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Molecular Weight and Tacticity Fractionations in Successive Extraction of Highly Isotactic Polypropylene with *n*-Alkane Solvents

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ABSTRACT: The highly isotactic polypropylene prepared with a δ-$TiCl_3/Et_2AlCl$ catalytic system was fractionated by successive extraction with *n*-alkane solvents. The pentad tacticities in the respective fractions and the whole polymer were determined from the ^{13}C NMR spectra. A mechanism of stereospecific polymerization was statistically analyzed from the values of pentad tacticities on the basis of the two-site model, in which at one site (APP site) polymerization proceeds according to the Bernoullian model of selection between meso and racemo configurations and at the other site (IPP site) according to selection between dextro and levo. Further, molecular weights of the respective fractions and the whole polymer were measured. From these results, it was indicated that both molecular weight and tacticity fractionations occur for the isotactic polymer produced at the IPP site and molecular weight fractionation mainly occurs for the atactic polymer produced at the APP site in the successive extraction. Also indicated was that the number-average molecular weight of the isotactic polymer is much larger than that of the atactic polymer. This suggests that the ratio rate of the propylene propagation reaction/rate of the chain transfer reaction at the IPP site is much larger than that at the APP site.

Introduction

Polypropylenes having high crystallinity can be prepared with stereospecific Ziegler–Natta catalytic systems. It is well-known that the less crystalline polymer can be removed by a suitable extraction. It is possible to isolate fractions having different melting points (106–175 °C) and crystallinities (15–66%) by the extractions with different *n*-alkane solvents.[1] Nakajima et al.[2] fractionated polypropylene by extraction with boiling hydrocarbons with different boiling points and confirmed that the respective polymer fractions have different molecular weights and isotacticities. Their results suggest that the tacticity and molecular weight fractionations occur in the *n*-alkane extraction. Further, it has been confirmed that the respective fractions obtained with the successive extraction of polypropylenes with boiling *n*-alkane solvents have different pentad tacticities,[3-5] indicating the occurrence of the tacticity fractionation. On the basis of these previous results, Kissin[6] considered the continuous distribution of active centers with different stereoregularity.

The mechanism of stereospecific polymerization has been statistically analyzed from the values of tacticities in polypropylenes prepared with various Ziegler–Natta catalytic systems.[7-16] It has been concluded that neither Bernoullian[10] nor first-order Markovian[11] statistical models describe the polymerization mechanism of propylene except the syndiotactic sample prepared with a VCl_4–$Al(CH_3)_2Cl$–anisole catalytic system, which obeys Bernoullian statistics (polymerization proceeds through the selection between meso (*m*) and racemo (*r*)).[13] Zambelli et al.[13] and Chûjô[14] proposed the two-site model for the mechanism of propylene polymerization, in which at one site polymerization proceeds according to the Bernoullian model of selection between meso and racemo configurations (symmetric model) and at the other site (IPP site) according to selection between dextro (*d*) and levo (*l*) (asymmetric

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model).[17] The applicability of the two-site model for atactic and isotactic polypropylenes has been confirmed from the good correspondence between the observed and calculated fractions of the respective pentad stereoisomers by Chûjô et al.[15,16] Their results indicate that the asymmetric model corresponds to a site (IPP site) producing highly isotactic polypropylene and the symmetric model to a site (APP site) producing atactic polypropylene. Heptad configurational analysis of isotactic polypropylene also supports the reasonableness of the two-site model for the propylene polymerization mechanism.[9]

Therefore, the fractionation of polypropylene by the extraction with boiling *n*-alkane solvents should be separately investigated for the isotactic and atactic polymers. However, the details of the fractionation behavior, that is, whether the tacticity fractionation, or molecular weight fractionation, or both fractionations occur in the boiling *n*-alkane extraction of polypropylene, have never been investigated from the viewpoint of the two-site polymerization mechanism.

In this study, highly isotactic polypropylene prepared with a δ-$TiCl_3/Et_2AlCl$ catalytic system in the presence of hydrogen is fractionated by successive extraction with boiling *n*-hexane, *n*-heptane, and *n*-octane. The pentad tacticities in the respective fractions and the whole polymer are determined from the ^{13}C NMR spectra. The molecular weight of each fraction is determined from the ^{13}C NMR spectra and from the chromatograms of gel permeation chromatography. The polymerization mechanism is analyzed from the pentad tacticities on the basis of the two-site model. From these results, detailed fractionation behavior of the isotactic and atactic polymers (defined by the two-site model) in the successive extraction is discussed. Further, the number-average molecular weights and molecular weight distributions of the isotactic and atactic polymers are evaluated through the analysis of molecular weight and tacticity fractionations of the highly isotactic polypropylene.

Experimental Section

Materials and Fractionation. The highly isotactic polypropylene (PP) prepared with the δ-$TiCl_3/Et_2AlCl$ catalytic system was donated by Tokuyama Soda Co., Ltd. The polymerization was carried out at 65 °C for 2 h in the presence of molecular hydrogen in a slurry process. Propylene monomer was used as a solvent and the conversion of propylene was less than 20%. The whole polymer, PP, was fractionated by the successive extraction with boiling *n*-hexane (n-C_6), *n*-heptane (n-C_7), and *n*-octane (n-C_8), using a Soxhlet-type extractor. From ^{13}C NMR measurement, it was confirmed that PP does not contain any detectable amounts of head-to-head and tail-to-tail arranged units, referring to the study on regioirregular polypropylenes.[18-20] Thus, this polymer is suitable for the investigation of the propylene polymerization mechanism.

Molecular Weight Measurements. The weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights of PP and of high molecular weight fractions obtained by the successive extraction were determined by gel permeation chromatography (GPC) on a Waters Instrument (Model 150C) with mixed gel columns GMH-HT (10^3–10^7 pore sizes from Toso Co., Ltd.). The solvent used was *o*-dichlorobenzene and the flow rate was 1.0 $cm^3\ min^{-1}$. A molecular weight calibration curve for polypropylene was obtained on the basis of universal calibration[21,22] from the calibration curve for polystyrene determined from seven standard polystyrenes of molecular weights from 950 to 6 750 000. The number-average molecular weights of low molecular weight fractions were determined from the relative peak areas of inner methyl carbons and of the chain-end methyl carbons in the ^{13}C NMR spectra by using a curve resolution method.[12]

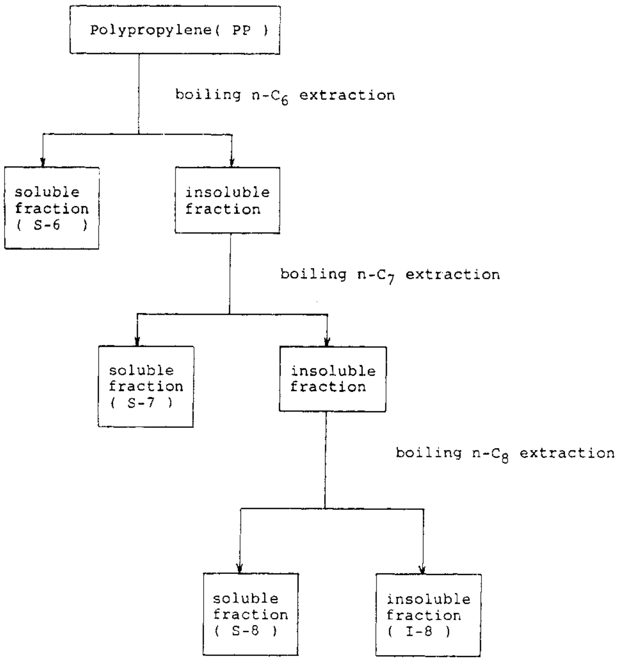


Figure 1. Scheme of successive fractionation with *n*-alkane solvents.

Table I
Weight- and Number-Average Molecular Weights of PP and the Fractions S-6, S-7, S-8, and I-8

sample	wt fractn	$\bar{M}_w/10^4$	$\bar{M}_n/10^4$	$\bar{M}_w/\bar{M}_n$
PP		30.0	4.50	6.4
S-6	0.011		0.09[a]	
S-7	0.039		0.46[a]	
S-8	0.224	18.0	2.30	7.8
I-8	0.726	42.0	8.20	6.4

[a] Determined from NMR measurements.

NMR Measurements. ^{13}C NMR spectra were recorded at 120 °C on a JEOL GSX-270 spectrometer operated at 67.8 MHz. The sample solutions in a 10-mm-o.d. glass tube were prepared in *o*-dichlorobenzene (90 vol %)/benzene-d_6 (10 vol %) to give 0.15 g (polymer) cm^{-3} (solvent). Benzene-d_6 was used for the ^2H NMR internal lock. In all measurements, broad-band noise decoupling was used to remove ^{13}C–^1H couplings, the pulse angle was 90°, and 10000 free induction decays were stored in 32K data points using a spectral window of 10 000 Hz. Hexamethyldisiloxane was used as an internal reference (2.03 ppm downfield from the resonance of tetramethylsilane). For the quantitative measurements, the pulse repetition time was set to be 25 s, which is more than five times the spin–lattice relaxation times of the most mobile methyl carbons at the chain end (4.0–4.8 s[23]).

Results and Discussion

Highly isotactic polypropylene (PP) was fractionated by successive extraction into extraction into four fractions S-6, S-7, S-8, and I-8, as shown in Figure 1. The weight fractions of these samples are shown in Table I. In Figure 2a are shown the GPC chromatograms of PP and the individual fractions. These chromatograms apparently indicate that the molecular weight increases in the order from fraction S-6 to S-7, to S-8, to I-8. In Figure 2b are shown the molecular weight calibration curves for polystyrene (1) and for polypropylene (2). The molecular weights of PP, S-8, and I-8 were determined from the GPC chromatograms by using the calibration curve for polypropylene, which were obtained on the basis of universal calibration from that for polystyrene. Unfortunately, molecular weights of S-6 and S-7 were not accurately determined from GPC measurement owing to the poor reliability of the calibration curve in the range of molecular weight less than 10^3.

According to the schemes for the formation of chain-end structures in polypropylene prepared with a δ-$TiCl_3/$

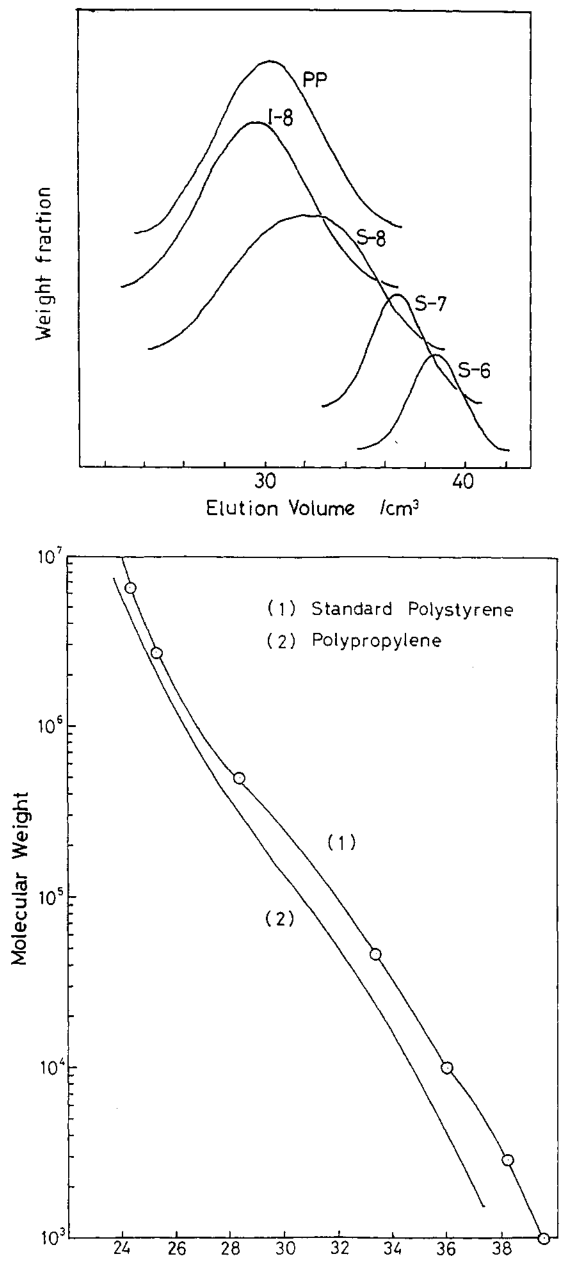
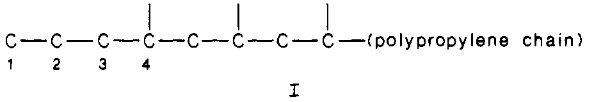


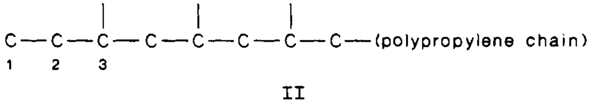
Figure 2. (a, Top) GPC chromatograms of polypropylene and fractions of the whole polymer obtained by successive extraction. (b, Bottom) Molecular weight calibration curve (1) obtained with standard polystyrenes and the calibration curve (2) for polypropylene obtained on the basis of universal calibration from (1) for polystyrene.

Et_2AlCl catalytic system in the presence of hydrogen,[24] chan-end structures I and II are produced through initiation reactions and the subsequent primary insertions of propylene.



$$\underset{1}{C}{-}\underset{2}{C}{-}\underset{3}{C}{-}\underset{4}{\overset{\displaystyle C}{\overset{|}{C}}}{-}C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}\text{(polypropylene chain)}$$

I



$$\underset{1}{C}{-}\underset{2}{C}{-}\underset{3}{\overset{\displaystyle C}{\overset{|}{C}}}{-}C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}C{-}\text{(polypropylene chain)}$$

II

The initiation reactions producing the chain-end structure I are the primary insertions of propylene monomer on a metal (M)–hydrogen (H) bond and on a M–C_3H_7 bond, which are formed by the chain-transfer reactions of propagation species to hydrogen and propylene, respectively. The initiation reaction for the formation of structure II is the primary insertion of propylene on the M–CH_2CH_3 bond, where CH_2CH_3 is derived from Et_2AlCl.

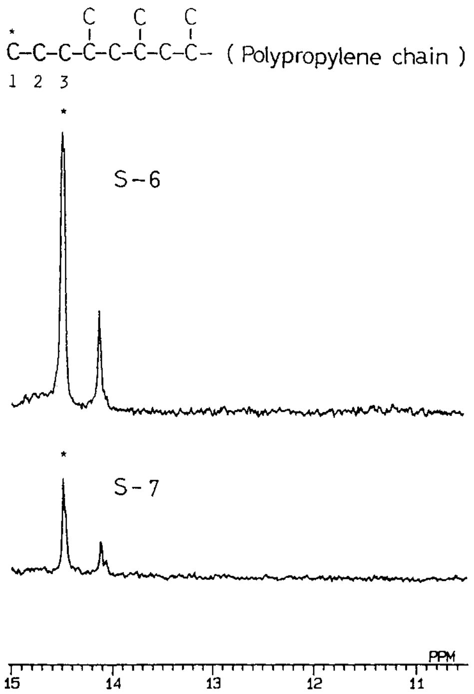


Figure 3. Chain-end methyl carbon resonance regions in the ^{13}C NMR spectra of S-6 and S-7.

In Figure 3 are shown the chain-end methyl resonance regions in the ^{13}C NMR spectra of S-6 and S-7. Referring to ^{13}C chemical shifts of the chain-end methyl carbons previously reported,[24] it is confirmed that the peaks (marked by asterisks) of the methyl carbon 1 in structure I are observed in both spectra and that no peaks are detected at 11.1 ppm, the chemical shifts of the methyl carbon 1 in structure II. Thus, the extent of the initiation reaction producing structure II is negligible under the polymerization condition in this study. This indicates that the rate of chain-transfer reactions with hydrogen and propylene monomer is much higher than that with Et_2AlCl. In Figure 4 are shown the methyl (inner methyl) resonance regions in the ^{13}C NMR spectra of PP and the fractions S-6, S-7, S-8, and I-8. Number-average molecular weights of S-6 and S-7 were determined from the relative peak areas of methyl carbon 1 in structure I and of inner methyl carbons. In Table I are shown the results of molecular weight measurements. The number-average molecular weight increases in the order from S-6, to S-7, to S-8, to I-8.

The pentad assignments of ^{13}C chemical shifts proposed by Zambelli et al.,[25] which have been confirmed from the chemical shift calculation[8,9] via the γ-effect, are shown in Figure 4. The pentad tacticities were accurately determined from the relative peak areas using a curve resolution method.[12] The determined values of pentad tacticities are shown in Table II. These values indicate that the fractions (I-8 and S-8) having higher molecular weights are more isotactic than those (S-6 and S-7) having lower molecular weights, referring to the number-average molecular weights of the fractions (Table I).

From the determined values of the pentad tacticities in PP and the fractions S-6, S-7, S-8, and I-8, the propylene polymerization mechanism was analyzed on the basis of the two-site model. The parameters of the two-site model

Table II
Pentad Tacticities of PP and the Fractions S-6, S-7, S-8, and I-8

	PP		S-6		S-7		S-8		I-8	
pentad	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
mmmm	0.925	0.928	0.208	0.216	0.454	0.455	0.895	0.894	0.951	0.952
mmmr	0.015	0.015	0.108	0.099	0.073	0.081	0.018	0.021	0.013	0.014
rmmr	0.006	0.002	0.028	0.025	0.022	0.014	0.004	0.002	0.003	0.001
mmrr	0.015	0.017	0.119	0.118	0.103	0.096	0.027	0.024	0.015	0.014
mrmm + *rmrr*	0.010	0.009	0.149	0.146	0.088	0.088	0.013	0.014	0.004	0.004
mrmr	0.002	0.003	0.032	0.049	0.018	0.027	0.002	0.004	0.001	0.002
rrrr	0.010	0.010	0.161	0.174	0.115	0.117	0.016	0.016	0.004	0.003
mrrr	0.007	0.008	0.130	0.115	0.075	0.075	0.012	0.012	0.003	0.003
mrrm	0.009	0.009	0.064	0.059	0.051	0.048	0.014	0.012	0.006	0.007
SD[a]/10^{-3}		1.886		9.843		5.497		1.886		1.054

[a] Standard deviations between the observed and calculated pentad sequence distributions.

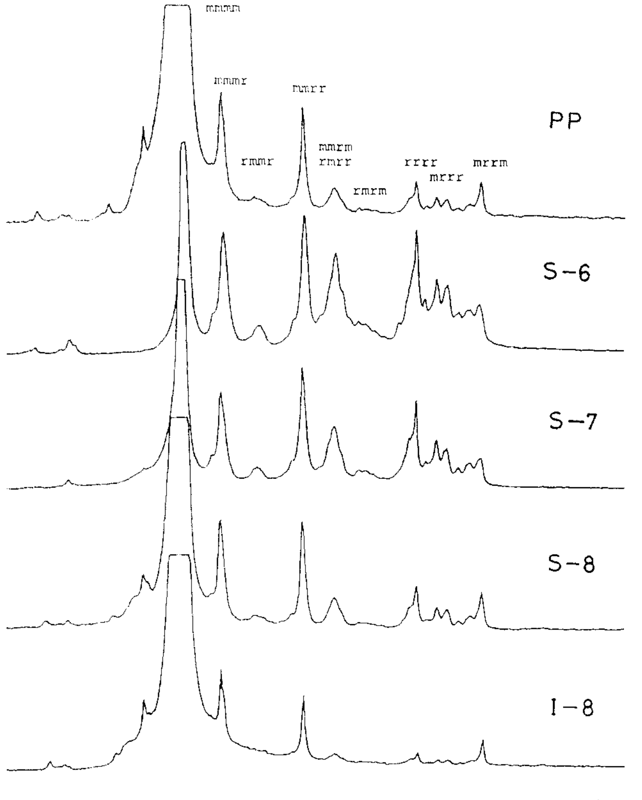


Figure 4. Methyl resonance regions in ^{13}C NMR spectra of PP and the fractions S-6, S-7, S-8, and I-8.

are as follows: α, the probability of selecting a *d* unit at a *d*-preferring site in the asymmetric model site; σ, the probability of selecting a meso dyad configuration in the symmetric model site; ω, the weight fraction of the polymer produced at the asymmetric model site. The optimum values of these parameters were determined by the nonlinear least-square method. Pentad stereosequence distributions in these samples predicted by the two-site model are shown in Table II. The calculated fractions of pentad sequences well correspond with the observed ones. Standard deviations between the observed and calculated fractions of pentads are less than 0.01. These results indicate the suitability of the two-site model for the mechanism of propylene polymerization. In Table III are shown the optimum values of the parameters. These optimum values confirm our previous conclusion[9,15,16] that the isotactic polymer is predominantly produced at the asymmetric model site (IPP site) and that the atactic polymer (strictly syndiotactic rich) is predominantly produced at the symmetric model site (APP site). Thus, the fractionation of the isotactic polypropylene in the successive extraction should be separately investigated for the isotactic and atactic polymers.

Table III
Optimum Values of the Parameters for the Two-Site Model

sample	ω	α	σ	$\bar{M}_n/10^4$
PP	0.963	0.993	0.280	4.50
S-6	0.559	0.826	0.221	0.09
S-7	0.675	0.924	0.231	0.46
S-8	0.944	0.989	0.258	2.30
I-8	0.987	0.993	0.265	8.20

Table IV
Molecular Weight and Tacticity Distributions in the Isotactic (IPP) and Atactic (APP) Polymers

	IPP			APP		
$\bar{M}_n/10^4$	w_i	w_c	Fm(I)	w_i	w_c	Fm(A)
0.09	0.006	0.006	0.712	0.125	0.125	0.221
0.46	0.027	0.033	0.860	0.325	0.450	0.231
2.30	0.220	0.253	0.978	0.325	0.775	0.258
8.20	0.747	1.000	0.986	0.225	1.000	0.265

In Table IV are shown the molecular weight and tacticity distributions in the isotactic and atactic polymers, where the respective weight fractions (w_i) in both polymers are normalized. (The respective weight fractions in the isotactic and atactic polymers were calculated by multiplying the respective weight fractions of S-6, S-7, S-8, and I-8 by ω and $(1 - \omega)$ of those and normalized to 1.0.) The fraction (Fm(A)) of meso dyad in the atactic polymer is equal to σ and that (Fm(I)) in the isotactic polymer is calculated by the following equation:

$$\mathrm{Fm(I)} = \alpha^2 + (1 - \alpha)^2$$

In Figure 5a are shown the plots of the cumulative weight fractions (w_c) of the isotactic (IPP) and atactic (APP) polymers against the number-average molecular weight. These plots clearly indicate that the molecular weight fractionation occurs in the successive extraction. In Figure 5b are shown the plots of w_c against Fm(I) and Fm(A), respectively. The isotactic polymer is fractionated into the highly isotactic (Fm(I) = 0.978 and 0.986) and relatively low isotactic (Fm(I) = 0.712 and 0.860) fractions. This indicates the occurrence of tacticity fractionation for the isotactic polymer in the successive extraction with boiling *n*-hexane and *n*-heptane. Thus, both the molecular weight and tacticity fractionations occur for the isotactic polymer in the successive extraction. The values of Fm(A) in the respective fractions of the atactic polymer are almost constant (0.221–0.265) among four fractions. This indicates that the molecular weight fractionation mainly occurs for the atactic polymer in the successive extraction.

As shown in Figure 5a, it is indicated that the low molecular weight fractions S-6 and S-7 are composed of a very

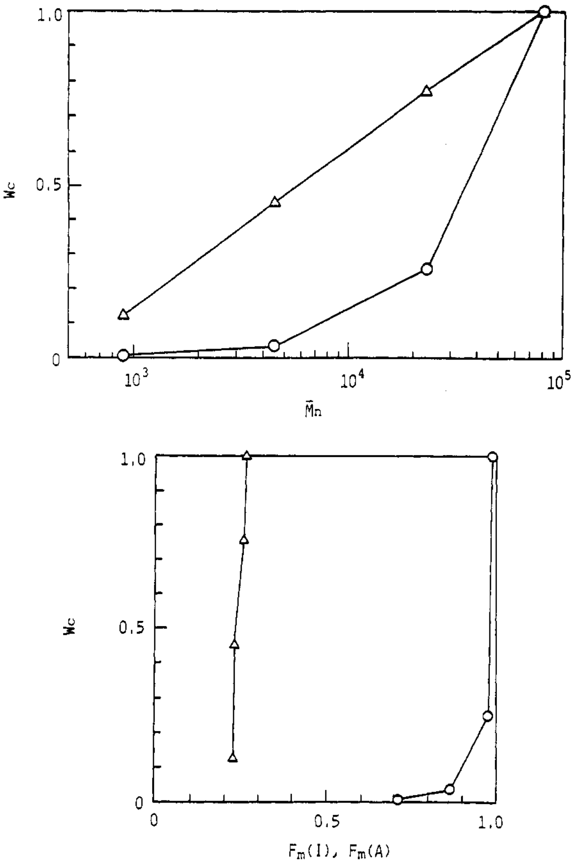


Figure 5. Plots of the cumulative weight fractions (w_c) of the isotactic (○) and atactic (△) polymers against (a, top) the number-average molecular weight and (b, bottom) the fractions (Fm(I) and Fm(A)) of meso dyad.

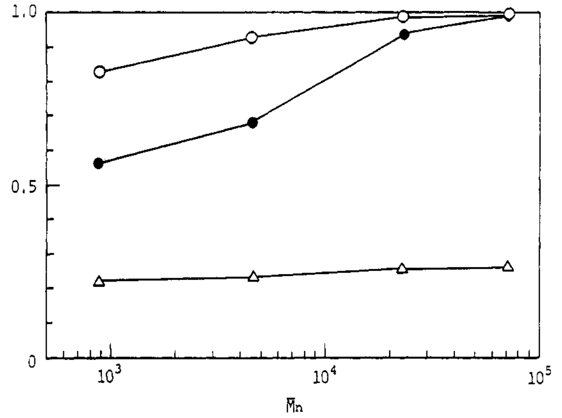


Figure 6. Molecular weight dependences of the optimum values of the parameters ω (●), α (○), and σ (△).

small portion of the isotactic polymer and of the low molecular weight fractions of the atactic polymer. Thus, the extraction of isotactic polypropylene with boiling *n*-heptane,[26-28] which has been widely used to provide the index of isotacticity, removes parts of atactic polymer and very small portions of isotactic polymer. In Figure 6 are shown the molecular weight dependence of the optimum values of the parameters. Since the values of ω in the fractions S-6 and S-7 are larger than 0.5, the amount of isotactic polymer in the *n*-heptane extract is never negligible. The content ($F(\mathrm{IPP})_{\mathrm{S7}}$) of isotactic polymer in the mixture (boiling *n*-heptane extract) of the fractions S-6 and S-7 is 0.65, which is estimated by the following equation:

$$F(\mathrm{IPP})_{\mathrm{S7}} = \frac{W_{\mathrm{S6}}\omega_{\mathrm{S6}} + W_{\mathrm{S7}}\omega_{\mathrm{S7}}}{W_{\mathrm{S6}} + W_{\mathrm{S7}}}$$

where W is the weight fraction and the subscripts S6 and S7 denote the fractions S-6 and S-7, respectively. Boiling *n*-heptane extract is not an atactic polymer but a mixture of the isotactic and atactic polymers. The content of the atactic polymer in the mixture of the fractions S-8 and I-8 is similarly calculated to be 0.044. Thus, the fraction of the whole polymer insoluble in boiling *n*-heptane is not a good estimation for the isotactic index of polypropylene.

On the basis of the molecular weight dependence of the optimum values of the parameters, the relative intensities of methyl pentad peaks in the ^{13}C NMR spectra of the respective fractions are reasonably described. As shown in Figure 3, only the isolated *rr* triads in the isotactic polypropylene sequences are detected as a stereodefect in the spectrum of the high molecular weight fraction I-8, where the peak assigned to *mmmr* pentad is attributable to *mmmmrr* heptad on the basis of heptad analysis.[9] Since the optimum value of α is 0.993, the IPP site produces only an *rr* defect. The *rr* defect is mainly produced at the IPP site and the amount of *rr* defect produced at the APP site is negligible, because the weight fraction ω of the polymer produced at IPP site is 0.987. The intensities of the methyl peaks corresponding to the *rr* defect and the other stereodefects increase in the order from S-6 to S-7, to S-8, to I-8. The decrease of the α value with the decrease of molecular weight leads to an increase of *rr* defects. The increases of the other stereodefects arise from the decrease of ω, because σ is almost constant.

As shown in Figure 5a, the molecular weight distribution in the isotactic polymer is different from that in the atactic polymer. This suggests that there exists a difference between distributions in the IPP and APP sites with respect to polymerization kinetics (rates of the propagation, termination, and initiation reactions). The number-average molecular weights of the isotactic and atactic polymers are calculated from

$$\bar{M}_{\mathrm{n}} = 1/\left(\frac{w_i}{\bar{M}_{\mathrm{n}_i}}\right) \tag{1}$$

where w_i and $\bar{M}_{\mathrm{n}_i}$ are the weight fraction and the number-average molecular weight of *i*th component. The number-average molecular weights, $\bar{M}_{\mathrm{n}}(\mathrm{I})$ and $\bar{M}_{\mathrm{n}}(\mathrm{A})$, of isotactic and atactic polymers calculated from the data listed in Table IV are 32000, and 4400, respectively (where I and A represent the isotactic and atactic polymers, respectively). The calculated value for IPP is rather small compared to the $\bar{M}_{\mathrm{n}}$ of the whole polymer. The reasons of this discrepancy are the poor reliability of the calibration curve in the range of molecular weight less than 10^3 and the very small amount of S-6, which is too small to be detected from the GPC measurement of the whole polymer. These values indicate that the number-average molecular weight of isotactic polymer produced at the IPP site is much larger than that of atactic polymer produced at the APP site.

According to the basic kinetics of propylene polymerization,[29-31] the number-average degree ($\bar{P}_{\mathrm{n}}$) of polymerization of polypropylene produced during stationary polymerization is expressed by

$$\bar{P}_{\mathrm{n}} = \frac{R_{\mathrm{p}}}{R_{\mathrm{t}} + R_{\mathrm{tr}}} \tag{2}$$

where R_{p} is the rate of the propagation reaction, R_{t} is the rate of the termination reaction, and R_{tr} is the rate of the chain-transfer reaction.

Since the polymerization rate is very high because of the extremely high concentration of propylene (propylene was used as a solvent), the chain-end structure II is not detected in the spectra of low molecular weight fractions, and $\bar{M}_n$ and pentad tacticity of the whole polymer are independent of polymerization time in the presence of hydrogen (not published), eq 2 is simplified to

$$\bar{P}_n = R_p/R_{tr} \tag{3}$$

where $R_p = k_p[M][C]$ and $R_{tr} = [C](k_M[M] + k_H[H_2]^n)$. [M], [C], and $[H_2]$ are the concentrations of propylene, catalytic sites, and molecular hydrogen; k_p is the rate constant of the propagation reaction; k_M and k_H are the rate constants of chain transfer reactions with propylene monomer and hydrogen.

The ratio $\bar{M}_n(I)/\bar{M}_n(A)$ is given by

$$\frac{\bar{M}_n(I)}{\bar{M}_n(A)} = \frac{\bar{P}_n(I)}{\bar{P}_n(A)} = \frac{R_p(IS)R_{tr}(AS)}{R_{tr}(IS)R_p(AS)} \tag{4}$$

where IS and AS represent the IPP and APP sites, respectively.

Since $\bar{M}_n(I)/\bar{M}_n(A)$ is 7.3 (32000/4400), the ratio rate of the propagation reaction/rate of the chain transfer reaction at the IPP site is seven times as large as that at the APP site.

Conclusions

According to the two-site model for the mechanism of propylene polymerization, isotactic polypropylene is a mixture of the isotactic and atactic polymers produced at two different sites. In the successive extraction of isotactic polypropylene with boiling *n*-alkane solvents, tacticity and molecular weight fractionations occur for the isotactic polymer, while the molecular weight fractionation mainly occurs for the atactic polymer. The number-average molecular weight of the isotactic polymer is much larger than that of the atactic polymer. This suggests that the ratio rate of the propagation reaction/rate of the chain transfer reaction at the IPP site is much larger than that at the APP site.

Registry No. IPP, 25085-53-4; propylene, 115-07-1.

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Isotactic Polymerization of Propene: Homogeneous Catalysts Based on Group 4 Metallocenes without Methylalumoxane

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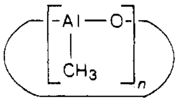
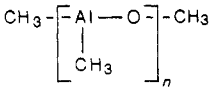
ABSTRACT: Propylene has been polymerized in the presence of stereospecific homogeneous catalytic systems consisting of group 4 metallocenes and mixtures of trimethylaluminum and dimethylaluminum fluoride. The polymers obtained are isotactic with a molecular structure very much like that of the polymers prepared in the presence of the same group 4 metallocenes and methylalumoxane.

Methylalumoxane (MAO), the reaction product of $Al(CH_3)_3$ with the appropriate amount of water, having the general formula[1]





$$CH_3-\left[Al(CH_3)-O\right]_n-CH_3$$

is a key ingredient of homogeneous catalysts that promote isotactic polymerization of propene. As reported by Ewen[2] and Kaminsky,[3] this organometallic compound activates group 4[4] metallocenes, which become able to promote polymerization of propene to (a) classical isotactic polypropylene, consisting essentially of blocks of isotactic diads *m* separated by pairs of syndiotactic diads *r*, i.e., ... *mmmrrmmm*...*mmmrrmmm*... (hereinafter called type I polypropylene as proposed by Ewen[2]), to (b) type II isotactic polypropylene, consisting of blocks of *m* diads sep-