Stereoelective Copolymerization: A New Method for Preparing Optically Active Polymers

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ON copolymerization of racemic 3,7-dimethyloct-1-ene and (*S*)-3-methylpent-1-ene (optical purity 89%) with the stereoselective[1] catalyst system obtained from $TiCl_4$ and $ZnBu^{i}_{2}$, we have found that the (*S*)-3-methylpent-1-ene molecules are incorporated selectively in the macromolecules which contain predominantly units derived from (*S*)-3,7-dimethyloct-1-ene.

By extracting the product successively with boiling acetone, ethyl acetate, and ether, fractions have been obtained (Table) which have positive optical activity and which contain an appreciable amount of units derived from (*S*)-3-methylpent-1-ene (Figure 1C, Figure 1D). The fraction which is soluble in di-isopropyl ether but insoluble in diethyl ether has been shown by infrared examination (Figure 1E) to be substantially poly-3,7-dimethyloct-1-ene. As the fraction has a high negative rotatory power, it must contain principally (*R*)-3,7-dimethyloct-1-ene units.[2]

The non-polymerized 3,7-dimethyloct-1-ene has a slight negative optical activity (optical purity: 1·2%) showing that the antipode of the racemic monomer having the same absolute structure as the optically active comonomer is preferentially polymerized.

The most reasonable explanation of the last result is the formation of stereoelective catalytic centres, the isobutyl group originally bound to the catalyst being at least partially displaced by the optically active comonomer [Reaction (**1**)].

In order to test whether catalysts containing 3-methylpentyl groups are stereoelective some experiments have been carried out using catalyst prepared from $TiCl_4$ with bis-[(*S*)-3-methylpentyl]-zinc of high optical purity ($\sim$93%).[3]

This catalyst has a stereoelectivity comparable (conversion: 32·6%; optical purity of recovered (*R*)-3,7-dimethyloct-1-ene 2·1%) to that of the catalyst prepared from $TiCl_4$ and bis-[(*S*)-2-methylbutyl]zinc[4]; working with very high ($\sim$7) monomer : ZnR_2 molar ratios, small amounts of (*S*)-3-methylpent-1-ene have been detected in the

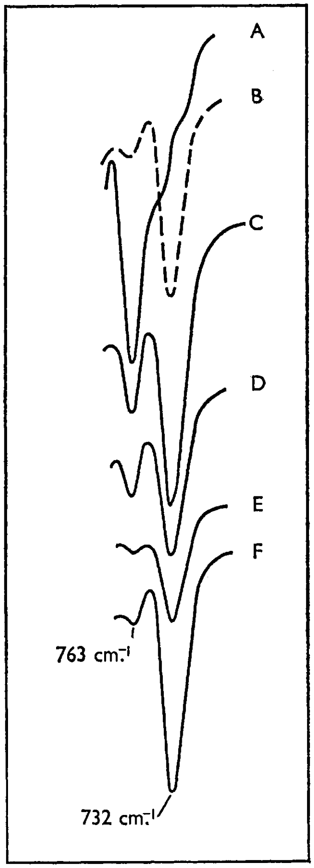

FIGURE 1

i.r. Spectra in CS_2 solution 700—800 cm.$^{-1}$ for: (A) *Poly-*(S)-3-*methylpent*-1-*ene;* (B) *Poly-*(R)-3,7-*dimethyloct*-1-*ene;* (C) *Ethyl acetate-soluble, acetone-insoluble,* (D) *Diethyl ether-soluble, ethyl acetate-insoluble, and* (E) *Di-isopropyl ether-soluble,* diethyl ether-insoluble fraction of polymer obtained by copolymerisation of* (S)-3-*methylpent*-1-*ene with racemic* 3,7-*dimethyloct*-1-*ene, using $TiCl_4$ and $ZnBu^{i}_{2}$;* (F) *Cyclohexane-soluble, di-isopropyl ether-insoluble fraction of the polymer obtained by polymerisation of racemic* 3,7-*dimethyloct*-1-*ene, using $TiCl_4$ and bis-*[(S)-3-*methylpentyl*]*zinc.*

* *This fraction contains traces of silicone grease.*

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[1] P. Pino, F. Ciardelli, G. Montagnoli, and E. Benedetti, Paper presented at the Meeting of the Sections of the National Centre of Macromolecular Chemistry of C.N.R., Varenna (Italy), 1964, *Ricerca Sci.*, in press.

[2] P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, *Makromol. Chem.*, 1963, **61**, 207.

[3] L. Lardicci and L. Lucarini, *Ann. Chim. (Italy)*, 1964, **54**, 1233.

[4] P. Pino, F. Ciardelli, and G. P. Lorenzi, *Makromol. Chem.*, 1964, **70**, 182.

purified non-polymerized monomer, which could arise either from the decomposition of the catalyst accompanied by hydride formation[5] or from the reaction [**2**] analogous to reaction [**1**].

$$\{\text{Cat}\}\text{—CH}_2\cdot\text{CHMe}_2 + \text{CH}_2\text{=CH—}^{*}\text{CH(Me)(Et)}$$
$$\rightarrow \{\text{Cat}\}\text{—CH}_2\cdot\text{CH}_2\text{—}^{*}\text{CH(Me)(Et)} + \text{CH}_2\text{=CMe}_2 \qquad (\mathbf{1})$$

$$\{\text{Cat}\}\text{—CH}_2\cdot\text{CH}_2\text{—}^{*}\text{CH(Me)(Et)} + \text{CH}_2\text{=CH}\cdot\text{CHMe}\cdot(\text{CH}_2)_3\cdot\text{CHMe}_2$$
$$\rightarrow \{\text{Cat}\}\text{—CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot(\text{CH}_2)_3\cdot\text{CHMe}_2 + \text{CH}_2\text{=CH—}^{*}\text{CH(Me)(Et)} \qquad (\mathbf{2})$$

Owing to the (*S*)-3-methylpent-1-ene present in solution, the stereoelective copolymerization takes place also in this case.

In fact, the acetone-, ethyl acetate-, and diethyl ether-soluble fractions have positive rotatory power, increasing in the above order, the di-isopropyl ether-soluble fraction has also positive rotatory power but lower than the preceeding one and the di-isopropyl ether-insoluble, cyclohexane-soluble fraction has a high negative rotatory power (Table 1) and consists of practically pure poly-3,7-dimethyloct-1-ene (Fig. 1F) having a large prevalence of (*R*)-asymmetric carbon atoms in the lateral chains.

TABLE

Rotatory powers of the fractions extracted by boiling solvents from the products obtained copolymerizing (R)(S)-3,7-*dimethyl-oct*-1-*ene with* (S)-3-*methylpent*-1-*ene* (*a*) *and polymerizing* (R)(S)- *and* (R)-3,7-*dimethyl-oct*-1-*ene* (*b*)

Monomer	(*R*)(*S*)-3,7-dimethyl-oct-1-ene[c] + (*S*)-3-methylpent-1-ene		(*R*)(*S*)-3,7-dimethyloct-1-ene[d]		(*R*)-3,7-dimethyloct-1-ene[e]	
Catalyst	$\text{TiCl}_4\text{–ZnBu}^{\text{i}}_2$		$\text{TiCl}_4\text{–Zn[CH}_2\cdot\text{CH}_2{}^{*}\text{CH(Me)(Et)]}_2$		$\text{TiCl}_4\text{–ZnBu}^{\text{i}}_2$	
	%	$[\alpha]^{25}_{\text{D}}$ [f]	%	$[\alpha]^{25}_{\text{D}}$ [f]	%	$[\alpha]^{25}_{\text{D}}$ [g]
Acetone-sol. fraction	29·2	+26·1	16·9	+8·6	18·3	−15·3
Acetone-ins., ethyl acetate-sol. fraction	51·1	+64·9	24·5	+19·7	16·0	−54·4[f]
Ethyl acetate ins., diethyl ether-sol. fraction	14·6	+38·0	21·2	+33·7	11·3	−74·3
Diethyl ether-ins., di-isopropyl ether-sol. fraction	5·1	−51·6	29·0	+21·3	11·9	−79·5
Di-isopropyl ether-ins., cyclohexane-sol. fraction	0	—	8·4	−70·3	42·5	−92·5

(a) Monomer optical purity: 89%; (b) Monomer optical purity: 95%; (c) Moles: (*S*)-3-methylpent-1-ene: $0{\cdot}61 \times 10^{-2}$, (*R*)(*S*)-3,7-dimethyloct-1-ene: $2{\cdot}08 \times 10^{-2}$, ZnBu^{i}_2: $3{\cdot}35 \times 10^{-3}$, TiCl_4 $1{\cdot}06 \times 10^{-3}$; (d) Moles: (*R*)(*S*)-3,7-dimethyloct-1-ene: $2{\cdot}58 \times 10^{-2}$, $\text{Zn[CH}_2\cdot\text{CH}_2{}^{*}\text{CH(Me)(Et)]}_2$: $4{\cdot}17 \times 10^{-3}$, TiCl_4: $1{\cdot}39 \times 10^{-3}$; (e) Moles: (*R*)-3,7-dimethyloct-1-ene: $1{\cdot}46 \times 10^{-2}$, ZnBu^{i}_2: $2{\cdot}4 \times 10^{-3}$, TiCl_4: $1{\cdot}02 \times 10^{-3}$; (f) In cyclohexane, (g) In toluene.

From the above results the following conclusions can be drawn:

(i) it is possible to prepare optically active polymers of rather high optical purity from racemic monomers using small amounts of optically active comonomers;

(ii) stereoelective catalysts can be prepared from organometallic compounds containing alkyl groups with an asymmetric carbon atom either in the β-[4] or in the γ-position with respect to the metal atom;

(iii) the low stereoelectivity[4] found up to now in the polymerization of the racemic α-olefins might be due, at least in part, to displacement reactions of type [**2**].

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[5] G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, and M. Peraldo, *Chimica e Industria*, 1956, **38**, 124.