nearly monodisperse polymers of controlled molecular weights.

Acknowledgment. This work was supported in part by a Grant for International Joint Research Project from the New Energy and Industrial Technology Development Organization (NEDO), for which we are grateful.

References and Notes

(1) Higashimura, T.; Kojima, K.; Sawamoto, M. *Polym. Bull. (Berlin)* **1988**, *19*, 7.

(2) Higashimura, T.; Kishiro, O. *Polym. J. (Tokyo)* **1977**, *9*, 87.

(3) Higashimura, T.; Mitsuhashi, M.; Sawamoto, M. *Macromolecules* **1979**, *12*, 178.

(4) For a review, Higashimura, T.; Sawamoto, M. *Adv. Polym. Sci.* **1984**, *62*, 49.

(5) (a) Masuda, T.; Higashimura, T. *J. Polym. Sci., Part B* **1971**, *9*, 783. (b) Higashimura, T.; Kishiro, O. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 967.

(6) Pepper, D. C. *Makromol. Chem.* **1974**, *175*, 1077.

(7) Higashimura, T.; Kishiro, O.; Takeda, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1089.

(8) Tanizaki, A.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 87.

(9) (a) Marvel, C. S.; Schertz, G. L. *J. Am. Chem. Soc.* **1943**, *65*, 2054. (b) Nystrom, R. F.; Brown, W. G. *Ibid.* **1947**, *69*, 1197.

(10) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265, 2228.

(11) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* **1987**, *20*, 2693.

(12) Nuyken, O.; Kröner, H. *Polm. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 87.

(13) Enoki, T.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci., Part A, Polym. Chem.* **1986**, *24*, 2261.

(14) Ohtori, T.; Hirokawa, Y.; Higashimura, T. *Polym. J.* **1979**, *11*, 471.

Copolymerization of Styrene and Substituted Styrenes with $Ti(OMen)_4$–Methylaluminoxane Catalyst

Kazuo Soga,*,† Hisayuki Nakatani,† and Takashi Monoi‡

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan, and Oita Research Laboratory, Showa Denko K.K., 2, Nakanosu, Oita 870-01, Japan.

Received March 14, 1989; Revised Manuscript Received July 3, 1989

ABSTRACT: Copolymerizations of styrene and substituted styrenes were carried out at room temperature with a $Ti(OMen)_4$–methylaluminoxane catalyst and the monomer reactivity ratios (r) were estimated by using the Fineman–Ross method. From the plot of log r versus σ in the Hammett equation, log $r = \rho\sigma$, ρ was approximately −1.2. The negative value of ρ suggested that polymerization of these styrene monomers proceeds not via a coordinated anionic but via a coordinated cationic mechanism. The results of copolymerization between styrene and α-olefins supported the mechanism.

Introduction

Ishihara et al.[1] have succeeded in preparing syndiotactic polystyrene by using a kind of Kaminsky–Sinn catalysts composed of some titanium compounds and methylaluminoxane (MAO). Zambelli et al.[2,3] later found that some zirconium compounds are also effective for the syndiotactic polymerization of styrene when MAO is used as cocatalyst. Ishihara et al.[4] have recently reported that corresponding syndiotactic polymers can also be similarly obtained for ring-substituted styrenes (*p*- and *m*-methylstyrene, *p-tert*-butylstyrene, *p*- and *m*-chlorostyrene, *p*-fluorostyrene, etc.) with a similar catalyst system. More recently, Grassi et al.[5] have also carried out the polymerization of substituted styrenes and found that syndiotactic polymer is obtained from *p*-methylstyrene, whereas atactic polymers are obtained from *p*-methoxystyrene and *p*-, *m*-, and *o*-chlorostyrene.

It is evident that MAO plays an important role in producing syndiotactic polystyrene. However, the catalyst system composed of Cp_2MCl_2 (M = Ti, Zr) and MAO, which is well-known to catalyze olefin polymerization, does not give syndiotactic polystyrene, whereas the $Ti(OR)_4$–MAO system, which produces syndiotactic polystyrene, also gives polyolefins[6] but not copolymers of styrene and olefins. These facts may indicate that the active species that produce syndiotactic polystyrene are different from those producing polyolefins.

To obtain more information on the active species for syndiotactic polymerization of styrene, we have carried out the copolymerization of styrene and analyzed the results by using the Hammett law.

Experimental Section

Materials. Styrene and substituted styrenes commercially obtained from Kanto Chemical Co. were washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. Toluene used as solvent was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. $Ti(OMen)_4$ was prepared from $TiCl_4$ and L-(−)-menthol and purified by distillation. $AlMe_3$ (TMA) and $CuSO_4·5H_2O$ were commercially obtained and used without further purification. Methylaluminoxane (MAO) was prepared from TMA and $CuSO_4·5H_2O$ according to the literature[7] and reserved as stock solution in toluene, 0.40 mmol/dm^3. Nitrogen of 99.9989% purity was used after passing it through a column of 3A molecular sieve.

Polymerization and Analytical Procedures. Polymerizations were carried out in a 100-cm^3 glass reactor equipped with a magnetic stirrer. Polymerization was stopped by adding a mixture of hydrochloric acid and methanol, filtered, and dried under reduced pressure at 60 °C. The structures and compositions of the copolymers were determined by ^1H NMR, ^{13}C

---

† Tokyo Institute of Technology.

‡ Oita Research Laboratory.

0024-9297/90/2223-0953$02.50/0 © 1990 American Chemical Society

Table I
Results of Copolymerization of Styrene (M_1) and *p*-Methylstyrene (M_2)[a]

$[M_1]$, mol %	$[M_2]$, mol %	$d[M_1]$, mol %[b]	$d[M_2]$, mol %[b]	F	f	F^2/f	$F(f-1)/f$
27.4	72.6	19.2	80.8	0.377	0.238	0.597	-1.21
53.1	46.9	39.4	60.6	1.13	0.650	1.96	-0.608
62.9	37.1	45.9	54.1	1.70	0.848	3.41	-0.305
72.6	27.4	57.7	42.3	2.65	1.36	5.16	0.701

[a] Polymerization conditions: polym temp = 27 °C; styrene + *p*-methylstyrene = 10 cm^3; Ti(OMen)$_4$ = 0.1 mmol; MAO = 2.0 mmol; toluene = 30 cm^3. [b] Determined from ^{1}H NMR.

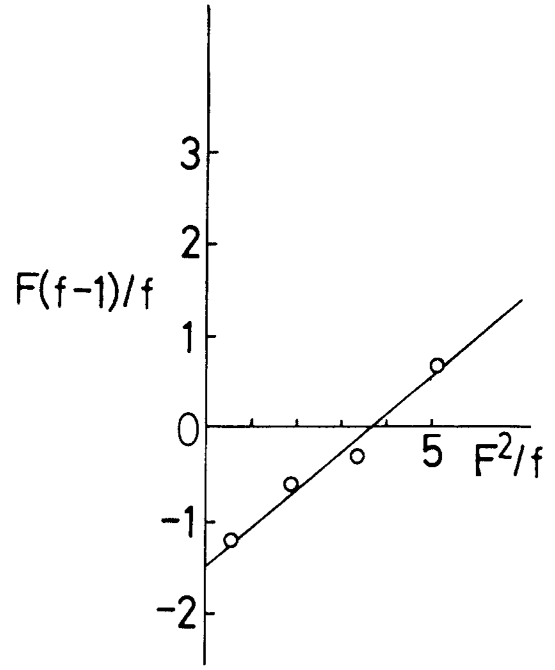

Figure 1. Fineman–Ross plots for the copolymerization of styrene (M_1) and *p*-methylstyrene (M_2): polym temp = 27 °C; styrene + *p*-methylstyrene, 10 cm^3; Ti(OMen)$_4$, 0.1 mmol; MAO, 2.0 mmol; toluene, 30 cm^3.

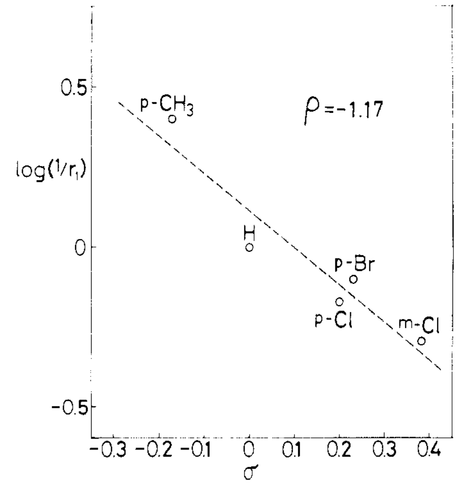

Figure 2. Plots of log $(1/r_1)$ against σ: polym temp = 27 °C; styrene + substituted styrene, 10 cm^3; Ti(OMen)$_4$, 0.1 mmol; MAO, 2.0 mmol; toluene, 30 cm^3.

Table II
Monomer Reactivity Ratios for Styrene and Substituted Styrenes[a]

monomer	r_1	r_2	r_1r_2
p-CH$_3$St	0.40	1.47	0.59
St	1	1	1
p-ClSt	1.49	0.19	0.29
p-BrSt	1.26	0.79	1.00
m-ClSt	1.95	0.23	0.45

[a] Polymerization conditions: polym temp = 27 °C, styrene + substituted styrene = 10 cm^3; Ti(OMen)$_4$ = 0.1 mmol; MAO = 2.0 mmol; toluene = 30 cm^3.

NMR, and elemental analysis. The ^{13}C NMR spectra of the polymers were measured at 25.1 MHz in chloroform-*d* at 60 °C with a JEOL FX-100 spectrometer. The chemical shifts were referred to HMDS added as an internal standard for δ = 2.0 ppm. Molecular weight and molecular mass distributions of the homopolymers were determined at 140 °C with a Waters Associates Model 150GPC chromatograph using 1,2,4-trichlorobenzene as solvent, whereas those of copolymers were determined at 40 °C with a Shimadzu liquid chromatograph HIC-6A using chloroform as solvent. $\bar{M}_n$ and $\bar{M}_w$ were obtained by using standard polystyrene gels. (Since we have no calibration curves between polystyrene and present polymers, $\bar{M}_n$ and $\bar{M}_w$ thus determined might not be correct.)

Results and Discussion

Copolymerizations were usually conducted at 27 °C by using 0.1 mmol of Ti(OMen)$_4$, 2.0 mmol (referred to AlMe$_3$) of MAO, 10 cm^3 of monomers (styrene + substituted styrene), and 30 cm^3 of toluene.

As an example, the results of copolymerization between styrene (M_1) and *p*-methylstyrene (M_2) are given in Table I. By use of the Fineman–Ross plots shown in Figure 1 as well as eq 1, the monomer reactivity ratios for styrene (r_1) and *p*-methylstyrene (r_2) were obtained to be r_1 = 0.40 and r_2 = 1.47, respectively.

$$F(f-1)/f = r_1F^2/f - r_2 \qquad (1)$$

$$\text{with} \quad F = [M_1]/[M_2] \quad \text{and} \quad f = d[M_1]/d[M_2]$$

The results obtained with the other copolymerizations were also analyzed in a similar way. The experimental data satisfactorily fitted the Fineman–Ross plots for all copolymerizations. The r_1, r_2 and r_1r_2 values obtained are summarized in Table II. In Figure 2 are plotted the log $(1/r_1)$ values against σ from the Hammett equation (log $(1/r_1) = \rho\sigma$). From the slope in Figure 2, ρ was obtained to be -1.17. The negative value of ρ indicates that these copolymerization reactions proceed not via an anionic but via a cationic mechanism.

Typical ^{13}C NMR spectra of the copolymers are illustrated in Figure 3. The styrene–*p*-methylstyrene copolymer is highly syndiotactic, whereas the syndiotacticity of the other copolymers is not as high.

To get more information on this point, homopolymerizations of these substituted styrenes were carried out under similar conditions. In Figure 4 are shown the ^{13}C NMR spectra of the polymers obtained together with assignments. Numeration of the carbon atoms of the monomer units is illustrated in Figure 5. The spectra in phenyl C-1 and methylene regions clearly indicate that highly syndiotactic polymers are obtained with styrene and *p*-methylstyrene, whereas atactic polymers are obtained with *p*-chlorostyrene, *p*-bromostyrene, and *m*-chlorostyrene. This tendency agrees well with the copolymerization results. Ishihara et al.[4] conducted the polymerization of substituted styrene monomers by using (η^5-C$_5$H$_5$)TiCl$_3$–MAO catalyst and concluded that corresponding syndiotactic polymers were obtained according to the analysis of the ^{13}C NMR spectra in the phenyl C-1 carbon region. The present results are in good agreement with those reported by Grassi et al.[5] but do not agree with those reported by Ishihara et al.[4] The

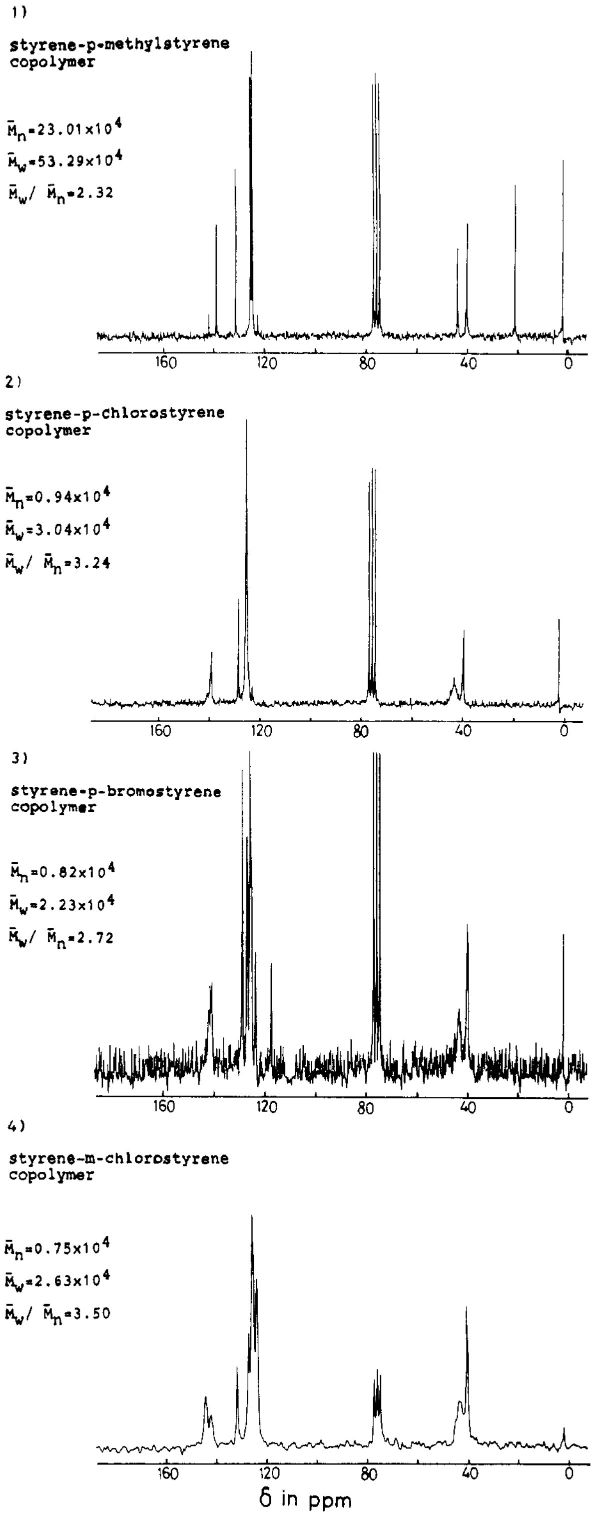

Figure 3. (1) ^{13}C NMR spectrum of the styrene–*p*-methylstyrene copolymer. Monomer contents: styrene, 19.2 mol %; *p*-methylstyrene, 80.8 mol %; polym temp = 27 °C; styrene, 2.5 cm^3; *p*-methylstyrene, 7.5 cm^3; Ti(OMen)$_4$, 0.1 mmol; MAO, 2.0 mmol; toluene, 30 cm^3. (2) ^{13}C NMR spectrum of the styrene–*p*-chlorostyrene copolymer. Monomer contents: styrene, 18.4 mol %; *p*-chlorostyrene, 81.6 mol %; polym temp = 60 °C; styrene, 1 cm^3; *p*-chlorostyrene, 9 cm^3; Ti(OMen)$_4$, 0.1 mmol; MAO, 2.0 mmol; toluene, 30 cm^3. (3) ^{13}C NMR spectrum of the styrene–*p*-bromostyrene copolymer. Monomer contents: styrene, 49.0 mol %; *p*-bromostyrene, 51.0 mol %; polym temp = 60 °C; styrene, 5 cm^3; *p*-bromostyrene, 5 cm^3; Ti(OMen)$_4$, 0.1 mmol; MAO, 2.0 mmol; toluene, 30 cm^3. (4) ^{13}C NMR spectrum of the styrene–*m*-chlorostyrene copolymer. Monomer contents: styrene, 9.3 mol %; *m*-chlorostyrene, 90.7 mol %; polym temp = 27 °C; styrene, 4 cm^3; *m*-chlorostyrene, 6 cm^3; Ti(OMen)$_4$, 0.1 mmol; MAO, 2.0 mmol; toluene, 30 cm^3.

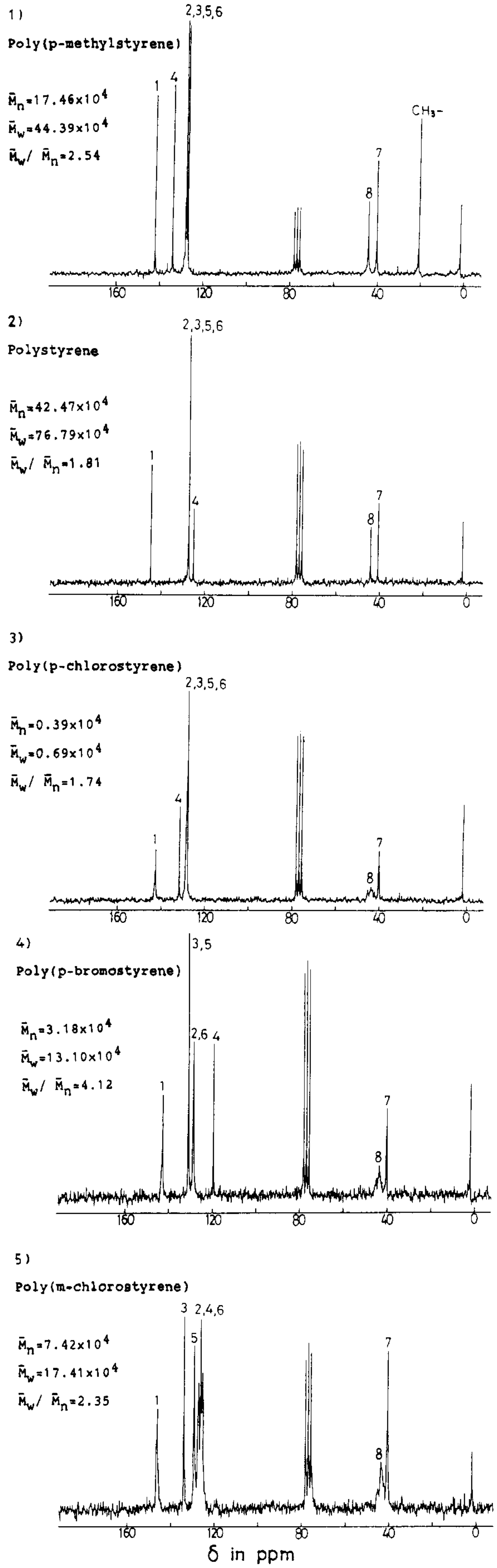

Figure 4. ^{13}C NMR spectra of the homopolymers of the substituted styrenes: (1) poly(*p*-CH$_3$St); (2) polySt; (3) poly(*p*-ClSt); (4) poly(*p*-BrSt); (5) poly(*m*-ClSt); poly temp = 27 °C for 1 and 2 and 60 °C for 3–5; substituted styrene, 10 cm^3; Ti(OMen)$_4$, 0.1 mmol; AMO, 2.0 mmol; toluene, 30 cm^3.

Table III
Copolymerization of Styrene (M_1) with Some Olefins (M_2) by $Ti(O^nBu)_4$–MAO[a]

comonomer	M_2 in feed, mol %	polym temp, °C	polym time, h	yield, mg	polym obtained[b]
ethylene	95	40	1	83	polyethylene
	5	27	40	320	atactic polystyrene (major) + polyethylene (trace)
1-hexene	73.2	27	3	35	atactic polystyrene

[a] Polymerization conditions: $Ti(O^nBu)_4$ = 0.1 mmol; MAO = 2.0 mmol; toluene = 30 cm^3. [b] Analyzed by ^{13}C NMR of extracted polymers.

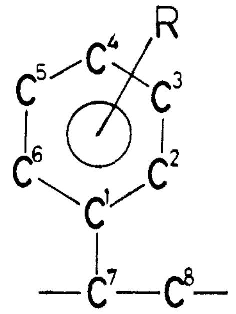

Figure 5. Numeration of the carbon atoms of the monomer units (R = CH_3, Cl, Br).

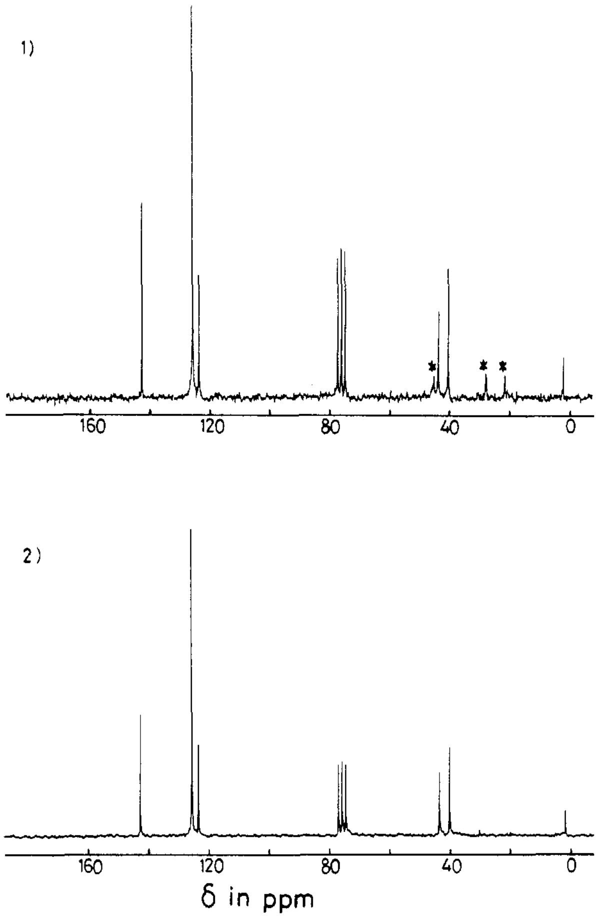

Figure 6. ^{13}C NMR spectra of the polymer obtained in the block copolymerization between styrene and propylene. (1) Crude polymer, before extraction with $CHCl_3$. The labeled peaks are assigned to polypropylene. (2) Soluble polymer, after extraction with $CHCl_3$: polym temp = 0 °C; propylene, 2.2 dm^3; styrene, 20 cm^3; $Ti(OMen)_4$, 0.2 mmol; MAO, 5.0 mmol; toluene, 51 cm^3.

precise reason for such disagreement in polymer structures is not obvious at present.

As is well-known, most of the α-olefin polymerizes via an anionic mechanism, whereas Eisch et al.[8] reported that some cationic species like dicyclopentadienylmethyltitanium(IV) tetrachloroaluminate initiate ethylene polymerization. From such a viewpoint, copolymerization of styrene with ethylene or 1-hexene was then conducted under similar conditions. The polymers obtained were separated by extraction with $CHCl_3$ and both fractions were analyzed by ^{13}C NMR. Typical results are shown in Table III. The polymers obtained were essentially composed of polyolefin and atactic polystyrene. No detectable amount of the ethylene–styrene or 1-hexene–styrene copolymer was obtained with this catalyst system. The possibility of producing a block copolymer between styrene and propylene was also examined with the following experiments. After the polymerization of propylene was carried out at 0 °C for 24 h, propylene monomer was quickly substituted by styrene at 0 °C and the reaction was continued for 24 h at 0 °C. In Figure 6-1 is illustrated the ^{13}C NMR spectrum of the crude polymer, which indicates the small peaks attributable to polypropylene. The polymer was then extracted with $CHCl_3$, in which a very small quantity was insoluble. The ^{13}C NMR spectrum of the soluble part is shown in Figure 6-2. The peaks attributed to polypropylene disappeared completely. Although we could not measure the ^{13}C NMR spectrum of the insoluble part due to very small amount, it might be homopolypropylene. No block polymer was formed by this procedure.

Thus, the present catalyst produces both polyolefins and polystyrene but not any copolymer between them. These results can be rationalized by the presence of both coordinated cationic and coordinated anionic species, and the former gives syndiotactic polystyrene while the latter polyolefins. The change in structure of polystyrene from syndiotactic to atactic in the presence of olefins may suggest that the coordinated cationic species has also some interaction with olefin monomers.

Natta et al.[9,10] carried out the copolymerization of styrene with substituted styrenes by using $TiCl_4$–$AlEt_3$ catalyst and obtained a Hammett ρ parameter of approximately −1, which agrees well with the present result. However, usual Ziegler–Natta catalysts like $TiCl_4$–$AlEt_3$ are known to be active also for the copolymerization of styrene with olefins. Therefore, there seems to be a big differences in catalytic centers from usual Zieger–Natta catalysts and the present catalyst system. To obtain more information about this, experiments are under way to copolymerize styrene with monomers that are known to polymerize via a cationic mechanism. The results will be reported in another paper.

References and Notes

(1) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.
(2) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277.
(3) Grassi, A.; Pellecchia, C.; Longo, P.; Zambelli, a. *Gazz. Chim. Ital.* **1987**, *117*, 249.
(4) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356.
(5) Grassi, A.; Longo, P.; Proto, A.; Zambelli, A. *Macromolecules* **1989**, *22*, 104.
(6) Oliva, L.; Longo, P.; Pellecchia, C. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 51.

Macromolecules **1990,** *23,* 957–959

(7) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980,** *19,* 390.
(8) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985,** *107,* 7219.
(9) Natta, G.; Danusso, F.; Sianesi, D.; Macchi, A. *Chim. Ind. (Milan)* **1959,** *41,* 968.
(10) Sianesi, D.; Pajaro, G.; Danusso, F. *Chim. Ind. (Milan)* **1959,** *41,* 1176.

Syndiotactic Polymerization of Styrene with Supported Kaminsky–Sinn Catalysts

Kazuo Soga* and Hisayuki Nakatani

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan.
Received March 22, 1989; Revised Manuscript Received July 17, 1989

ABSTRACT: Two kinds of supported catalysts, $Ti(OBu)_4/SiO_2$ (A) and $Ti(OBu)_4/MAO/SiO_2$ (B), were prepared and styrene polymerization was conducted by using the catalyst systems of A with methylaluminoxane (MAO) and B alone. In the case of A with MAO, the rate of polymerization rapidly increased to reach a nearly constant value at a MAO/Ti ratio near 1 (Al/Ti = 20) with a slow increase as the molar ratio MAO/Ti is increased. On the other hand, very high activity was obtained when bulk polymerization was carried out using B. All the polymers obtained with these catalysts were highly syndiotactic (approximately 100%) with narrow molecular mass distributions.

Introduction

Idemitsu Kosan Co. Ltd.[1] has recently succeeded in preparing syndiotactic polystyrene by using Kaminsky–Sinn catalysts composed of some titanium compounds and methylaluminoxane (MAO).[2-4] Zambelli et al.[5,6] reported that some zirconium compounds are also effective for the polymerization when MAO is used as cocatalyst.

More recently, we have succeeded in preparing supported Kaminsky–Sinn catalysts that effectively catalyze syndiotactic polymerization of styrene at a low molar ratio of MAO/Ti. The catalyst systems seem to be useful not only for the production of syndiotactic polystyrene but also for the investigation of the active species in the Kaminsky–Sinn catalyst.

This paper reports the preparation of the catalysts as well as brief results of styrene polymerization with these supported catalysts.

Experimental Section

Materials. Toluene (from Kanto Chemicals Co. Ltd.) was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. Styrene (from the same company) was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. SiO_2 (350 m^2/g, from Fuji-Davison Chemicals Ltd., grade 952) and γ-Al_2O_3 (150 m^2/g, from Nishio Industry Co.) were heated under reduced pressure at 300 °C for 4 h. $AlMe_3$, $CuSO_4{\cdot}5H_2O$, and $Ti(OBu)_4$ were commercially obtained and used without further purification. Nitrogen (99.9989%, from Toyo Oxygen Co.) was used after passing through a 3A molecular sieve column. Methylaluminoxane (MAO) was prepared from $AlMe_3$ and $CuSO_4{\cdot}5H_2O$ according to literature.[2] It is said that an appreciable amount of the unreacted $AlMe_3$ remains in the MAO.[7] Since $AlMe_3$ is considered to be more reactive than MAO, it is recommended to remove the unreacted $AlMe_3$. From such a viewpoint, 22 mmol of MAO (referred to $AlMe_3$) was brought into contact with 1.2 g of γ-Al_2O_3 for 24 h at room temperature. The MAO thus treated was reserved as a stock solution in toluene (0.40 $mmol/dm^3$). Sinn et al.[7] measured the CH_3/Al ratio of their MAO by complete hydrolysis and obtained $CH_3/Al = 1.59$. The CH_3/Al ratios of untreated and γ-Al_2O_3-treated MAO were analyzed by a similar method (HCl/H_2O) by using approximately 4-mL samples. The results obtained were as follows: untreated MAO, Al = 2.0 mmol, CH_4 evolved = 3.42 mmol, $CH_3/Al = 1.71$; treated MAO, Al = 2.0 mmol, CH_4 evolved = 3.12 mmol, $CH_3/Al = 1.56$. Thus, the treatment of MAO with γ-Al_2O_3 caused a slight decrease in the CH_3/Al ratio, suggesting that $AlMe_3$ contained in MAO is partly removed. However, the CH_3/Al ratio is still much higher than unity, which indicates that the structure of MAO is very complicated.

Preparation of Supported Catalysts. $Ti(OBu)_4/SiO_2$ catalyst (catalyst A): To a solution of $Ti(OBu)_4$ in toluene (51.4 cm^3, 0.747 mol/dm^3) at room temperature was added 2.3 g of SiO_2. After raising the temperature to the boiling point, the mixture was kept standing for 8 h with vigorous stirring. Then the precipitate was filtered under nitrogen, washed five times with plenty of toluene, and dried under reduced pressure at 40 °C for 4 h. $MAO/Ti(OBu)_4/SiO_2$ catalyst (catalyst B): 9.76 mmol of the MAO (referred to $AlMe_3$) was added dropwise at −20 °C to the slurry containing 10 cm^3 of toluene and 0.30 g of the $Ti(OBu)_4/SiO_2$ catalyst, which had been prepared from 1.5 g of SiO_2 and 37.6 cm^3 of $Ti(OBu)_4$ solution in toluene (0.747 mol/dm^3). Then the mixture was kept standing at room temperature for 1 h. The precipitate was filtered, washed with toluene, and dried under reduced pressure at 40 °C for 4 h.

Polymerization and Analytical Procedures. Polymerization of styrene was carried out in a 0.1 dm^3 glass reactor equipped with a magnetic stirrer. Measured amounts of catalyst A and MAO or catalyst B were placed in the reactor containing styrene or styrene and toluene at room temperature. Polymerization was stopped by adding a mixture of hydrochloric acid and methanol; the mixture was filtered and dried under reduced pressure at 60 °C.

The ^{13}C NMR spectra of the polymers were measured at 25.1 Hz in chloroform-*d* at 60 °C with a JEOL JNH FX-100 spectrometer. The amounts of titanium and aluminum contained in the supported catalysts were determined by atomic absorp-

0024-9297/90/2223-0957$02.50/0 © 1990 American Chemical Society