

(η^5 -Indenyl)trichlorotitanium-catalyzed Copolymerization of Styrene and Styrenic Macromonomer Carrying a Functional Group

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Abstract : Styrenic macromonomers with/without a silyloxy-functional group were synthesized via chain-end functionalization using 4-vinylbenzyl chloride as a terminating agent in *sec*-butyllithium-initiated polymerization of styrene. The yields were 92 mol% for the silyloxy group and 88 mol% for the styrenic unit. Crystalline polystyrene-*g*-amorphous polystyrenes were synthesized by (η^5 -indenyl)-trichlorotitanium ((Ind)TiCl₃)-catalyzed copolymerizations of the macromonomers with styrene in the presence of methylaluminumoxane (MAO) in toluene at 40 °C. The macromonomer having α, α' -bis(4-*tert*-butyldimethylsilyloxy)phenyl) group was also utilized for the preparation of a precursor of hydroxyl-functionalized syndiotactic polystyrene. The obtained polymers were characterized by a combination of ¹H, ¹³C NMR spectroscopic, size exclusion chromatographic, and differential scanning calorimetric analysis. The (Ind)TiCl₃-catalyzed copolymerization of styrene with the macromonomer carrying the silyloxy functional group was found to be an efficient method to modify syndiotactic polystyrene without a great loss of physical property by controlling the feed ratio of the macromonomer.

Introduction

Recent advances in metallocene-catalyzed polymerizations of α -olefins have opened a new era in the polymer industry since the finding of a remarkable efficiency of partially hydrolyzed trialkylaluminum as a cocatalyst.¹ Further interests in metallocene-catalyzed polymerization arise from the production of stereoregular polymers of α -olefins,^{2,4} vinyls,⁵ and cycloolefins.⁶ More recent improvements in a synthetic challenge are the successful synthesis of polyolefin elastomer using a sandwich type of metallocene catalyst and of linear low density polyethylene by Insite[®] Technology.^{7,8} These advances may contribute to expansion of the application fields of the final products. In spite of these successful syntheses of polymeric materials,

there are still much unsolved problems to expand their potential applications because of poor interaction with other polymers in polymer blends leading to phase separation.⁹ To expand the limited end uses, metallocene-based poly(α -olefin) graft copolymer has been synthesized by a combination of free-radical polymerization.¹⁰ One of the known methodologies to modify the physical properties of polymers is the incorporation of functional groups into the polymer chain leading to the increase of compatibility with other materials by chemical reactions or physical interaction such as hydrogen bonding.¹¹

Syndiotactic polystyrene ($T_m=270$ °C) as a new engineering plastics produced by metallocene catalysis exhibits very interesting and important polymorphisms.¹²⁻¹⁴ Although it may retain an advantage in a variety of application fields because of fast re-crystallization rate,¹³ its application is still

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limited due to the incompatibility with other polymers arising from a high crystallinity. In this respect, a modification of its physical property may provide a new insight for broadening its application field. It has been reported that sulfonated syndiotactic polystyrene exhibited the reduced crystallization temperature ($T_c = 158^\circ\text{C}$ for 2 mol% sulfonation) and a little reduction (250°C) of the melting temperature.^{15,16} This phenomenon can be readily deduced by a breakdown of the high crystallinity and by an aggregates of the sulfonated group. In addition, copolymerizations of styrene with substituted styrene by homogeneous Ti-based catalysis have been reported by several research groups.¹⁷ The activities of substituted styrenes in relation to the Hammett's values to cationic d^0 titanium center have been also investigated by other groups.¹⁸ More recently, a synthetic methodology was reported to modify the physical properties of syndiotactic polystyrene via CpTiCl_2 -catalyzed copolymerization of styrene with styrenic type macromonomer having the polyisoprene backbone at the same time during this study.¹⁹

Furthermore, there is few report on the synthesis of functionalized syndiotactic polystyrene. The authors have reported that a precursor of hydroxyl-functionalized syndiotactic polystyrene can be prepared by titanocene-catalyzed copolymerization of styrene with 4-[(*tert*-butyldimethylsilyl)oxy]styrene.²⁰ It is interesting to develop new synthetic method for the synthesis of graft or block copolymer with functional groups.

In this communication, we will report the results for the synthesis of syndiotactic polystyrene carrying α, α' -disilyloxy-functional group via titanocene-catalyzed copolymerization of styrene with styrenic type macromonomer.

Experimental

Materials. Styrene (Dong Yang Chem. Co., 98%) was purified by following the literature procedures.²¹ Benzene (Dong Yang Chemical Co., reagent grade), toluene (Dong Yang Chemical Co., reagent grade), and tetrahydrofuran (Dong Yang Chem., Co. reagent) as solvents were also purified by following the procedures in the litera-

ture.²¹ 4-Vinylbenzyl chloride (Dajac, 97%) was purified by stirring over grounded calcium hydride (CaH_2 , Aldrich Chem. Co., 98%) for at least 30 h, followed by distillation into a graduated cylindrical ampule. 4,4'-Dihydroxybenzophenone (Aldrich Chemical Co. 99%) was used as a precursor for the synthesis of diphenylethylene derivative. Bis-(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2 ; Aldrich Chemical Co., 97%) and trimethylaluminum ($\text{Al}(\text{CH}_3)_3$; 2.0 M solution in toluene) were used for synthesizing the 'Tebbe' reagent as methylenating agent without further purification. *sec*-Buthyllithium (*sec*-BuLi; Aldrich Chemical Co.; 1.3 M in cyclohexane) was used as anionic initiator for the synthesis of macromonomer carrying functional group. (η^5 -Indenyl)trichlorotitanium ($(\text{Ind})\text{-TiCl}_3$; Strem Chem. Inc., 99%) and methylaluminoxane (MAO; Aldrich Chem. Co., 10 wt% solution in toluene) were used as the syndiospecific catalyst for styrene polymerization as purchased.

Synthesis of Macromonomer. 4,4'-Dihydroxybenzophenone was first converted to the α -corresponding 1,1-bis(4-*t*-butyldimethylsilyloxyphenyl)ethylene through hydroxyl group protection,²² followed by the 'Wittig-type' reaction using the Tebbe reagent, the similar reaction and purification procedures as described in the literatures.^{23,24}

Styrenic type macromonomers with a functional group was first prepared by α, ω -difunctionalization of 'living' polymers formed by alkyllithium-initiated polymerization. *sec*-BuLi-initiated polymerization of styrene was carried out in benzene at 25°C for 24 h. The poly(styryl)lithium (PSLi) was delivered into the reactor containing 4-vinylbenzyl chloride (Cl-ST)/THF solution with vigorously stirring by the break-seal delivery technique in a high vacuum line, followed by keeping the reactor at room temperature for at least 24 h ($[\text{Cl-ST}]/[\text{PSLi}] = 20/1$). Analogously, to prepare macromonomer having a functional group, *sec*-BuLi was crossover reacted with 1,1-bis(4-*t*-butyldimethylsilyloxyphenyl)ethylene in the mixture of benzene/THF (10/1, v/v) for at least 6 h, in which the diphenylethylene derivative was first converted from 4,4'-dihydroxybenzophenone after protection of the hydroxyl group using *t*-butyldimethylchlorosilane. The 1,1-bis(*t*-butyldimethylsilyloxyphenyl)hexyllithium was then used as the

anionic initiator to polymerize styrene effecting the generation of α,α' -disilyloxyphenyl-functionalized PSLi. Again, the PSLi was reacted with 4-vinylbenzyl chloride ($[\text{Cl}]/[\text{Li}] = 20/1$) at room temperature for at least 6 h, followed by termination with degassed methanol. In this process, completion of all the reactions was determined through UV/Visible spectroscopic monitoring as described in the literatures.²² The resulting products were precipitated in excess methanol and dried in vacuum oven at 40 °C for 48 h prior to characterization and use in the other reactions.

(η^5 -Indenyl)trichlorotitanium-catalyzed

Copolymerization. All the reactions were carried out in all glass, sealed reactor using break-seals and standard high techniques.²¹ Copolymerizations of styrene and the styrenic type macromonomer having the disilyloxy group or not, with the different monomer feed ratio, were performed using $(\text{Ind})\text{TiCl}_3$ in the presence of methylaluminumoxane (MAO) in toluene at 40 °C for 6 h ($[\text{Al}]/[\text{Ti}] = 2000$). After termination with acidic methanol (0.1 M HCl), the product was precipitated in excess methanol, followed by extraction via the acetone reflux using a Soxhlet apparatus at 40 °C for 30 h. The final products were dried for characterization in vacuum oven at 50 °C for at least 48 h.

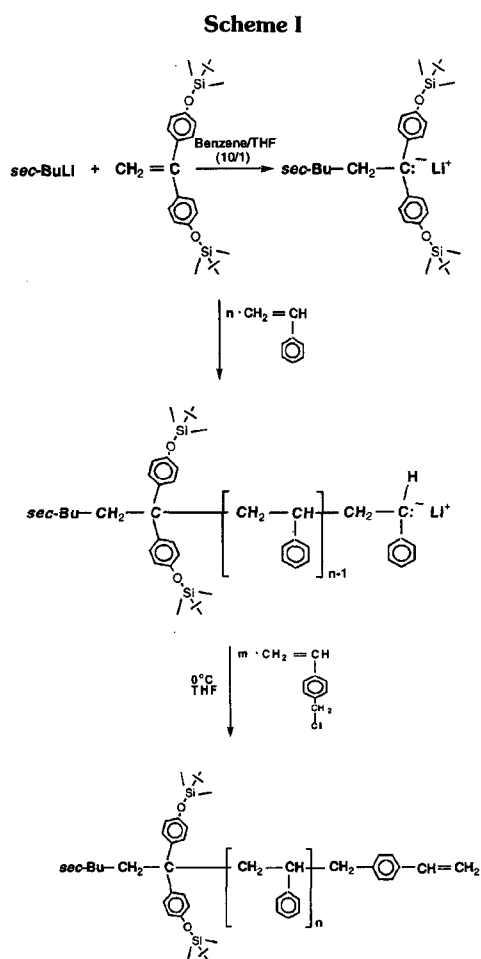
Characterization. Size exclusion chromatograms (SECs) of the macromonomers were obtained at a flow rate of 1.0 mL/min in THF at 30 °C using a Water HPLC component system equipped with five ultra- μ -Styragel[®] columns (two 10⁵, 10⁴, 10³, and 500 Å) after calibration with standard polystyrene samples (Polysciences). SECs of syndiotactic polystyrenes were obtained at a flow rate of 0.3 mL/min in *o*-dichlorobenzene as the eluent at 135 °C using a Waters 150C ALC/GPC System equipped with two columns (Styragel HT4 and HT5[™]) after calibration with standard polystyrene samples (Polysciences). ¹H- & ¹³C-NMR spectra were obtained using a Varian spectrometer (Model Gemini 200 (200 MHz)) in CDCl₃ at 25 °C for the macromonomers and a Bruker Arx 600 (600 MHz) in deuterated dichlorobenzene (Aldrich Chem. Co. 99%+) as solvent at 90 °C for the crystalline polymers. Differential scanning calorimetric (DSC) thermograms were obtained by

scanning the samples with a 20 °C/min heating rate (2nd scan) using a Perkin-Elmer DSC-7 instrument under inert N₂ gas after annealing at 300 °C for 2 min.

Results and Discussion

Synthesis of Macromonomers. Anionic synthesis of macromonomers has been well described by several research groups.²⁵⁻²⁷ The authors have already reported that functionalized macromonomers were successfully prepared through chain-end functionalization of poly(styryl)lithium or poly(isoprenyl)lithium using diphenylethylene derivatives carrying functional groups and *meta*-substituted double diphenylethylene (MDDPE).²⁸ To synthesize styrenic type macromonomer having amorphous polystyrene backbone, we followed the chain-end functionalization method in alkyllithium-initiated polymerizations. *sec*-BuLi-initiated polymerization of styrene was first performed in benzene for 24 h, followed by adding 4-vinylbenzyl chloride/THF ($[\text{Cl}]/[\text{Li}] = 20/1$, mol/mol) solution at room temperature with vigorously stirring leading to the production of styrenic type macromonomer.

In addition, diphenylethylene derivatives having a protected functional group have been found to be powerful and efficient substances for functionalization of 'living' polymers in alkyllithium-initiated polymerization.²⁹ In this respect, styrenic type macromonomer carrying a protected functional group can be prepared by following the modified procedures described in the literature.^{28,30} As shown in Scheme I, the complete formation of 1,1-bis(*t*-butyldimethylsilyloxyphenyl)hexyllithium from the reaction of *sec*-BuLi with 1,1-bis([4-(*tert*-butyldimethylsilyloxy)phenyl]ethylene can be readily determined through UV/Visible spectroscopic analysis under a high vacuum.²² The above diphenylalkyllithium can readily initiate other vinyl monomers or dienes resulting in the production of the corresponding 'living' polymer carrying α,α' -disilyloxy group. The functionalized PSLi can be reacted with 4-vinylbenzyl chloride leading to the formation of the corresponding styrene type macromonomer having α,α' -disilyloxyphenyl group. The results for the styrenic macromonomers having polystyrene backbone with or with-



out functional groups are shown in Table I. The functionalization yields for the styrene unit of both Macro PS 1 and Macro PS 2 were not over 90 mol% because of the 'Wurtz' coupling reaction via lithium-halogen exchange between poly(styryl)lithium and 4-vinylbenzyl chloride.^{30,31} The typical ¹H-NMR spectra of α -disilyloxyphenyl-functionalized polystyrene (α -Silyloxy PS) and the corresponding macromonomer (Macro PS 2) in Table I are compared in Figure 1. In Figure 1(a), the chemical shift at $\delta = 0.2$ ppm is assigned to the protons on the methyl groups adjacent the Si atom ($f = 1.84$ for silyloxy group). In Figure 1(b), the chemical shifts at $\delta = 4.9$ and 5.5 ppm are assigned to the protons on the vinyl group of the styrene unit at the chain-end. The chemical shift at $\delta = 6.4$ ppm corresponding to the proton on the methine group of the styrene unit was overlapped with the protons of the phenyl ring of polystyrene. The functionality for the styrene unit was 0.88 on the basis of ¹H-NMR spectral analysis. Figure 2 represents size exclusion chromatograms of di(silyloxyphenyl)-functionalized polystyrene and the corresponding styrenic type macromonomer. The molecular weight distributions seem to be monomodal. On the basis of the results, the di(silyloxyphenyl)-functionalized styrenic type macromonomer is found to be successfully prepared ($f = 0.88$ for the styrene unit)

Table I. The Analytical Results of Homopolymer, Functionalized Polymer, and the Corresponding Styrenic Type Macromonomers

Sample	\bar{M}_n ($\times 10^{-3}$)		PDI ^b	Functionality ^c	
	SEC	¹ H NMR ^d			
Polystyrene	5.7	5.2	1.09	-	-
Macro PS 1 ^d	6.0	5.3	1.09	-	0.72
α -Silyloxy PS ^e	3.2	4.0	1.10	1.84	-
Macro PS 2 ^f	3.5	4.2	1.09	1.84	0.88

^aThe number average molecular weight is obtained from calculation based on the initiator fragment.

^bThe molecular weight distribution data obtained from size exclusion chromatographic analysis.

^cThe data obtained from ¹H NMR spectral analysis.

^dStyrenic type macromonomer without functional group having polystyrene backbone.

^e α -Disilyloxy-functionalized polystyrene.

^fStyrenic type macromonomer carrying silyloxy functional group.

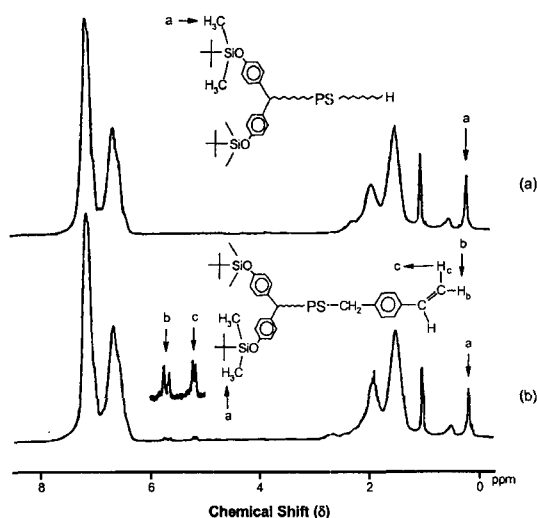


Figure 1. ^1H NMR spectra of α -di(*t*-butyldimethylsilyloxyphenyl)-functionalized polystyrene (a) and the corresponding styrene type of Macro PS 2 (b) in Table I.

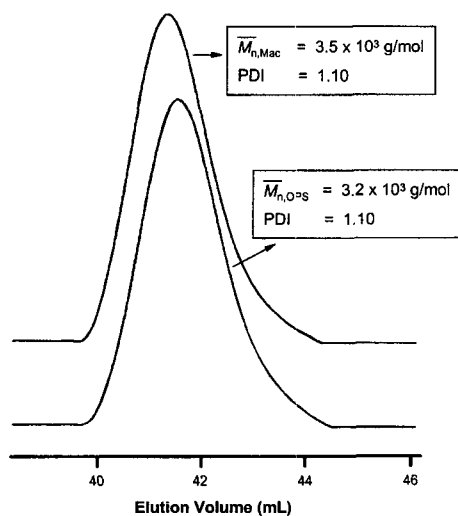
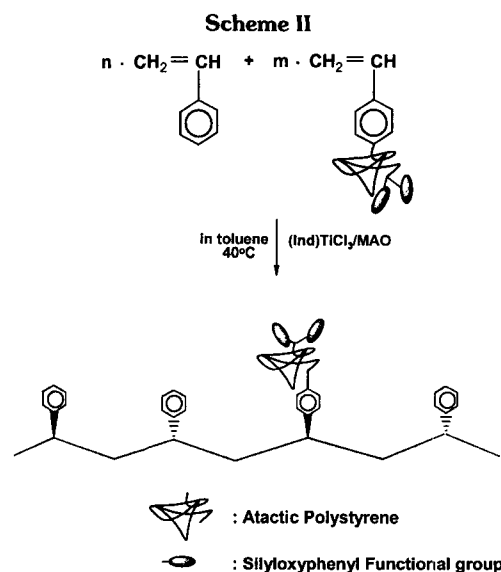


Figure 2. Size exclusion chromatograms of α -di(*t*-butyldimethylsilyloxyphenyl)-functionalized polystyrene and the corresponding styrene type of Macro PS 2 in Table I.

despite of the inclusion of α,ω -tetrakis(*t*-butyldimethylsilyloxyphenyl)-functionalized polystyrene by the 'Wurtz' coupling or α -di(*t*-butyldimethylsilyloxyphenyl)-functionalized polystyrene in the Macro PS.

(Ind)TiCl₃-catalyzed Copolymerization.

Most homogeneous Ti-catalysts have been well-



known to produce efficiently syndiotactic polystyrene and its analogues in the presence of methylaluminoxane (MAO).^{12,32} Furthermore, (Ind)TiCl₃-catalyzed copolymerization of styrene with its analogue carrying the silyloxy group has been found to produce effectively the corresponding copolymer as a precursor of hydroxyl-functionalized syndiotactic polystyrene.³³ With regard to this, we employed the (Ind)TiCl₃/MAO ([Al]/[Ti] = 2,000/1, mol/mol) catalytic system in toluene to copolymerize styrene with the styrene type of macromonomers as shown in Scheme I. The reaction conditions and their results for copolymerizations of styrene with the macromonomers are listed in Table II and Table III, respectively. Concerning the functionalities of the macromonomers ($f = 0.72$ for the Macro PS 1, $f = 0.88$ for the Macro PS 2 in Table I), some fractions of amorphous polystyrenes are inevitably included in the formed graft copolymers. In this respect, the amorphous fractions should be completely removed from the formed graft copolymers by the acetone reflux. As expected, the acetone insoluble fraction after removal of the unreacted polymers decreases with increasing the feed ratio of the Macro PS 1 as shown in Table II. Despite of not much difference between the molecular weights of the copolymers 1 and 2, the degree of incorporation of the Macro PS 1 increases with increasing

Table II. The Reaction Conditions and Characterization Results for Syndiotactic Poly(styrene- co-macromonomer)s in Toluene at 40 °C^a

Sample	Feed Ratio ^b ([St]/[M]) (g/g)	Reaction Time (h)	Yield ^c (g)	Acetone ^d Insoluble Fraction(wt%)
Copolymer 1 ^e	18.1/1.5	0.5	11.1	82
Copolymer 2 ^e	9.1/3.0	0.5	5.1	78
Copolymer 3 ^e	4.5/3.0	3.0	4.1	21
Copolymer 4 ^f	18.1/1.0	0.5	16.6	78
Copolymer 5 ^f	18.1/2.0	0.5	8.1	80
Copolymer 6 ^f	9.1/2.0	1.0	7.3	46

^a All copolymerizations were performed using (Ind)TiCl₃ (1×10⁻⁴ mol) and MAO (0.1 mol) in 300 mL toluene at 40 °C.

^b The feed ratio of styrene to macromonomer used in copolymerization.

^c The weight of polymer obtained after extraction of the crude copolymer using *o*-dichlorobenzene.

^d The insoluble fraction after extraction using acetone.

^e Polymer by copolymerization of styrene with Macro PS 1 in Table I (without functional group).

^f Polymer by copolymerization of styrene with Macro PS 2 in Table I (with functional group).

Table III. The Results for the Characterization of Poly(styrene- co-macromonomer)s Obtained from Syndiospecific Copolymerization by the (Ind)TiCl₃/MAO Catalytic System

Sample	\bar{M}_n^a (g/mol)	PDI	Macromonomer ^b Content (mol%)	# of Grafts	T_m (°C)
Copolymer 1	16,700	2.1	9.2	2.6	267
Copolymer 2	18,200	2.3	17.8	3.2	261
Copolymer 3	14,400	1.9	29.7	2.5	253
Copolymer 4	15,000	2.4	11.5	3.0	263
Copolymer 5	13,600	2.8	14.5	2.8	261
Copolymer 6	10,500	2.3	13.0	2.3	249

^a The number average molecular weight obtained by using a high temperature GPC instrument.

^b The value obtained from ¹H NMR spectroscopic analysis.

its feed ratio. Clearly, the decrease of the melting point of the copolymer in the cases of copolymers 1 and 2 as shown in Figure 3 must be attributed to the incorporation of amorphous macromonomer. Interestingly, the catalytic activity seems to be independent of the feed ratio of macromonomer and the reaction time as in the cases of copolymers 2 and 3 (see the yield). However, the molecular weight of the latter is small and the incorporation of the Macro PS 1 is much higher than that of the former. These play the major role in decreasing the melting point.

As already described in the previous publica-

tion,³³ a polar group on monomer may effect the reduction of the activity of the Group IV transition-metal center. With regard to this, analogous results are expected in this experiment utilizing the macromonomer carrying the silyloxy group. As described in the previous section, the Macro PS 2 may contain amorphous polystyrenes including α -disilyloxy- or α,ω -tetrakis(silyloxy)-functional groups without the styrene unit at the chain-end ($f = 0.88$ for the styrene unit). With regard to this, the decrease of the catalytic activity in the (Ind)TiCl₃-catalyzed copolymerization with styrene may be attributed to the silyloxy group concerning the 14-

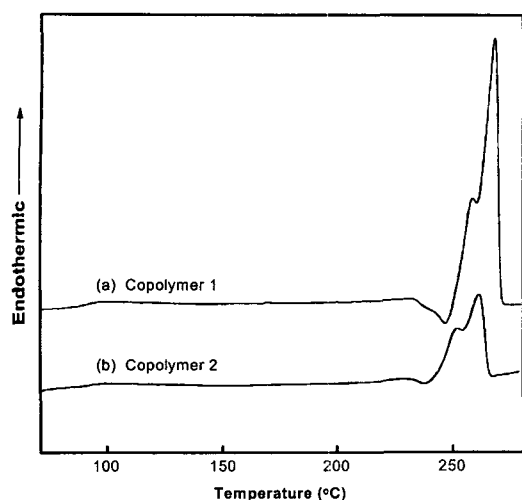


Figure 3. DSC thermograms of crystalline polystyrene-g-amorphous polystyrene without the silyloxy group: (a) Copolymer 1 and (b) Copolymer 2 in Table II.

electron valence of cationic d^0 titanium center. The production yield of the copolymer 5 is much lower compared to that of the copolymer 4 irrespective of the acetone insoluble fraction as shown in Table II as described elsewhere.³³ It may be rationalized by the factors that the silyloxy group effects the reduction of the catalytic activity via the formation of complex with cationic Ti atom but also this copolymerization seems to be a kinetic-controlled reaction arising from steric hindrance by the *t*-butyldimethylsilyloxy group.³³ On the other hand, even in the cases using the Macro PS 1 without the silyloxy group, most production yields of the graft copolymers 1~3 are lower than those of the graft copolymers 4~6 independent of the reaction time as shown in Table II. These lower yields may be due to the higher feed ratios of the macromonomer concerning the diffusion-controlled reaction. Analogous phenomenon has been observed in radical copolymerization using macromonomer.³⁴

Despite of not much differences on the production yield and the macromonomer content in the formed product between copolymers 5 and 6 as shown in Table II, the great melting point reduction of the graft copolymer 6 seems to arise from the lower molecular weight. This informs that the crystallinity of the graft copolymer 6 must be rela-

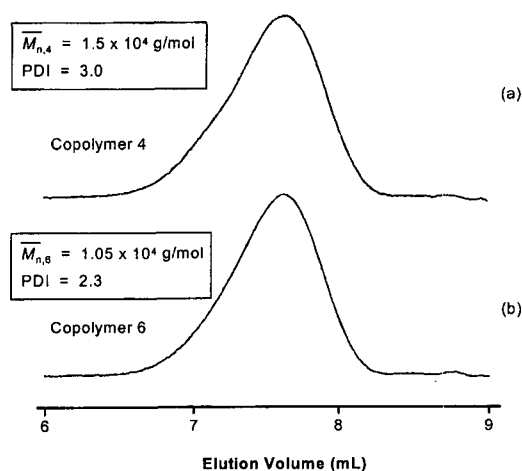


Figure 4. SECs of crystalline polystyrene-g-amorphous polystyrenes carrying the silyloxy group in the grafted chain: (a) Copolymer 4 and (b) Copolymer 6 in Table III.

tively lower than that of the graft copolymer 5 concerning the similar macromonomer content. Furthermore, concerning all the reaction conditions, the lower production yield of the graft copolymer 6 compared to the copolymer 4 must arise from a higher feed ratio of the macromonomer leading both the decrease of the catalytic activity by lone pair electron on the silyloxy groups and the kinetic-controlled reaction.

A polar group has been reported to effect profoundly the catalytic activities arising from the formation of a dative σ -bond between the polar group and cationic d^0 transition-metal center concerning the 14-electron structure of the neutral Group IV transition-metals.³³ With regard to this, the (Ind)TiCl₃-catalyzed copolymerizations of styrene with the Macro PS 2 seem to lead to the production of a blocky type of a graft copolymer arising from a higher local concentration of the Macro PS 2 in the case of the copolymer 6 (not confirmed).³³ Figure 4 is the comparison of SECs of the copolymers 4 and 6. Although the molecular weight of the copolymer 4 is larger than that of the copolymer 6, the multimodal distribution is observed. The rationale is that a low concentration of the silyloxy group in the case of the copolymer 4 effects the formation of the growing active species with different activities leading to the different chain lengths even in homogeneous condi-

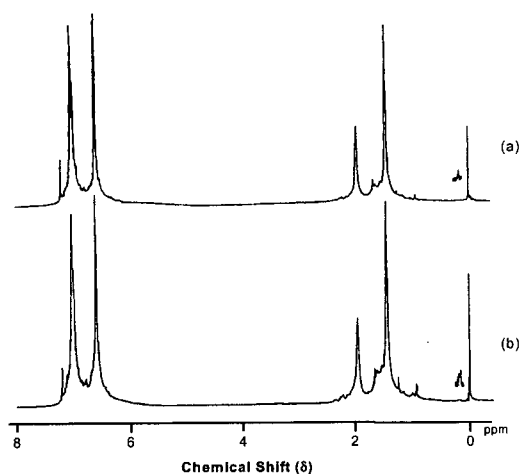


Figure 5. ^1H NMR spectra of crystalline polystyrene-g-amorphous polystyrene carrying the silyloxy groups in the grafted chain: (a) Copolymer 4 and (b) Copolymer 6 in Table II.

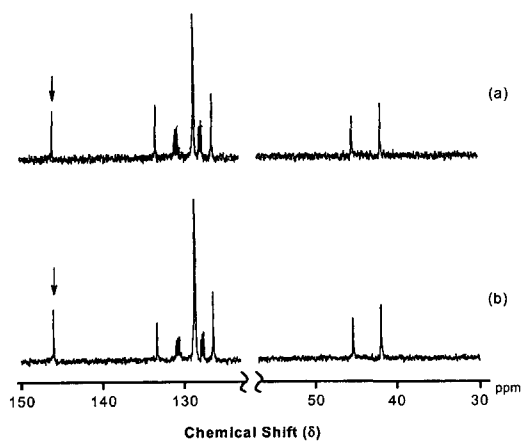


Figure 6. ^{13}C NMR spectra of crystalline polystyrene-g-amorphous polystyrenes carrying the silyloxy group in the grafted chain: (a) Copolymer 4 and (b) Copolymer 6 in Table III.

tions. However, in the case of the copolymer 6, a higher local concentration of the Macro PS 2 around cationic Ti-metal center arising from the electron-donating effect of the silyloxy group seems to contribute to the generation of the homogeneous growing species with a same activity. Figures 5 and 6 represent the ^1H and ^{13}C NMR spectra of the copolymer 4 and 6 in Table II, respectively. In Figure 5, the sharp spectra in the chemical shift range of 6.8~7.5 ppm inform indi-

rectly that the phenyl ring on the formed copolymers still retains the racemic pentad (*rrrr*) configuration leading to a crystalline phase. The absorption peak at $\delta = 0.2$ ppm is clearly assigned to the protons on the methyl group adjacent to the Si atom ($-\text{OSi}(t\text{-C}_4\text{H}_9)(\text{CH}_3)_2$). Furthermore, in Figure 6, the very sharp absorption near $\delta = 146$ ppm corresponding to the C-1 atom on the phenyl ring of styrene and its area reveal the racemic pentad configuration of the formed copolymer.³³ On the base of the results, the (Ind)- TiCl_3 -catalyzed copolymerization of styrene with the Macro PS 2 produces crystalline polystyrene-g-amorphous polystyrene as a precursor of hydroxyl-functionalized syndiotactic polystyrene. It can be concluded that titanocene-catalyzed copolymerization of styrene with macromonomers carrying a protected polar group may be a method to produce the corresponding graft copolymer to modify syndiotactic polystyrene without a great loss of the physical properties.

Conclusion

The styrenic type macromonomer carrying a silyloxy-functional group was successfully synthesized via the chain-end functionalization in alkyl-lithium-initiated polymerization of styrene. The functionalization yields were 92 and 88 mol% for the silyloxy group and the styrene unit, respectively. Even concerning the diffusion-controlled reaction, the unfunctionalized fraction in the formed macromonomer seemed to affect to the reaction rate in the (Ind) TiCl_3 -catalyzed copolymerization of styrene with the macromonomer in the presence of MAO. The silyloxy group contributed to the reduction of the activity of cationic d^0 transition-metal center concerning the 14-electron structure of the Group IV transition-metals. The (Ind) TiCl_3 -catalyzed copolymerizations of styrene with macromonomers carrying a protected polar group produce effectively the corresponding graft copolymer to modify syndiotactic polystyrene.

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References

- (1) H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, **18**, 99 (1980).
- (2) H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.*, **34**, 1143 (1995).
- (3) W. Kaminsky, *Macromol. Chem. Phys.*, **197**, 3907 (1996).
- (4) (a) R. W. Barnhart and G. C. Bazan, *J. Am. Chem. Soc.*, **120**, 1082 (1998); (b) L. Resconi, F. Piemontesi, I. Camurati, O. Scedmeijer, I. E. Nifantev, P. V. Ivchenko, and L. G. Kuzmina, *J. Am. Chem. Soc.*, **120**, 2308 (1998).
- (5) (a) N. Ishihara, M. Kuramoto, and M. Uoi, *Macromolecules*, **21**, 3356 (1988); (b) D. J. Duncalf, H. J. Wade, C. Waterson, P. J. Derrick, D. M. Haddleton, and A. McCamley, *Macromolecules*, **26**, 6399 (1996); (c) Y. Li, D. G. Ward, S. S. Reddy, and S. Collins, *Macromolecules*, **30**, 1875 (1997); (d) A. Zambelli, L. Oliva, and C. Pellecchia, *Macromolecules*, **22**, 2129 (1989).
- (6) (a) S. Collins and W. M. Kelly, *Macromolecules*, **25**, 233 (1995); (b) W. M. Kelly, S. Wang, and S. Collins, *Macromolecules*, **30**, 3151 (1997); (c) M. Arndt and W. Kaminsky, *Macromol. Symp.*, **95**, 167 (1995).
- (7) R. Kravchenko, A. Masood, R. M. Waymouth, and C. L. Myers, *J. Am. Chem. Soc.*, **120**, 2039 (1998).
- (8) (a) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, and J. E. Bercaw, *J. Am. Chem. Soc.*, **114**, 4623 (1994); (b) D. Schwank, *Modern Plastics Int.*, **Aug.**, 33 (1993).
- (9) (a) T. C. Chung and D. Rhubright, *J. Polym. Sci.; Part A; Polym. Chem.*, **33**, 829 (1996); (b) T. C. Chung, *Macromolecules*, **21**, 865 (1988).
- (10) U. M. Stehling, E. E. Malmstrom, R. M. Waymouth, and C. J. Hawker, *Macromolecules*, **31**, 4396 (1998).
- (11) B. De Roover, M. Sclavons, V. Carlier, J. Devaux, R. Legras, and A. Momtaz, *J. Polym. Sci.; Part A; Polym. Chem.*, **33**, 829 (1996).
- (12) M. Ishihara, *Macromol. Symp.*, **89**, 553 (1995).
- (13) E. J. C. Kellar, C. Galiotis, and E. H. Andrews, *Macromolecules*, **29**, 3515 (1996).
- (14) W. Kaminsky and Y.-W. Park, *Macromol. Rapid Commun.*, **16**, 343 (1995).
- (15) Z. Su, X. Li, and S. L. Hsu, *Macromolecules*, **27**, 2635 (1994).
- (16) E. Bruce Orier, D. J. Yontz, and R. B. Moore, *Macromolecules*, **26**, 5157 (1993).
- (17) (a) K. Soga and T. Monoi, *Macromolecules*, **22**, 3823 (1989); (b) C. Pellecchia, D. Pappalardo, M. Darco, and A. Zambelli, *Macromolecules*, **29**, 1158 (1996).
- (18) N. Tomostu, N. Ishihara, T. H. Newman, and M. T. Malanga, *J. Mol. Catal. A: Chem.*, **128**, 167 (1998).
- (19) K. Endo and K. Senoo, *Macromol. Rapid Commun.*, **19**, 563 (1998).
- (20) K. H. Kim, W. H. Jo, S. Kwak, K. U. Kim, and J. Kim, *Macromol. Rapid Commun.*, **20**, 175 (1999).
- (21) M. Morton and L. J. Fetters, *Rubber Chem. Technol.*, **48**, 359 (1975).
- (22) J. C. Cho, K. U. Kim, K. H. Kim, H. J. Kim, J. Kim, M. S. Chun, C. H. Lee, and W. H. Jo, in *Abstract of International Symposium on Ionic Polymerization, IP '97*, Paris, 1997, pp 206.
- (23) S. H. Pine, G. S. Shen, and H. Hoang, *Synthesis*, 165 (1990).
- (24) J. Kim, S. Kwak, K. U. Kim, K. H. Kim, J. C. Cho, W. H. Jo, D. Lim, and D. Kim, *Macromol. Chem. Phys.*, **199**, 2185 (1998).
- (25) G. O. Schulz and R. Milkovich, *J. Appl. Polym. Sci.*, **27**, 4773 (1982).
- (26) P. Rempp and F. Franta, *Adv. Polym. Sci.*, **58**, 1 (1984).
- (27) R. P. Quirk and J. Kim, in *Ring-Opening Polymerization: Mechanism, Catalysis, Structure, Utility*, D. J. Brunelle, Ed., Hanser Publisher, Munich, 1993, Chap. 9, pp 263.
- (28) J. Kim, J. C. Cho, K. H. Kim, K. U. Kim, W. H. Jo, and R. P. Quirk, in *Functional Polymers: Modern Synthetic Methods and Novel Structure; ACS Symp. Series # 704*, A. O. Patil, D. N. Schulz, and B. M. Novak, Eds., Am. Chem. Soc., Washington, D. C., 1998, Chap. 7, pp 85.
- (29) R. P. Quirk, *Anionic Synthesis of Polymers with Functional Groups*, in *Comprehensive Polymer Science*, G. Allen, S. L. Aggarwal, and S. Russo, Eds., Pergamon Press, Seoul, 1992, 1st Suppl. Vol., pp 83.
- (30) R. Asami, M. Takai, and H. Hanahata, *Macromolecules*, **16**, 628 (1983).
- (31) B. J. Wakefield, *Organolithium Method*, Academic Press, New York, 1988, pp 107.
- (32) J. Kim, K. H. Kim, J. C. Cho, S. Kwak, K. U. Kim, W. H. Jo, H. S. Yoon, and D. Lim, *J. Polym. Sci.; Part A; Polym. Chem.*, **36**, 1733 (1998).
- (33) K. H. Kim, W. H. Jo, S. Kwak, K. U. Kim, S. S. Hwang, and J. Kim, *Macromolecules*, **32**, 8703 (1999).
- (34) G. O. Schulz and R. Milkovich, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1633 (1984).