Difference in propagation profiles between isotactic and atactic polymerizations with Ziegler–Natta catalysts

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Polymerizations of propene and 1-hexene were conducted with two sets of catalyst systems with completely different stereospecificity: aspecific catalyst, $TiCl_3/MgCl_2/Al_2(C_2H_5)_3Cl_3/Al(C_2H_5)_3$ (solid) and Cp_2ZrCl_2/MAO (soluble); isospecific catalyst, Solvay type $TiCl_3/Cp_2Ti(CH_3)_2$ (solid) and *rac*-$Et[IndH_4]_2ZrCl_2$/MAO (soluble). The molecular mass distributions (MMDs) of both oligomers and high polymers obtained with these catalysts were measured by mass spectrometer and g.p.c. The pattern of oligomer distributions was found to be markedly different between the aspecific and isospecific catalysts. The aspecific catalyst gave a continuous distribution in a wide mass range, whereas the isospecific catalyst gave a discontinuous distribution, i.e. oligomers having more than 10–20 monomer units could not be detected. On the other hand, short periods of polymerization gave high polymers, the MMDs of which did not change so much with increasing the polymerization time. These results suggest that atactic polymerization proceeds steadily while the propagation rate of isotactic polymerization becomes very fast after the polymer chains grow to a critical number of monomer units (10–20).

(Keywords: Ziegler–Natta catalyst; aspecific; isospecific; propagation rate; oligomer distribution; helix conformation)

INTRODUCTION

In olefin polymerizations with Ziegler–Natta catalysts, isotactic polymerization usually proceeds faster than atactic polymerization[1–3]. However, the precise reason for such a difference in propagation rate has not yet been clarified, probably due to the complexities arising from the heterogeneity of active species. For example, even recent commercial catalysts contain appreciable amounts of aspecific centres.

We have succeeded in preparing both very highly isospecific and completely aspecific solid catalysts[4,5]. Kaminsky *et al.*[6] have also developed excellent homogeneous catalysts which completely differ in stereospecificity. We have thus carried out the polymerization of propene and 1-hexene using these catalyst systems and analysed the oligomers and high polymers in detail. It was found that the profile of oligomer distributions is strongly dependent upon the catalyst stereospecificity.

EXPERIMENTAL

Materials

1-Hexene (Tokyo Kasei Chemical Co.) was distilled over CaH_2 and stored under nitrogen. Propene (Mitsubishi Petrochemical Co.) was purified by passing through NaOH and P_2O_5 columns. $MgCl_2$, $TiCl_4$ (Toho Titanium Co.) and $TiCl_3$ (Solvay type, Showa Denko Co.) and methylaluminoxane (MAO, $M_n = 890$, Tosoh Akzo Co.) were used without further treatment. Ethylenebis(tetrahydroindenyl)zirconiumdichloride ($Et(IndH_4)_2$-$ZrCl_2$) was prepared according to the literature[7]. Bis(cyclopentadienyl)titanium dimethyl ($Cp_2Ti(CH_3)_2$) was prepared by reacting bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) with a slight excess of methyl lithium, dissolved in diethyl ether at −20°C under nitrogen atmosphere. After the temperature was raised to 0°C, the reaction mixture was hydrolysed with cold deaerated water. The organic layer was separated, dried over sodium sulphate, and the solvent was removed by distillation *in vacuo* to give orange $Cp_2Ti(CH_3)_2$ crystals. The aspecific $TiCl_3 \cdot 3py$ (py = pyridine)/$MgCl_2$ catalyst was prepared according to the same procedures as described previously[5].

Polymerization

Polymerization of 1-hexene was carried out at 0°C using heptane as solvent in a 100 cm^3 glass reactor equipped with a magnetic stirrer. Polymerization of propene was carried out in a 100 cm^3 autoclave provided with a magnetic stirrer. Solvent, catalyst, monomer and cocatalyst were added in this order. After completion of polymerization the products were repeatedly washed with excess H_2O/HCl solution using a dropping funnel and dried *in vacuo*. Isotactic polymerization of propene was terminated by adding a dilute hydrochloric acid solution in methanol. The polymer produced was washed with methanol and dried *in vacuo* at 60°C.

Measurements

Mass spectra of oligomers were recorded at ambient temperature with a Hitachi M-80 double focused mass spectrometer equipped with a field desorption ionizer.

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Molecular ions were continuously recorded and processed by a Hitachi M-003 data system. Molecular mass distributions (MMDs) of poly(1-hexene) and atactic polypropylene were determined by g.p.c. (Shimadzu HIC 6A) with polystyrene gel columns (Shodex KF-802, KF-80M) using chloroform as solvent at 40°C. The MMD of isotactic polypropylene was measured at 145°C by g.p.c. (Waters 150C) using *o*-dichlorobenzene as solvent. ^{13}C n.m.r. spectra of the products were recorded at 120°C on a Jeol GX-270 n.m.r. spectrometer operating at 67.8 MHz. Polymers were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (9/1 in volume) up to 10 wt%. The X-ray diffraction patterns of polymers were obtained with an X-ray diffractometer (Casio RAD-B, Rigaku C.) in the range of 2θ between 6 and 40°.

RESULTS AND DISCUSSION

Heterogeneous catalyst systems

Poly(1-hexene), even when highly isotactic with high molecular weight, is easily soluble in the usual organic solvents, whereas isotactic polypropylene is insoluble. For this reason we started with 1-hexene polymerization. Polymerization of 1-hexene was performed in heptane solvent at 0°C using the highly isospecific (Solvay type $TiCl_3$–$Cp_2Ti(CH_3)_2$) and completely aspecific ($TiCl_3 \cdot 3py/MgCl_2/Al(C_2H_5)_3$) catalyst systems. After a given time of polymerization, the catalyst was deactivated by adding methanol. An excess amount of H_2O/HCl solution was added to the reactor to dissolve the catalyst residue, and the mixture was agitated. The organic layer was then separated using a dropping funnel and evacuated to remove heptane, methanol and unreacted monomer. The residues were analysed by mass spectrometer and g.p.c.

Figure 1 shows the mass spectra of oligo(1-hexene) obtained by polymerization for 5 min. Appreciable amounts of high polymers were already formed at this time, as shown in *Table 1*. In the case of atactic polymerization (*Figure 1a*), the ion fragments (m/z) appeared continuously in a very wide range, where each main m/z value was observed to be higher than that of the corresponding oligo(1-hexene) by 30 (equivalent to the total mass of C_2H_5 and H). It may be said, therefore, that atactic polymerization proceeds steadily via the insertion of 1-hexene monomer into the Ti–C_2H_5 bonds. On the contrary, oligomers having more than approximately 10 monomer units could not be detected in the case of isotactic polymerization (*Figure 1b*), suggesting that isotactic propagation starts to proceed very rapidly after the polymer chains grow to approximately 10 monomer units. The precise reason why so many fragments were observed in this case is not clear, but it might be plausible to speculate that the isotactic polymer is more liable to decomposition. Each main m/z value in this case agreed with the corresponding oligomer's mass, which might be closely related to the appearance of many fragments. These profiles of oligomer distributions remained unchanged even when the polymerization time was increased to 10 and 30 min. *Table 1* shows the analytical results for high polymers. With increasing the polymerization time, the polymer yield increased without changing the MMD. The number average molecular weights determined by g.p.c. were approximately 2.2×10^5 and 1.2×10^5 for isotactic and atactic polymers. These values may be statistically regulated by the ratio of propagation and transfer rate constants.

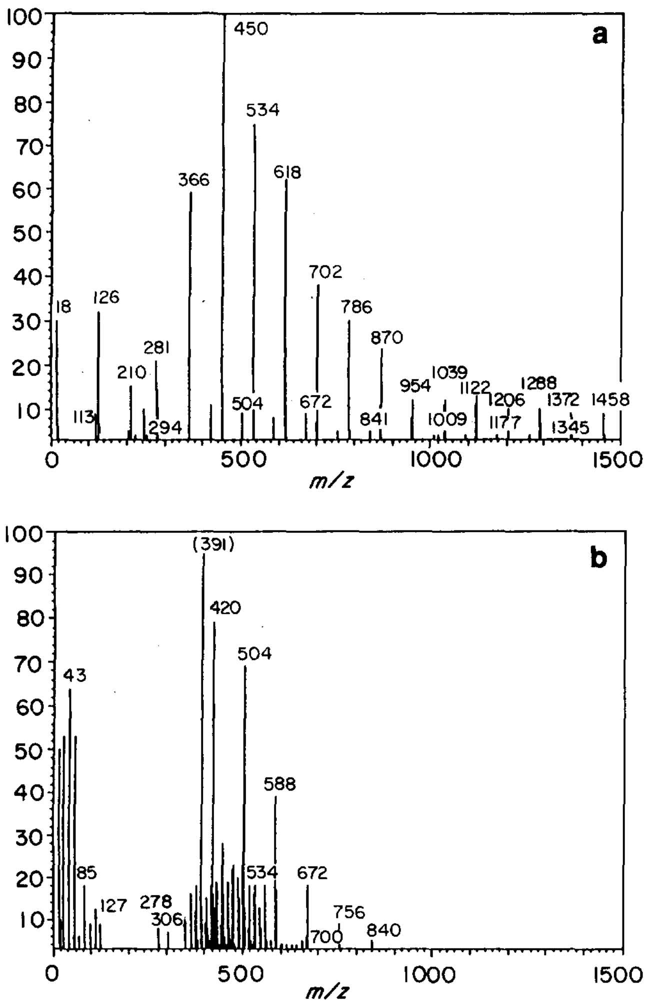

Figure 1 Mass spectra of poly(1-hexene). Polymerization conditions: [1-hexene] = 0.2 mol l^{-1}, [cocatalyst] = 10 mmol l^{-1}, heptane = 100 cm^3, 0°C, 5 min. (a) $TiCl_3/MgCl_2$ (1.26 g; 0.03 wt% Ti)/$Al(C_2H_5)_3$ catalyst; (b) Solvay $TiCl_3$ (0.08 g)/$Cp_2Ti(CH_3)_2$ catalyst

Table 1 Results of 1-hexene polymerization[a] with heterogeneous catalyst systems

Catalyst system	Reaction time (min)	Conversion[b] (%)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$
Solvay type,	5	2	222000	2.2
$TiCl_3/Cp_2TiMe_2$	10	4	218000	2.6
(highly isospecific)	30	11	218000	3.6
$TiCl_3/MgCl_2/AlEt_3$	5	4	125000	1.8
(aspecific)	30	18	123000	1.9

[a] Polymerization conditions as in *Figure 1*
[b] Including oligomers
[c] For high polymers, calculated by polystyrene

From the ^{13}C n.m.r. analysis, the [*mmmm*] pentad fractions were estimated to be approximately 0.45 and 0.98 for the polymers produced with aspecific and isospecific catalysts, respectively.

Homogeneous catalyst systems

Polymerization of 1-hexene was first performed at 0°C in toluene using both isospecific ($Et[IndH_4]_2ZrCl_2$/MAO) and aspecific (Cp_2ZrCl_2/MAO) homogeneous

Table 2 Results of 1-hexene polymerization[a] with homogeneous catalyst systems

Catalyst system	Reaction time (min)	Conversion[b] (%)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$
Et $[IndH_4]_2ZrCl_2$	5	0.7	17 300	1.4
/MAO	10	2.6	16 800	1.7
(isospecific)	60	7.8	18 100	1.9
Cp_2ZrCl_2	2	1.2	2200	1.5
/MAO	5	1.6	2300	1.4
(aspecific)	10	3.6	2300	1.4

[a] Polymerization conditions: [1-hexene] = 0.67 mol l^{-1}, toluene = 100 cm^3, [catalyst] = 3×10^{-4} mol l^{-1}, Al/Zr = 1700, 0°C

[b] Including oligomers

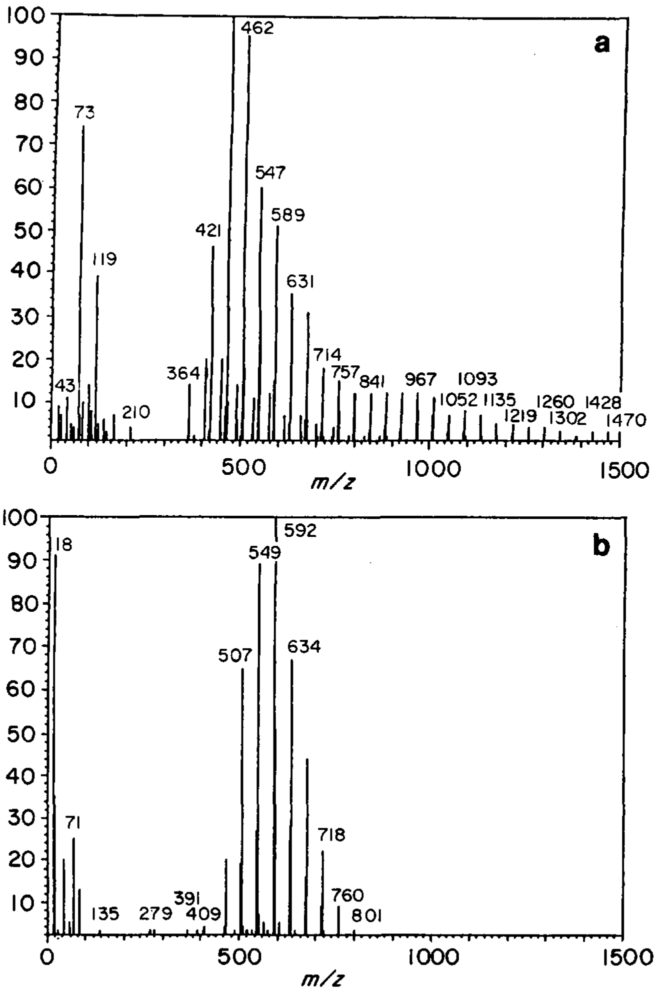

Figure 2 Mass spectra of polypropylene. Polymerization conditions: propene = 7 dm^3, toluene = 50 cm^3, [catalyst] = 1.5×10^{-4} mol l^{-1}, Al/Zr = 1700, 0°C, 5 min. (a) Cp_2ZrCl_2/MAO catalyst; (b) $Et[IndH_4]_2ZrCl_2$/MAO catalyst

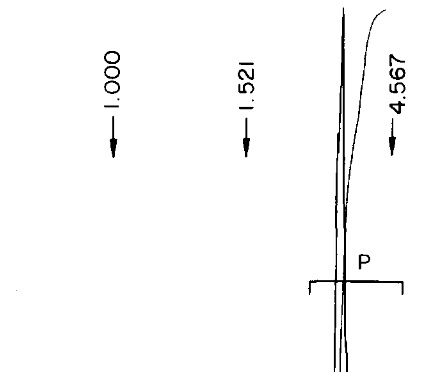

Figure 3 ^1H n.m.r. spectrum of the propene oligomers soluble in boiling methanol. Propene = 7 dm^3, toluene = 50 cm^3, $[Et[IndH_4]_2ZrCl_2]$ = 1.5×10^{-4} mol l^{-1}, Al/Zr = 1700, 0°C, 5 min

catalyst systems. The fractions of *meso* diad in atactic and isotactic polymers estimated from the ^{13}C n.m.r. spectra were 0.20 and 0.96, respectively. The ion fragments (m/z) of the oligomers produced with the aspecific catalyst appeared continuously in a wide range, each value of which agreed well with the corresponding oligomers. In the case of isotactic polymerization, on the other hand, peaks corresponding to the oligomers above 14 monomer units could not be detected. Although the critical value (14) was slightly higher than that (10) observed in the heterogeneous isospecific catalyst, the results obtained in the homogeneous systems also lead us to believe that isotactic polymerization proceeds rapidly after the polymer chains grow to the critical monomer sequence.

Table 2 shows the changes in polymer yield and molecular weight with polymerization time, again indicating that molecular weights of both atactic and isotactic polymers remain almost unchanged.

Polymerization of propene was then performed at 0°C for 5 min with these homogeneous catalyst systems. In the case of atactic polymerization, an excess amount of HCl/H_2O solution was added to the reaction mixture and the aqueous and organic layers were separated using a dropping funnel. The organic layer was evacuated at 40°C for 30 min using a rotary evaporator, followed by further drying *in vacuo* at 60°C for 8 h. The viscous products thus obtained were analysed by mass spectrometry and g.p.c.

In the case of isotactic polymerization, on the other hand, an excess amount of HCl/methanol solution was added to the reaction mixture. After stirring for 10 h at room temperature, the precipitates obtained were separated by filtration and extracted with boiling methanol.

Figures 2a and *2b* display the mass spectra of oligo(propene) obtained with the aspecific catalyst (whole products) and that produced with the isospecific catalyst (part soluble in boiling methanol), respectively. The ion fragments (m/z) of atactic oligomers (*Figure 2a*) appeared continuously in a wide range while those of isotactic ones (*Figure 2b*) showed a discontinuous distribution. The fraction soluble in boiling methanol obtained with the isospecific catalyst was further analysed by ^1H n.m.r. and X-ray. *Figure 3* shows the ^1H n.m.r. spectrum of the part soluble in boiling methanol. According to Pino *et al.*[8], the peaks appearing above 1.45 (T) and below 0.98 ppm (P) can be assigned to the methyne protons and methyl protons + one methylene proton of isotactic propene units. The ratio of P/T in

Figure 3 was estimated to be approximately 4.57, indicating that the isotacticity index defined by Pino *et al.*[8] is very high (~100%).

It is well known that common isotactic polypropylene displays strong absorption peaks at $2\theta = 14.0°$, $17.0°$, $18.5°$ and $21.2°$. The parts both soluble and insoluble in boiling methanol were analysed by X-ray. The insoluble part clearly showed those peaks (crystallinity = 62%)[9], whereas in the soluble part the corresponding peaks were barely detectable. Therefore, it may be assumed that the oligo(propene) obtained with the isospecific catalyst is isotactic but has no crystallinity.

As is well known, the most favoured conformation of isotactic polyolefins is a helix of the type 3_1, 7_2 or 4_1, which develops simultaneously with the growth of the polymer chain[10,11]. It may be plausible to consider that such a helical conformation is formed when the polymer chains grow to a critical number of monomer units. There might be a correlation between the above observation and this speculation. Although much additional data are necessary to predict the precise mechanism of polymerization, the present results may suggest different profiles for atactic and isotactic polymerizations:

Atactic polymerization

$M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow \cdots \rightarrow M_n$ (high polymer)

(each propagation step proceeds steadily)

Isotactic polymerization

$M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow \cdots M_k \longrightarrow M_n$ (high polymer)

(propagation is accelerated when the chains grow to the critical number of monomer units, M_k)

Similar phenomena have been found by Hatada *et al.* in the syndiotactic polymerization of triphenylmethyl methacrylate[12]. They have speculated that the propagation reaction is accelerated by the helical structure, which formed after the polymer chains grew to 7–9 monomer units.

The present results may also be explained in terms of the same mechanism. However, the precise reason for such an enhancement in the isotactic propagation is still open to discussion.

A more detailed study is now in progress and the results will be reported in a future publication.

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