtained by extracting with methanol, acetone, diethyl ether, diisopropyl ether and cyclohexane in that order. [b] Obtained by a second extraction with cyclohexane of the polymer, from which fractions 1–5 had been removed, previously treated with boiling decalin for 10 hr. [c] Residue to solvents extraction. [d] In cyclohexane (c = 0.5–3.0 g/dl). [e] On polymer films; base line points 700 and 892 cm^{-1}; for the homopolymer of 3-methyl-1-pentene this ratio was 13.0. [f] $[\alpha]^{25}\text{D} > 0$, measured in the solid state by suspending the powdered polymer in an acetophenone–tris-n-butylamine mixture.

1-octene and (S)-3-methyl-1-pentene are reported in Table III.

In run C_1, which was carried out using the $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ catalytic system and a rather low (3.4) molar ratio racemic monomer to optically active monomer, all the polymer was extractable with diisopropyl ether. In runs C_2 and C_3 the polymer was not completely extractable with the last solvent, but a residue, extractable with cyclohexane, was present.

The optical rotation in cyclohexane solution of the first extracted fractions is positive in all cases and increases going from the first to the third or fourth fraction, then decreases (runs C_1 and C_3) or remains practically constant (run C_2) and becomes negative for the last extracted fraction. The presence of units derived from 3,7-dimethyl-1-octene and 3-methyl-1-pentene in the fractions was tested by ir spectroscopic analysis on polymer nonoriented films or on solutions

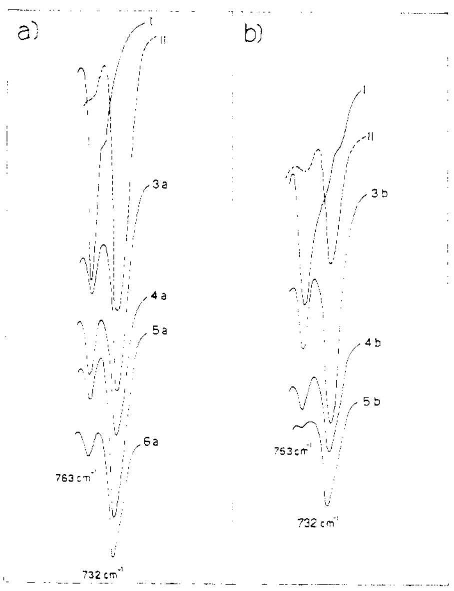

Figure 1. Infrared spectra between 700 and 800 cm^{-1} on nonoriented films (a) or on CS_2 solution (b) for I, poly-(*S*)-3-methyl-1-pentene; II, poly-(*R*)-3,7-dimethyl-1-octene; 3a, 4a, 5a, and 6a fractions extracted successively with ethyl acetate, diethyl ether, diisopropyl ether, and cyclohexane from the polymer obtained by copolymerization of racemic 3,7-dimethyl-1-octene with (*S*)-3-methyl-1-pentene using $TiCl_4$ and $Al(i\text{-}C_4H_9)_3$ (run C_3); 3b, 4b, and 5b (this fraction contained traces of silicon grease) fractions extracted successively with ethyl acetate, diethyl ether, and diisopropyl ether from the polymer obtained by copolymerization of racemic 3,7-dimethyl-1-octene with (*S*)-3-methyl-1-pentene using $TiCl_4$ and $Zn(i\text{-}C_4H_9)_2$ (run C_1).

of polymer in carbon disulfide. Poly-3-methyl-1-pentene shows in its ir spectrum a band at 763 cm^{-1} attributed to the rocking vibration of ethyl group of the side chains,[14] and poly-3,7-dimethyl-1-octene shows a band at 732 cm^{-1}, attributed to the sequence of three methylene groups[15] which are present in the side chains of the last polymer (Figures 1a and b, spectra I and II). Both bands are detectable in the infrared spectra of all copolymer fractions even if with different relative intensity (Figure 1, spectra 3a, 4a, 5a, 6a, 3b, 4b, and 5b), depending on the content of units derived from 3-methyl-1-pentene and 3,7-dimethyl-1-octene. As an index of the relative amount of both units the ratio D_B 763/D_B 732 was used (base line points 700 and 892 cm^{-1}); this ratio is 0.11 for homopolymers of 3,7-dimethyl-1-octene and 13.0 for homopolymers of 3-methyl-1-pentene. Although positive or negative optical activity indicates at least for the investigated polymers, a prevalence of *R* or *S* units,[12] respectively, the value of the optical rotation cannot give a quantitative indication of the chemical composition.

In fact the optical rotation of the above polymers depends on the content of *R* or *S* units, whatever their structure, on their relative distribution and on the stereoregularity; the same value of the optical rotation can then derive from several different possibilities.

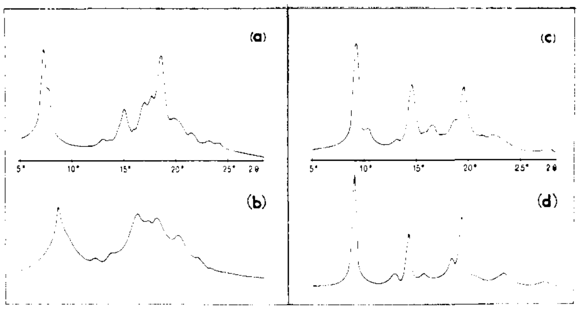

Figure 2. X-Ray powder spectra (Cu Kα) registered with a Geiger counter: (a) isotactic poly-(*R*)-3,7-dimethyl-1-octene; (b) fraction 4; and (c) fraction 7 of the polymer obtained by copolymerization of racemic 3-methyl-1-pentene with (*R*)-3,7-dimethyl-1-octene using $TiCl_4$ and $Zn(i\text{-}C_4H_9)_2$ (run C_4); (d) isotactic poly-(*S*)-3-methyl-1-pentene.

It is, however, interesting to remark that the highest value of the above optical density ratio corresponds to the highest positive optical rotation and the lowest value of the ratio was found for the last extracted fraction having negative optical activity (Table III). X-Ray powder spectra showed that fractions 3–5 of run C_1 and 3–6 of run C_2 are partially crystalline; in run C_3 only fraction 6, extracted with cyclohexane, was found to be moderately crystalline. In run C_4 which, conversely to the previous runs, was carried out using racemic 3-methyl-1-pentene and (*R*)-3,7-dimethyl-1-octene, the first four fractions have negative optical rotation in cyclohexane increasing in absolute value (Table IV). Fraction 5 has still negative rotatory power but lower, in absolute value, than fraction 4, and fraction 6 has positive optical activity. The rotatory power in solution of fraction 7 could not be determined owing to its insolubility in all tested solvents. Polarimetric investigation of a suspension of this polymer in the form of a fine powder in a mixture of acetophenone and tris-*n*-butylamine[16] indicated that, at least in the solid state, fraction 7 has positive optical activity.

The ratio D_B 763/D_B 732 in this case increases in the successively extracted fractions and reaches for fraction 6 the value of 4.5; this measurement could not be performed for fraction 7 due to impossibility to prepare nonoriented films. X-Ray powder spectra (Figure 2) indicate that fractions 3–6 are crystalline, the spectra being of intermediate type between that of isotactic poly-3,7-dimethyl-1-octene and that of isotactic poly-3-methyl-1-pentene; fraction 7 shows a X-ray diffraction spectrum practically identical with that of the crystalline isotactic homopolymer of 3-methyl-1-pentene.

Discussion

The data reported in the present paper indicate that by copolymerization, in the presence of stereospecific catalysts, of a racemic α-olefin (B) with an optically active one (A), both having structure of type I, the following main results are obtained.

(a) The recovered monomer B is optically active, the

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[14] M. C. Harvey and A. D. Ketley, *J. Appl. Polym. Sci.*, **5**, 247 (1961).

[15] J. van Schooten and S. Mostert, *Polymer*, **4**, 135 (1963).

[16] P. Pino, G. P. Lorenzi, and O. Bonsignori, *Chim. Ind.* (Milan), **48**, 760 (1966).

Table V

Fractionation with Boiling Solvents of Polymers of Racemic 3,7-Dimethyl-1-octene and of Its Copolymers with (*S*)-3-Methyl-1-pentene

Monomers	Catalytic system	Wt % of the fractions[a] 1	2	3	4	5	6
(*R*)(*S*)-3,7-Dimethyl-1-octene	$TiCl_4$–$Zn(i\text{-}C_4H_9)_2$	12.6	32.9	14.5	4.8	9.4	25.8
(*R*)(*S*)-3,7-Dimethyl-1-octene +	*b*	42.0	16.9	29.7	8.5	2.9	0
(*S*)-3-methyl-1-pentene	*c*	39.3	21.1	17.2	10.1	4.2	8.1
(*R*)(*S*)-3,7-Dimethyl-1-octene	$TiCl_4$–$Al(i\text{-}C_4H_9)_3$	∼0	4.2	9.2	14.8	34.7	37.1
(*R*)(*S*)-3,7-Dimethyl-1-octene + (*S*)-3-methyl-1-pentene	*d*	14.1	8.8	11.6	37.2	2.7	25.6

[a] Extracted successively with (1) methanol, (2) acetone, (3) ethyl acetate, (4) diethyl ether, (5) diisopropyl ether, (6) cyclohexane. [b] Run C_1. [c] Run C_2. [d] Run C_3.

antipode of B having the same absolute configuration as A being preferentially polymerized.[17]

(b) Solvent extraction of the polymeric products yields the optically active homopolymer of B, predominantly formed by units from the antipode having opposite absolute configuration to A, as well as fractions containing units from A and from the other antipode of B.

The former result demonstrates unequivocally that the process, as the polymerization of the same racemic α-olefins by optically active catalysts,[1,10] is stereoelective. According to Eliel's classification[18] the process can be defined as a "resolution by kinetic asymmetric transformation." The latter result can be explained by admitting that A copolymerizes preferentially with the antipode of B having the same chirality.

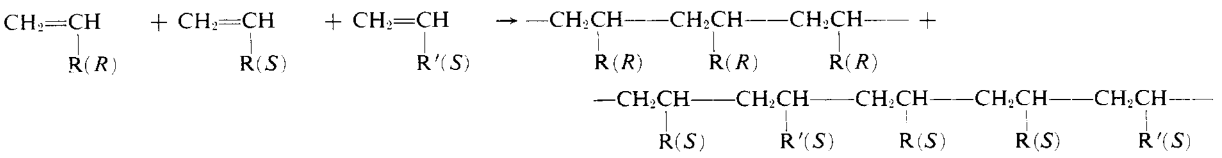
The polymeric products obtained in the copolymerization experiments are in fact extracted in larger extent than the corresponding homopolymers[4,5] with methanol, acetone, ethyl acetate, and diethyl ether (Table V). The most dramatic evidence is given by the fact that no residue to boiling cyclohexane was found in runs C_1, C_2 and C_3, thus excluding the presence of homopolymers of (*S*)-3-methyl-1-pentene which are not extractable with any solvent to more than 20%.[12]

Furthermore infrared spectroscopic analysis and optical activity measurements indicate, respectively, a different chemical and steric composition of the fractions collected in each run. The differences in steric composition are not limited to different tacticity, but consist also in different content of asymmetric carbon atoms of the side chains having *S* or *R* absolute configuration. In fact in each run fractions with positive and negative optical rotation have been obtained which therefore contain an excess of units with a *S* or *R* asymmetric carbon atom in the side chain.[12]

The same qualitative results were obtained in all experiments using a different molar ratio of comonomers or different catalysts. In runs C_1, C_2, and C_3, in which racemic 3,7-dimethyl-1-octene was used in combination with (*S*)-3-methyl-1-pentene, the first four (C_1) and five (C_2 and C_3) extracted fractions have positive optical activity and contain units from both monomers (Table III). These fractions should be mainly formed by copolymer between (*S*)-3-methyl-1-pentene and (*S*)-3,7-dimethyl-1-octene. The last fraction has negative optical rotation and contains an extremely low amount of units from (*S*)-3-methyl-1-pentene; it should be therefore predominantly formed by poly(*R*)-3,7-dimethyl-1-octene. Similar considerations can be extended to the results obtained for the copolymerization of racemic 3-methyl-1-pentene with (*R*)-3,7-dimethyl-1-octene (Table IV).

We can then conclude that the optically active comonomer [$CH_2{=}CHR'(S)$] copolymerizes preferentially with the antipode of the racemic monomer [$CH_2{=}CHR(S)$] having the same absolute configuration whereas the other antipode gives the corresponding homopolymer (Scheme I).

Scheme I



$$\underset{\mathrm{R}(R)}{\mathrm{CH_2{=}CH}} + \underset{\mathrm{R}(S)}{\mathrm{CH_2{=}CH}} + \underset{\mathrm{R'}(S)}{\mathrm{CH_2{=}CH}} \rightarrow -\underset{\mathrm{R}(R)}{\mathrm{CH_2CH}}-\underset{\mathrm{R}(R)}{\mathrm{CH_2CH}}-\underset{\mathrm{R}(R)}{\mathrm{CH_2CH}}- + -\underset{\mathrm{R}(S)}{\mathrm{CH_2CH}}-\underset{\mathrm{R'}(S)}{\mathrm{CH_2CH}}-\underset{\mathrm{R}(S)}{\mathrm{CH_2CH}}-\underset{\mathrm{R}(S)}{\mathrm{CH_2CH}}-\underset{\mathrm{R'}(S)}{\mathrm{CH_2CH}}-$$

The stereoselective character of the stereospecific polymerization of racemic α-olefins previously proposed[1,2] is therefore nicely confirmed.

Further interesting informations can be obtained from an even rough quantitative evaluation of the stereoelectivity and stereoselectivity of the process investigated.

The stereoelectivity, evaluated from the relative polymerization rate (R_p) of the two antipodes of B, seems to be higher using $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ than $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalyst as found in the polymerization of racemic α-olefins by catalysts from optically active zinc and aluminum alkyls.[10]

The stereoelectivity increases in the presence of the same catalyst (Table II) with increasing the relative amount of A, that is, decreasing R_m. This results could be interpreted considering that the asymmetric induction is mainly due to the last monomeric unit of the

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(17) 3,7-Dimethyl-1-octene with negative optical activity has in fact *R* absolute configuration[9] and 3-methyl-1-pentene with positive optical activity has *S* absolute configuration [P. Pino, L. Lardicci, and L. Centoni, *J. Org. Chem.*, **24,** 1399 (1959)].

(18) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., and Kogakusha Co., Ltd., 1962, p 65.

TABLE VI
POLY-(R)-3,7-DIMETHYL-1-OCTENE OBTAINED BY COPOLYMERIZATION OF RACEMIC 3,7-DIMETHYL-1-OCTENE WITH (S)-3-METHYL-1-PENTENE

			—Homopolymer of 3,7-dimethyl-1-octene[b]—		
Run	R_m[a]	Catalyst	$[\alpha]^{25}D$[c]	Wt %[d] (W_h)	Prevalence (P_r) of R units,[e] %
C_1	3.41	$TiCl_4$–$Zn(i\text{-}C_4H_9)_2$	−51.6	3.4	27
C_2	26.0		−25.2	8.3	12
C_3	3.36	$TiCl_4$–$Al(i\text{-}C_4H_9)_3$	−19.6	30.2	10

[a] (Moles of racemic 3,7-dimethyl-1-octene)/(moles of (S)-3-methyl-1-pentene). [b] On the basis of the last fraction obtained by solvents extraction of the polymeric products (see Table III). [c] In cyclohexane. [d] Calculated[11] as [weight per cent of the fraction (Table III)][(weight of 3,7-dimethyl-1-octene + weight of (S)-3-methyl-1-pentene)/(weight of 3,7-dimethyl-1-octene)]. [e] Calculated using the rotatory power of the fraction and the curves polymer rotatory power *vs.* polymerized monomer optical purity.[13,20]

growing chain end. In fact the number of growing chain ends having an asymmetric carbon atom of a single absolute configuration in the side chain increases with increasing the amount of optically active comonomer.

This observation is, however, in contrast with the fact that the same stereoelectivity has been obtained using $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ and $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalyst (Table II) with R_m = 26 and 3.4, respectively. The contribution of the catalytic complex to the stereoelective character of the process seems therefore still actual.[19]

More complicated appears the quantitative evaluation of the dependence of stereoselectivity on the type of catalyst and on comonomers molar ratio.

The method of separation of copolymers from homopolymers, based on solvents extraction, is very simple, but also rather rough and its efficiency is certainly not very high. Furthermore the polymeric products obtained in the different experiments are different with respect to molecular weight, tacticity, and probably comonomers distribution and these factors affect remarkably the results of solvents extraction.

In the case of the copolymerization of racemic 3,7-dimethyl-1-octene with (S)-3-methyl-1-pentene a rough evaluation of the stereoselectivity obtained in the different experiments can be performed on the basis of the amount of poly-(R)-3,7-dimethyl-1-octene obtained. Considering, in substantial agreement with the infrared spectra, the fractions with negative optical activity as poly-3,7-dimethyl-1-octene, the prevalence (P_r) of R units in these fractions can be calculated using the curves polymer rotatory power *vs.* polymerized monomer optical purity.[13,20]

The data are reported in Table VI together with per cent weight (W_h) of homopolymer of 3,7-dimethyl-1-octene with respect to the polymerized amount of the same monomer[11]; they indicate that P_r and W_h are affected by both comonomers ratio and catalytic system. The differences between the $TiCl_4$–$Zn(i\text{-}C_4H_9)_2$ and $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ system, R_m being the same, appear to be too large to be attributed only to differences in efficiency of the separation of the homopolymer from the copolymer. It seems, therefore, that the catalytic complex plays an appreciable role in determining the stereoselective character of the polymerization process as proposed in previous papers.[1,19]

Further experiments as well as a more accurate quantitative analysis of the polymeric products are necessary for a better understanding of the parameters responsible of the particular steric requirements of the copolymerization of asymmetric α-olefins. This knowledge could allow an improvement of the stereoselectivity and eventually of the efficiency of the separation which are very useful in order to prepare optically active homopolymers by copolymerization of a racemic monomer with a small amount of suitable optically active comonomer.

Acknowledgment. The authors wish to express their appreciation to Professor P. Pino for many helpful and stimulating discussions and to Dr. E. Benedetti for recording and discussing infrared spectra. They wish to thank also Professor L. Porri for reading the manuscript before publication.

(19) P. Pino, *Advan. Polym. Sci.*, **4**, 393 (1965).
(20) F. Ciardelli, G. Montagnoli, O. Pieroni, D. Pini, and P. Pino, to be published.

Notes

On the Definition of a Permeability Function

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Received February 6, 1969

Permeation through membranes is normally described by a permeability coefficient, which is calculated by measuring the flux across the membrane and dividing this by the mean pressure gradient. Although this coefficient is the most useful representation of permeation where solubility behavior follows Henry's law and the diffusion coefficient is concentration independent, it has some drawbacks in more complex situations. A permeability coefficient is a lumped-parameter description of the permeation process, since it ignores the different local processes which contribute to the over-all phenomenon. In contrast the diffusion coefficient and the solubility coefficient form a distributed-parameter description, since they describe the