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Copolymerization of Propylene with Styrene Using the Catalyst System Composed of Solvay Type $TiCl_3$ and Cp_2TiMe_2

Kazuo Soga*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 227, Japan

Hisayoshi Yanagihara*

Oita Research Laboratory, Showa Denko Co. Ltd., 2, Nakanosu, Oaza, Oita 870-01, Japan.

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ABSTRACT: Copolymerization of propylene and styrene was first conducted at 40 °C with Solvay type $TiCl_3$ by using $AlEt_3$ (Et = ethyl) as cocatalyst, which gave mixtures of polypropylene, polystyrene, and a copolymer of both monomers. The copolymerization was then carried out under similar conditions by using Cp_2TiMe_2 (Cp = cyclopentadienyl; Me = methyl) as cocatalyst. The catalyst system was found selectively (more than 90 wt %) to give a random copolymer of propylene and styrene. From the copolymerization by changing the monomer feed ratio, the monomer reactivity ratios were estimated to be $r_P = 130$ and $r_S = 0.18$. The random copolymer was characterized in detail by ^{13}C NMR spectroscopy, differential scanning calorimetry, gel permeation chromatography, etc.

Introduction

Although copolymerization of olefins and styrene with the usual Ziegler–Natta catalysts has been reported frequently,[1] the structure of the copolymers has not yet been clarified. The usual Ziegler–Natta catalysts, even highly isospecific catalysts, contain multiple active species that differ in stereospecificity, oxidation states of titanium metals, etc., resulting in production of not only copolymers but appreciable amounts of homopolymers. Therefore, it is not easy to determine the structure of copolymers obtained with the usual catalysts.

More recently, we have developed an extremely highly isospecific catalyst that is composed of Solvay type $TiCl_3$ and $(RCp)_2TiMe_2$ (R = H, Me).[2,3] The catalyst gives highly isotactic polypropylene (isotacticity > 99%),[2] poly-1-butene (>98%),[2] and polystyrene (>99%)[3] as well as highly crystalline polyethylene that has no ethyl branches.[2] The catalyst has uniformly active species and does not give any homopolymer in the copolymerizations of various olefins with ethylene.[4]

In the present study, we have tried to apply the catalyst in the synthesis of a random copolymer of propylene and styrene.

Experimental Section

Materials. Propylene (from Mitsubishi Petrochemical Co.) was purified by passing through NaOH and P_2O_5 columns. Solvay type $TiCl_3$ was donated by Showa Denko Co. Ltd. Research grade heptane commercially obtained was purified according to the usual procedures.[5] Research grade styrene obtained from Kanto Chemicals Co. was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under a reduced pressure. Cp_2TiMe_2 was prepared according to the method reported by Clauss et al.[6] and diluted into 0.25 mol/dm^3 in heptane. $AlEt_3$ (from Toyo Stauffer Chemical Co.) was also diluted into 0.25 mol/dm^3 in heptane.

Copolymerization of Propylene with Styrene. In a 200-cm^3 glass reactor equipped with a magnetic stirrer were placed given amounts of heptane, styrene, and cocatalyst (Cp_2TiMe_2 or $AlEt_3$). The reactor was degassed under vacuum, followed by introduction of propylene. After the mixture was kept at 40 °C for 10 min, copolymerization was started by adding the Solvay type $TiCl_3$ catalyst. Propylene monomer was continuously supplied under a total pressure of 1 atm. The copolymerization was conducted at 40 °C for 15 min and terminated by adding a dilute hydrochloric acid solution in methanol and dried with vacuum.

Characterization of Polymers. The crude polymer was fractionated with boiling chloroform for 16 h. ^{13}C NMR spectra of the polymers (10 w/v % in 1,2,4-trichlorobenzene–deuteriobenzene) were recorded at 120 °C by using a JEOL JNH GX-500 spectrometer operating at 125.6 MHz under proton decoupling in the Fourier transform (FT) mode. The chemical shifts are reported in ppm downfield from internal hexamethyldisiloxane (HMDS). The molecular mass distribution (MMD) of polymer was measured at 140 °C with a Shodex LCHT-3 GPC equipped with a Shodex AD 80M/S column using standard polystyrene gels obtained from Waters chromatography division. *o*-Dichlorobenzene was used as solvent. M_n and M_w were determined by standard procedures from elution curves. (Since we have no calibration curve between polystyrene and the present copolymer, M_n and M_w thus determined might be incorrect.) The melting

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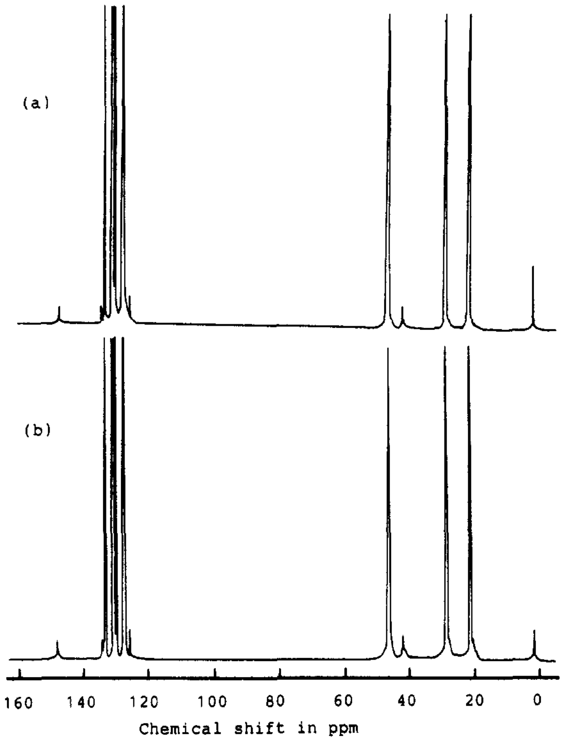

Figure 1. ^{13}C NMR spectra of boiling-chloroform-insoluble polymers obtained with two kinds of catalysts: (a) polymer obtained with Solvay type $TiCl_3$ and Cp_2TiMe_2 catalyst (run no. 4); (b) polymer obtained with Solvay type $TiCl_3$ and $AlEt_3$ catalyst (run no. 9).

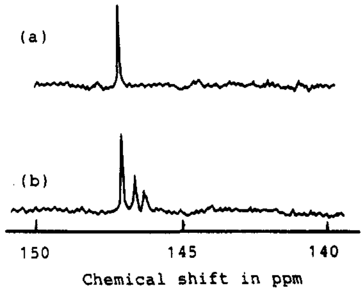

Figure 2. Expanded spectra of Ph–C_1 carbon region in Figure 1: (a) expanded spectrum of Figure 1a; (b) expanded spectrum of Figure 1b.

point (T_m) and heat of fusion (ΔH_f) of the polymers were determined from the peak of differential scanning calorimetric (DSC) curve. DSC measurements were made at a heating rate of 20 K/min with a Perkin-Elmer-II using aluminum sample pans.

Results and Discussion

Copolymerization of propylene and styrene was conducted at 40 °C for 15 min with the Solvay type $TiCl_3$ using both Cp_2TiMe_2 and $AlEt_3$ as cocatalyst. The polymers produced were analyzed by ^{13}C NMR spectroscopy. The soluble polymer could be easily assigned as atactic polystyrene, which might be produced via radical and/or cationic mechanism.[8]

In Figure 1 are shown the typical ^{13}C NMR spectra of the insoluble polymers obtained with two kinds of catalyst systems. Figure 2 shows the expanded spectra in the Ph–C_1 carbon region. The polymer obtained with the present catalyst shows a single peak at 147.2 ppm, whereas the polymer obtained with the usual Ziegler–Natta catalyst displays additional peaks at 146.8 and at around 146.4 ppm, which can be assigned to the Ph–C_1 carbons of isotactic and atactic polystyrene.[9]

In Figure 3 are shown the expanded spectra in the region of methine carbons of styrene.[9] Figure 3a displays a sharp peak at 42.2 ppm, while Figure 3b displays an additional broad peak at around 41.5–42.2 ppm assignable to the methine carbons of isotactic and atactic polystyrene.

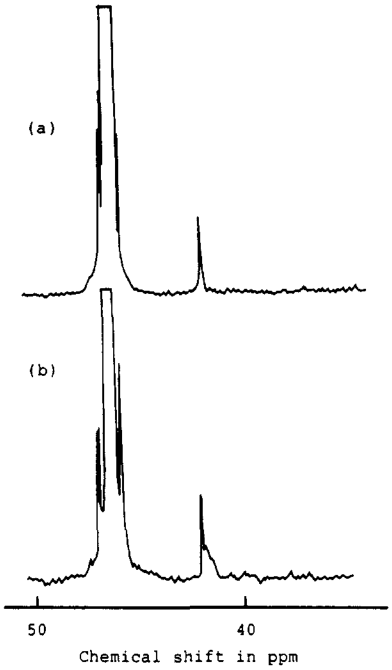

Figure 3. Expanded spectra of the methine carbon region of styrene in Figure 1: (a) expanded spectrum of Figure 1a; (b) expanded spectrum of Figure 1b.

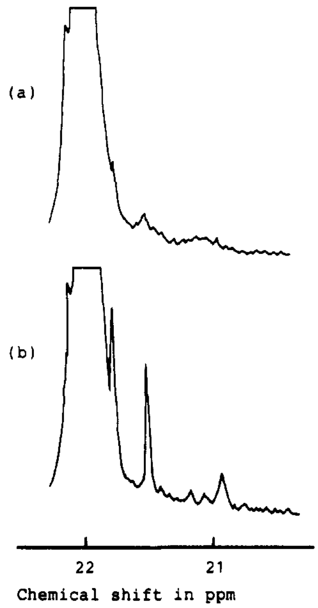

Figure 4. Expanded spectra of methyl carbon region of propylene: (a) expanded spectrum of Figure 1a; (b) expanded spectrum of Figure 1b.

From these results, it may be concluded that the insoluble polymer obtained with Cp_2TiMe_2 as cocatalyst is the real copolymer of propylene and styrene, whereas the insoluble polymer obtained with $AlEt_3$ contains appreciable amounts of isotactic and atactic polystyrene in addition to the copolymer.

On the other hand, Figure 4 shows the expanded spectra in the region of the methyl carbons of propylene. The values of [mm] triads calculated from these spectra were 99.5 and 94.5% for Figure 4, parts a and b, respectively, suggesting that the copolymer obtained with Cp_2TiMe_2 as cocatalyst has very few steric defects, i.e., polypropylene contained in the copolymer as a block is highly isotactic.

Table I
Results of Propylene–Styrene Copolymerization and Fractionation of Polymers[a]

run no.	concn of monomers[b] in heptane, mol/L		yield, g	extracted[c] fraction, %		concn of S[b] in I.Cl, mol %
	C_P	C_S		I.Cl	S.Cl	
1	0.450	2.18	2.241	92.7	7.3	4.4
2	0.450	1.04	1.958	94.8	5.2	2.8
3	0.450	0.620	1.950	96.0	4.0	1.8
4	0.450	0.522	1.900	96.4	3.6	1.4
5	0.450	0.261	1.892	98.6	1.4	0.40
6	0.450	0.087	1.550	99.0	1.0	0.15
7	0.450		1.340			
8		2.18	0.870			
9[d]	0.450	0.522	1.870	67.9	32.1	0.92[e]

[a] Copolymerization conditions: [Solvay type $TiCl_3$] = 1 mmol, [Cp_2TiMe_2] = 2 mmol, total solvent = 100 cm^3 (heptane + styrene), 40 °C, 15 min, P = 1 atm. [b] P and S denote propylene and styrene, respectively. [c] I.Cl and S.Cl denote boiling-chloroform-insoluble and -soluble parts, respectively. [d] 2 mmol of $AlEt_3$ was used as cocatalyst. [e] This value means total amount of styrene (copolymer and homopolymers).

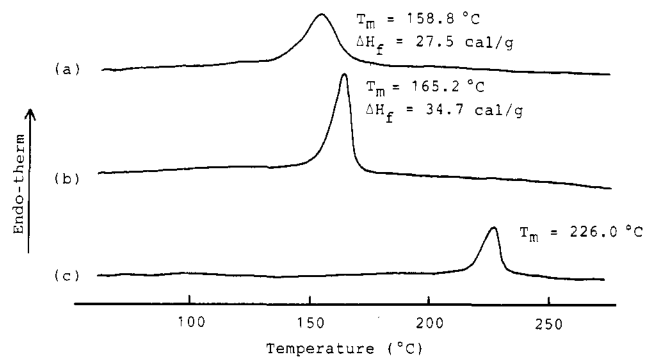

Figure 5. DSC thermograms of the polymers obtained with Solvay type $TiCl_3$ and Cp_2TiMe_2 catalyst: (a) propylene–styrene copolymer (run no. 4); (b) polypropylene (run no. 7); (c) polystyrene (run no. 8).

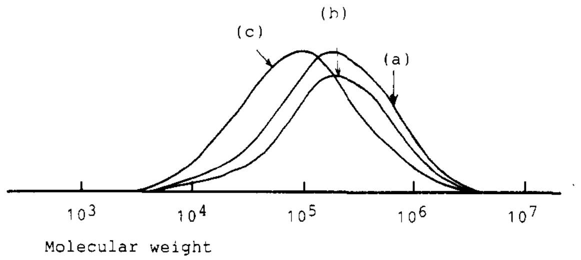

Figure 6. MMD curves of the polymers obtained with Solvay type $TiCl_3$ and Cp_2TiMe_2 catalyst: (a) propylene–styrene copolymer (run no. 4), M_n = 130 000, M_w = 1 003 000, M_w/M_n = 7.7; (b) polypropylene (run no. 7), M_n = 146 000, M_w = 1 138 000, M_w/M_n = 7.8; (c) polystyrene (run no. 8), M_n = 76 000, M_w = 650 000, M_w/M_n = 8.6.

The copolymerization of propylene and styrene was then carried out by changing the feed ratio of both monomers. The results obtained are summarized in Table I, where a typical result obtained with the use of $AlEt_3$ (under the same condition in run no. 4) is also shown for reference (run no. 9). It is evident from Table I that the Solvay type $TiCl_3$ catalyst combined with Cp_2TiMe_2 selectively gives the copolymer (>90 wt %) whereas the catalyst combined with $AlEt_3$ gives appreciable amount of homopolymers (copolymer = 68 wt %). The difference in selectivity between the two catalyst systems may be attributed to the difference in multiplicity of active species; the former system contains uniform active species, while the latter system contains several kinds of active species as described in the Introduction.

By using a Solvay type $TiCl_3$–Cp_2TiMe_2 catalyst system, highly isotactic polypropylene and polystyrene[3] were also synthesized under similar conditions as copolymerization (Table I, runs no. 7 and 8). These homopolymers and the copolymer were analyzed by DSC and GPC.

Figures 5 and 6 illustrate the results obtained. The copolymer displayed a single peak in its DSC curve (Figure 5a). Both the melting point (T_m) and heat of fusion (ΔH_f) for the copolymer were found to be lower than those for isotactic polypropylene (Figure 5b). The crystallinities of the copolymer and polypropylene were calculated from eq 1 by using ΔH_f, where ΔH_f is the heat of fusion of the

$$\text{crystallinity \%} = 100\Delta H_f/\Delta H_f^\circ \tag{1}$$

sample determined from the DSC curve and ΔH_f° is the thermodynamic heat of fusion of folded-chain polypropylene crystal (49.8 cal/g).[10] The crystallinities of the copolymer (run no. 4) and polypropylene (run no. 7) were obtained to be 55% and 70%, respectively. Both the copolymer and polypropylene were then fractionated with boiling octane for 8 h. Most of the polypropylene (98.0%) remained insoluble, whereas the copolymer was mostly (92.2%) soluble in boiling octane. Judging from the difference in the melting point, crystallinity, and solubility between the copolymer and polypropylene, it may be said that the present copolymer is not a mixture of copolymer and polypropylene but is essentially copolymer.

The molecular weight of the copolymer, on the other hand, was just between those of isotactic polypropylene and polystyrene (Figure 6). The polydispersities for three kinds of polymers were not very different, which may suggest that these polymerizations proceed over the same active species. The MMD curve for the copolymers shows a unimodal shape, indicating that it does not contain homopolymers. Broadening in polydispersity might be caused by the multiplicity of active species which differ in propagating rate constants (k_p) as reported previously.[11]

Since the polypropylene produced with the present catalyst contains neither head–head nor tail–tail unit (no inversion), there are four reactions to be considered in the present copolymerization:

$$\text{---P–Ti} + \text{P} \xrightarrow{k_{PP}} \text{---PP–Ti} \tag{2}$$

$$\text{---P–Ti} + \text{S} \xrightarrow{k_{PS}} \text{---PS–Ti} \tag{3}$$

$$\text{---S–Ti} + \text{P} \xrightarrow{k_{SP}} \text{---SP–Ti} \tag{4}$$

$$\text{---S–Ti} + \text{S} \xrightarrow{k_{SS}} \text{---SS–Ti} \tag{5}$$

where P and S represent propylene and styrene units, and k_{PP}, k_{PS}, k_{SP} and k_{SS} denote the propagation rate constants. Therefore, the monomer reactivity ratios, r_P (=k_{PP}/k_{PS})

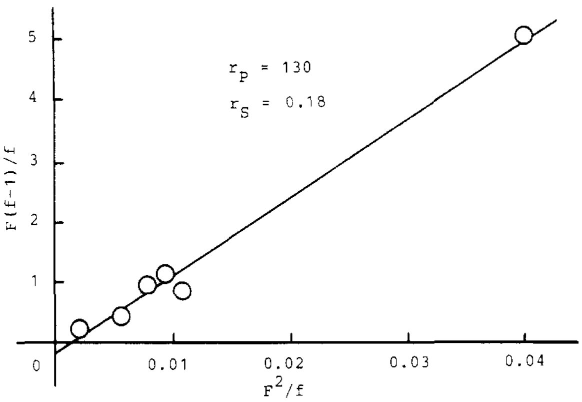

Figure 7. Fineman-Ross plots for propylene-styrene copolymerization.

Table II
Evaluation of $F(f-1)/f$ and F^2/f

run no.	F (C_P/C_S)	f (P/S)	$F(f-1)/f$	F^2/f
1	0.207	21.7	0.197	0.00197
2	0.432	34.7	0.420	0.00538
3	0.726	54.6	0.713	0.00965
4	0.863	70.4	0.854	0.0106
5	1.73	249	1.72	0.0102
6	5.18	666	5.10	0.0402

and r_S ($=k_{SS}/k_{SP}$), can be obtained by using the following Fineman-Ross equation:[12]

$$F(f-1)/f = (F^2/f)r_P - r_S \qquad (6)$$

where F and f are represented by

$$F = C_P/C_S$$

$$f = \frac{\text{moles of propylene in copolymer}}{\text{moles of styrene in copolymer}}$$

where C_P is the concentration of propylene in heptane and C_S is the concentration of styrene in heptane. The results obtained are summarized in Table II and Figure 7, which gave r_P = 130 and r_S = 0.18.

Although the present catalyst system is heterogeneous, the active species are considered to be uniform in the isospecificity. (There are multiple active species that differ in the propagation rate constant, resulting in broadening the polydispersity.[4]) Therefore, the results may be as reliable as the monomer reactivity ratios over the highly isospecific catalytic centers.

In conclusion, the catalyst composed of Solvay type $TiCl_3$ and Cp_2TiMe_2 was found to be effective for the production of copolymer between propylene and styrene.

Registry No. Cp_2TiMe_2, 1271-66-5; $TiCl_3$, 7705-07-9; propylene, 115-07-1; styrene, 100-42-5; (propylene)(styrene) (copolymer), 32555-67-2.

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Synthesis of Acryl- and Methacryl-Type Macromonomers and Telechelics by Utilizing Living Polymerization of 2-Oxazolines

Shiro Kobayashi,* Eiji Masuda, and Shin-ichiro Shoda

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Sendai 980, Japan

Yasuo Shimano

Hachinohe National College of Technology, Hachinohe 031, Japan.

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ABSTRACT: Acryl- and methacryl-type macromonomers and telechelics of poly(2-alkyl-2-oxazolines) (PROZO) have been prepared for the first time by terminating the living ends in the electrophilic (cationic) ring-opening polymerization of 2-alkyl-2-oxazolines (ROZO) with suitable reagents. The synthesis of macromonomers was achieved via the following two methods: (1) by the reaction of acryloyl or methacryloyl chloride with a PROZO alcohol obtained by the hydrolysis of the living PROZO propagating species under basic conditions (indirect method) and (2) by the termination of the living species with carboxylate anions of acrylic or methacrylic acids or with trimethylsilyl methacrylate (direct method). The production of telechelics of PROZO was achieved by using a bis(2-oxazolinium salt) initiator. Termination of both living ends of the PROZO with water, ammonia, or an alkylamine afforded the corresponding telechelics of PROZO as glycols and diamines in good yields.

Introduction

Chemical modification of polymer ends is an important topic in the field of polymer synthesis because these functionalized, end-reactive polymers can be used as prepolymers for the production of various materials. In electrophilic (cationic) polymerization,[1] one of the most effective methods for the introduction of functional groups onto polymer ends is the termination of living propagating