Macromolecules **1999,** *32,* 8703−8710

Synthesis and Characterization of Poly(styrene-*co*-4-[(*tert*-butyldimethylsilyl)oxy]styrene) as a Precursor of Hydroxyl-Functionalized Syndiotactic Polystyrene

Keon Hyeong Kim,[†] Won Ho Jo,[†] Soonjong Kwak,[‡] Kwang Ung Kim,[‡] Seung Sang Hwang,[‡] and Jungahn Kim*,[‡]

Hyperstructured Organic Materials Research Center, Seoul National University, Seoul, Korea, and Polymer Hybrids Center, Korea Institute of Science and Technology, P.O. Box 131 Cheongryang, Seoul, Korea

Received June 28, 1999; Revised Manuscript Received October 19, 1999

ABSTRACT: The ligand effects of homogeneous Ti-based catalysts for the copolymerization of styrene ([M$_1$]) with 4-[(*tert*-butyldimethylsilyl)oxy]styrene (TBDMSS; [M$_2$]) were investigated by the UV/visible spectroscopic analysis. Concerning the higher yields from the copolymerization of styrene with TBDMSS, the half-sandwich type of titanocene having π-ligands compared to titanium (IV) butoxide (Ti(OBu)$_4$) having σ-ligands was a more effective catalysts. The silyloxy group exhibiting a negative σ value in the Hammett $\sigma-\rho$ relationship reduced the activities of titanocenes. The stronger electron-donating substituent on the π-ligand leading to the increase in the catalytic activity in syndiospecific polymerization of styrene contributed to the decrease of the reactivity of the "cationlike" metal center due to both electronic and steric effects. The reactivity ratios, r_1 and r_2, in the η^5-indenyl trichlorotitanium ((Ind)TiCl$_3$)-catalyzed copolymerization of styrene with TBDMSS in the presence of methylaluminoxane (MAO) ([Al]/[Ti] = 2000) were 0.997 and 7.27 from the evaluation of Finmann and Ross, respectively. The r_1r_2 product value (7.25) indicates that a block type of copolymer may be produced in a relatively high feed range of TBDMSS to styrene.

Introduction

One of the useful and interesting products prepared via homogeneous group IV transition-metal catalysis including the MAO-free catalytic system is syndiotactic polystyrene.[1] A variety of homogeneous Ti-based catalysts involving σ-ligands or π-ligands exhibit different activities yet are particularly effective among the group IV metals in generating the syndiotactic configuration in polymerizations of styrene and its analogues, depending upon the reaction conditions.[2] The syndiotactic polymers or copolymers retain their unique physical properties depending upon their structural conformations. The potential for the unique polymorphism and the physical properties of syndiotactic polystyrene has encouraged the development of new polymerization processes.[3]

The synthesis of new syndiotactic polystyrene-based block and functionalized polymers may overcome a limited end-use of syndiotactic polystyrene analogues. Up until now, no synthetic methods of syndiotactic polystyrene-based block copolymers have been reported because of a lack of a "living" nature in the active species in the group IV metallocene-catalyzed polymerization. There are few reports on functionalized syndiotactic polystyrenes except for those with sulfonate or hydroxyl functionalities.[4−7] We believe copolymerization of styrene with functionalized styrenes may be the best method to produce the correspondingly functionalized copolymers. Concerning the Hammett σ value,[2b] the reactivity ratios in homogeneous Ti-catalyzed copolymerizations of styrene to substituted styrenes have been reported by means of the evaluation of Finemann and Ross following ^{13}C NMR spectroscopic analysis of the structural conformations.[8−10] It has also been reported that both the production yield and the structural conformation of the formed copolymers revealed a great dependency on the reaction conditions.[8b] With these observations, styrene analogues incorporated into a formed product may play an important role in controlling the physical property arising from a change of the structural conformation. Thus, a loss of syndiotacticity in a functionalized copolymer may not expand the limited end-use of syndiotactic polystyrene. To control the physical properties and the structural conformation, it is important to investigate the reactivity ratios of styrene and 4-[(*tert*-butyldimethylsilyl)oxy]styrene (TBDMSS), as a precursor of hydroxyl-functionalized styrene, in the homogeneous Ti-catalyzed copolymerization processes.

In this communication, we report the ligand effects on the catalytic reactivity in relation to the production yield using homogeneous Ti-based catalysts. The result for the reactivity ratios of styrene and TBDMSS will also be presented from the (Ind)TiCl$_3$-catalyzed copolymerizations in the presence of methylaluminoxane to optimize the production of the precursor for the preparation of hydroxyl-functionalized syndiotactic polystyrene.

Experimental Section

1. Materials. Styrene (Junsei Chemical Co., reagent grade) and toluene (Oriental Chemical Co., reagent grade) were purified by following the procedures reported elsewhere.[11] 4-Hydroxybenzaldehyde (Aldrich Chemical Co., 98%) and 4-acetoxystyrene (Aldrich Chemical Co., 96%) were used for the preparation of the precursor of hydroxyl-functionalized monomer. To synthesize the "Tebbe" reagent,[12] trimethylaluminum (Al(CH$_3$)$_3$; Aldrich Chemical Co., 2.0 M in toluene) and bis(cyclopentadienyl)titanium dichloride (Cp$_2$TiCl$_2$; Aldrich Chemical Co., 97%) were used as purchased without further

---

[†] Seoul National University.

[‡] Korea Institute of Science and Technology.

10.1021/ma991036i CCC: $18.00

purification. (η^5-Indenyl)trichloro-titanium ((Ind)$TiCl_3$; Strem Chemical Co., 99%), cyclopentadienyltitanium trichloride (Cp-$TiCl_3$; Aldrich Chemical Co., 97%), pentamethylcyclopentadienyltitanium trichloride (Cp*$TiCl_3$; Aldrich Chemical Co., 98%), and titanium (IV) butoxide ($Ti(OBu)_4$; Aldrich Chemical Co., 99%) were used as the syndiospecific catalysts without purification. Methylaluminoxane (MAO; Aldrich Chemical Co., 10 wt % in toluene) was purchased as cocatalyst and used without further purification.

2. Preparation of TBDMSS. 4-Hydroxybenzaldehyde was converted to TBDMSS by following the procedures described elsewhere.[7] Alternatively, TBDMSS was synthesized using authentic 4-acetoxystyrene by following the procedures described in the literature.[13] The yields were over 95 mol % on the basis of the incipient amount of the precursor used. The TBDMSS was further purified by double distillation at 85 °C on a high-vacuum line and then stored in an ampule.

3. Copolymerizations of Styrene with TBDMSS. The homogeneous Ti-catalyzed copolymerizations of styrene with TBDMSS were carried out under high vacuum at 50 °C for 60 min by following the same manner as described elsewhere.[11] First, the ampules of the (Ind)$TiCl_3$ toluene solution and MAO solution were made (1.0×10^{-5} mol [Ti], [Al]/[Ti] = 2000) in a high-vacuum line. The styrene and TBDMSS ampules were made prior to use, and the catalyst ampules were attached to a round-bottom flask (1 L) using a hand torch, followed by attaching to a high-vacuum line and evacuation. Toluene (50 mL) was distilled into the reactor, followed by adding a required amount of styrene and TBDMSS. MAO was delivered into the reaction solution using a break-seal technique in a high-vacuum line, followed by stirring the solution for at least 10 min and adding the catalyst solution. The solution was kept at 50 °C for 60 min with stirring, followed by termination with a 0.1 M HCl−methanolic solution. The same procedure was utilized in the Cp$TiCl_3$-, Cp*$TiCl_3$-, and the $Ti(OBu)_4$-catalyzed copolymerizations in the presence of methylaluminoxane ([Al]/[Ti] = 2000 for titanocenes, [Al]/[Ti] = 500 for $Ti(OBu)_4$). The (Ind)$TiCl_3$/MAO-catalyzed copolymerizations were carried out in the same manner with different feed ratios of styrene to TBDMSS ([Ti] = 1.0×10^{-5} mol, [Al]/[Ti] = 2000). The copolymers were dried in a vacuum oven at 40 °C for at least 48 h.

4. Characterization. The number-average molecular weight and the molecular weight distribution were characterized by size-exclusion chromatographic analysis using a Waters 150C ALC/GPC System equipped with two columns (Styragel HT4 and HT5) at a flow rate of 0.3 mL/min with *o*-dichlorobenzene as the eluent at 140 °C and at a flow rate of 1.0 mL/min in THF at 30 °C using a Waters HPLC component system equipped with a five ultra-μ-Styragel columns (two 10^5 and one each of 10^4, 10^3, and 500 Å) after calibration with standard polystyrene samples (Polymer Laboratories). The UV/visible spectroscopic analysis was performed in toluene at 25 °C using a Hewlett-Packard 8453 diode array spectrophotometer with a 0.5 cm UV cell. The UV/visible absorption spectra were obtained by following the procedures under high vacuum as described in the literature.[11] ^{1}H and ^{13}C NMR spectra were obtained on a Varian spectrometer (model Gemini 200 (200 MHz)) in $CDCl_3$ at 25 °C for the monomeric materials and a Varian UNITY plus-600 (600 MHz) in $C_2D_4Cl_2$ at 60 °C for the polymers. Differential scanning calorimetric (DSC) thermograms were obtained on a Perkin-Elmer DSC-7 instrument. The samples were annealed at 300 °C for 2 min, followed by scanning at 20 °C/min (second scan) under inert N_2 gas.

Results and Discussion

1. Activities of Homogeneous Ti-Based Catalysts. To synthesize hydroxyl-functionalized syndiotactic polystyrene copolymers, we used TBDMSS prepared via the "Wittig-type" reaction of 4-hydroxybenzaldehyde using the Tebbe reagent after protecting the hydroxyl group, as described elsewhere.[7,12] We also employed 4-acetoxystyrene as a precursor for the preparation of the styrene derivative carrying the hydroxyl group. The direct copolymerization of styrene with 4-acetoxystyrene did not produce the corresponding copolymers because of saponification or transesterification of the acetoxy group with organotitanium resulting in loss of the catalytic activity.[14]

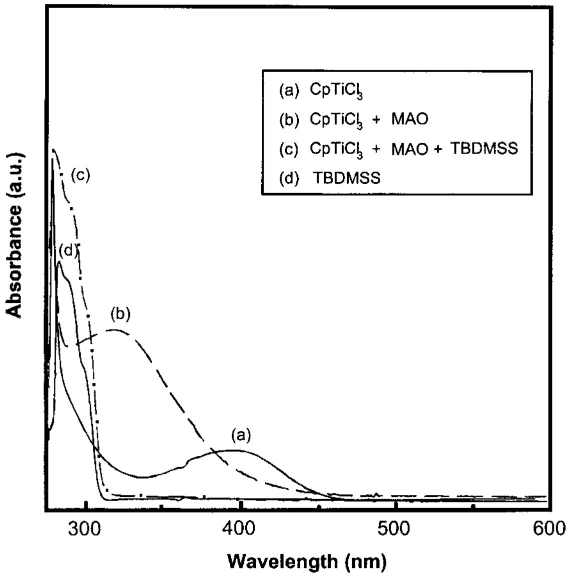


Figure 1. UV/visible spectra of the following: Cp$TiCl_3$, Cp$TiCl_3$/MAO, Cp$TiCl_3$/MAO/TBDMSS, and TBDMSS in toluene.

We have previously reported a relationship between the electronic spectral changes of homogeneous Ti-based catalysts depending on the concentration of methylaluminoxane (MAO) as cocatalyst and their activities.[11] As expected, the *hypsochromic* shift of the absorption maximum from $\lambda_{max} = 400$ to near 330 nm on adding MAO is also observed in this copolymerization system shown in Figure 1a,b. However, as shown in Figure 1c, a large excess addition of TBDMSS into the Cp$TiCl_3$/MAO solution ([TBDMSS]/[Ti] = 400/1) led to a remarkably hypsochromic shift (blueshift) of the absorption maximum at $\lambda_{max} = 330$ nm to the ultraviolet region ($\lambda_{max} = 286-296$ nm). The final electronic spectrum seems to be identical to the TBMDSS shown in Figure 1d. One possibility for this electronic spectral change may be that the alkylated cationlike metal center is fully saturated by complexation with the silyloxy group leading to a high local concentration of the TBDMSS. The electronic spectral change, resembling that of TBDMSS, of the complex presumably infers a removal of the longer conjugation between the Ti center and the η^5-Cp ligand. Concerning the 14-electron valence of Group 4 transition metals, no detection of the adsorption maximum at $\lambda_{max} = 330$ nm may be attributed to an η^5-cyclopentadienyl ring slippage, resulting in the generation of an η^1-C_5H_5 or η^3-C_5H_5 complex similar to the cases of indenyl or cyclopentadienyl *d*-block metal complexes.[15] On the other hand, a higher local concentration of the TBDMSS monomer around Ti-active center may give rise to a fast polymerization rate. The bulky silyloxy group may govern kinetically the reaction leading to a decrease of the reaction rate. Practically, Cp$TiCl_3$ seemed to be the most efficient catalyst with regards to the catalytic activity, irrespectively of the molecular weights of the copolymers, as shown in Table 1. This adverse order of the catalytic activities in

Table 1. Homogeneous Ti-Catalyzed Copolymerizations of Styrene and TBDMSS with the Mole Ratio of 98/2 in Toluene at 50 °C for 1 h[a]

copolym.	catalyst ($\times 10^{-5}$ mol)	[Al]/[Ti] (mol/mol)	activity[b]	incorp. TBDMSS (mol %)	$\bar{M}_n$[c] (PDI)	T_m (°C)
A[d]	Ti(OBu)$_4$ (1.0)	500/1	16	9.8	[e]	[f]
B[g]	CpTiCl$_3$ (1.0)	2000/1	71	2.5	8 000 (2.1)	243
C[h]	Cp*TiCl$_3$ (1.0)	2000/1	43	3.3	22 000 (2.0)	235
D[i]	(Ind)TiCl$_3$ (1.0)	2000/1	23	2.3	12 000 (2.1)	245

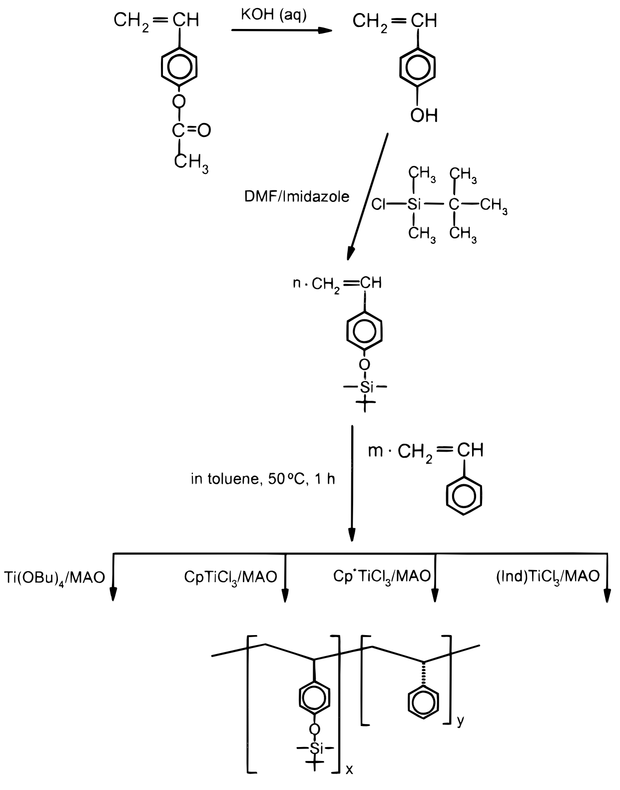
[a] Catalyst: 1.0×10^{-5}; MAO (0.02 mol, 6 mL) in 50 mL of toluene. The mole feed ratio of styrene to TBDMSS was 0.2/0.004. [b] In kilograms per mole of Ti per hour. [c] The number-average molecular weight obtained after calibration with the polystyrene standard sample. [d] Titanium tetrabutoxide-catalyzed copolymerization. [e] Multimodal. [f] Not measured. [g] Cyclopentadienyl trichlorotitanium-catalyzed copolymerization. [h] Pentamethylcyclopentadienyl trichlorotitanium-catalyzed copolymerization. [i] Indenyl trichlorotitanium-catalyzed copolymerization.

syndiospecific polymerization of styrene must arise from a kinetically controlled reaction.

Few methods to prepare functionalized syndiotactic polystyrenes have been reported.[4−7] As already described, copolymerization of vinyl monomers carrying functional groups is the best method to prepare the functionalized polymer. In this regard, the results for the copolymerization of styrene with styrenic type macromonomers to produce syndiotactic poly(styrene-*g*-isoprene) using the syndiospecific CpTiCl$_3$/MAO catalyst have been reported by others.[16] The authors have also synthesized syndiotactic graft polystyrenes carrying side-chain functional groups by copolymerization of styrene with α,α′-disilyloxy-functionalized macromonomers using the (Ind)TiCl$_3$/MAO catalyst.[17]

With a view to practicability, it would be useful directly to prepare hydroxyl-functionalized syndiotactic polystyrene. However, only preliminary results for the copolymerization of styrene with TBDMSS using the (Ind)TiCl$_3$/MAO catalyst have been reported.[7] Therefore, to investigate the most effective catalytic system, copolymerizations of styrene with TBDMSS using a variety of homogeneous Ti-based catalysts were carried out in toluene at 50 °C for 1 h in the presence of MAO, as shown in Scheme 1. All reaction conditions and the characterization results are listed in Table 1.

Scheme 1



Poly(styrene - *co*- 4-[(*t*-butyldimethylsilyl)oxy]styrene)

Analogous to the preparation of syndiotactic polystyrene,[1,2,12] the Ti(OBu)$_4$/MAO catalyst having only σ-ligands ([Al]/[Ti] = 500) exhibits a lower production than the half-sandwich titanocene catalysts shown in Table 1. From a mechanistic point of view, in the former case, not only the easier supplementation of the electron deficiency but also steric hindrance by the silyloxy group are main key factors that contribute to reduce the catalytic activity. In addition, the higher incorporation of the TBDMSS in the copolymer is due to not a higher reactivity but a higher local concentration concerning the dative bond formation between the silyloxy group and the alkylated active Ti center (see Table 1). Furthermore, the *tert*-butyldimethylsilyloxy group seems to make this catalytic system produce complicated metal-active sites, which will be discussed in more detail in relation to the SEC results.

On the other hand, it is well-known that the catalytic activities of half-sandwich titanocenes increase with the ratio [Al]/[Ti].[1,18] Electron-donating substituents on the π-ligands such as methyl, alkylsilyl, or phenyl groups effect the catalytic activity in the titanocene-catalyzed polymerization of styrene.[1,2b] In this respect, the production yields are expected to be dependent on the type of the ligand in the half-sandwich titanocene-catalyzed copolymerization systems. The electron-donating substituents on the ligand reduce the catalytic activity due to the electronic and the steric effects, as shown in Table 1. The TBDMSS incorporations determined by the ^{1}H NMR spectroscopic analysis shown in Figure 2 were not much different from each other in Table 1 (see copolymers B−D). However, the composition of copolymer A produced by Ti(OBu)$_4$ showed a great difference (9.8 mol % incorporation) at the same feed ratio within a limited conversion. One possible rationale is due to the existence of species very active to TBDMSS monomer among several active species generated from the Ti(OBu)$_4$ catalyst, depending upon the MAO concentration shown in Figure 3a.[11] Another is due to a high local concentration of TBDMSS around the Ti center arising from electronic effect of the silyloxy group. In the cases of the half-sandwich titanocenes, even though all the copolymers show the monomodal distributions shown in Figure 3, both the molecular weights and the production yields show a great difference in the copolymeriza-

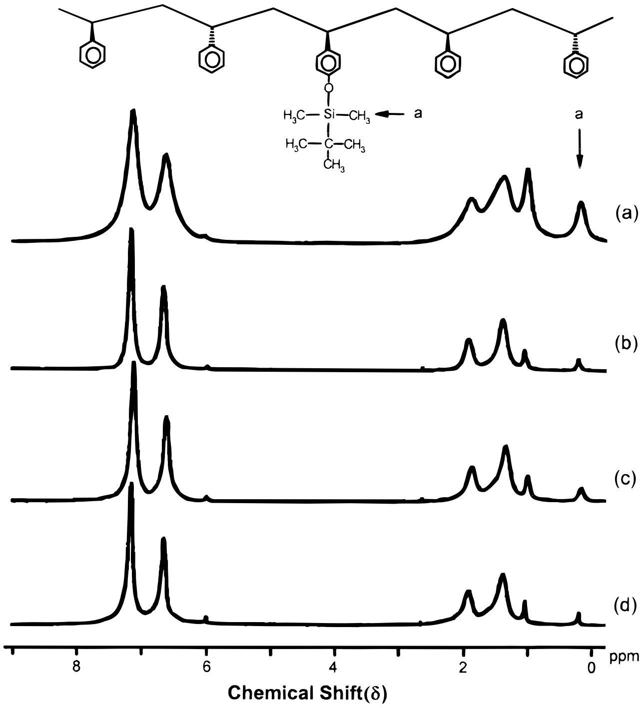


Figure 2. Comparison of ^{1}H NMR spectra of poly(styrene-*co*-4-[(*tert*-butyldimethylsilyl)oxy]styrene) prepared by using (a) Ti(OBu)$_4$, (b) CpTiCl$_3$, (c) Cp*TiCl$_3$, and (d) (Ind)TiCl$_3$ in the presence of MAO (see Table 1).

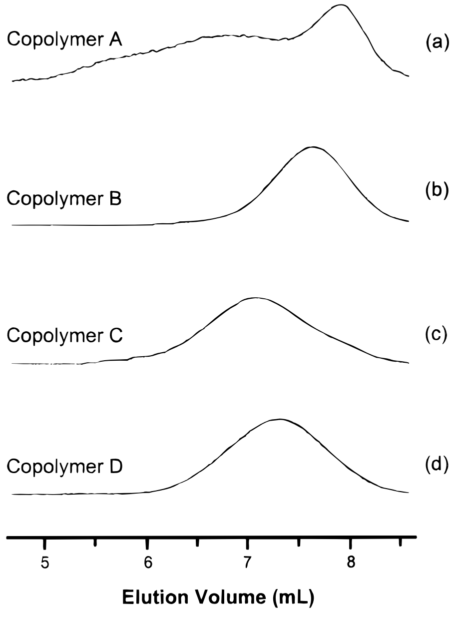


Figure 3. Comparison of SECs of the copolymers synthesized by homogeneous Ti-catalyzed copolymerizations of styrene with TBDMSS in toluene at 50 °C: (a) copolymer A by Ti(OBu)$_4$, (b) copolymer B by CpTiCl$_3$, (c) copolymer C by Cp*TiCl$_3$, and (d) copolymer D by (Ind)TiCl$_3$ (see Table 1).

tions under the same reaction conditions as shown in Table 1. The higher TBDMSS incorporations in the formed copolymers in relation the feed ratio are due to a fast reaction rate of TBDMSS compared to styrene within a limited conversion (short reaction time). The result for the production yields implies that the half-sandwich titanocene-catalyzed copolymerizations are far more affected by the kinetic-controlled mechanism compared to the effect on Ti(OBu)$_4$. For instance, the reaction rate seems to be mainly controlled by steric hindrance. Even under the same reaction conditions, each active site may experience a different equilibrium rate between fast chain transfer by α-agostic or β-agostic interaction and insertion of monomer.[19] Because the local concentration of monomer carrying the polar group near the cationlike metal center seems to be high, as illustrated in Figure 1, the relatively low feed of the TBDMSS (2 mol %) may lead to its 100% incorporation into the polymer chain during 1 h of the reaction time (not for the styrene monomer). Without any side reactions such as cyclopentadienyl ring slippage, the half-sandwich titanocenes can generate "single-site" active species, which can form a monomodal polymer distribution. However, production of a blocky type of copolymer exhibiting a lower melting point with increases in the feed ratio of the TBDMSS to styrene can be completely ruled out because of a higher local concentration of the TBDMSS. Similarly, a locally heterogeneous reaction in organolithium-initiated copolymerization of styrene with dienes in cyclohexane produced blocky types of copolymers, in which the diene block segments were first formed despite the low reactivities of dienes compared to those of styrene.[20] This rationale is due to a higher local concentration of diene around the growing active species arising from π-electron complexation with lithium.

2. Reactivity Ratio. Reactivity is greatly influenced by the reaction conditions, for instance, solvent, temperature, and catalysts. It is well-known that the (Ind)-TiCl$_3$-catalyzed syndiospecific polymerization of styrene provided the highest activity (9.6 kg/Ti mmol^{-1} M^{-1} h^{-1} for (Ind)TiCl$_3$ with [Al]/[Ti] = 2000 [21]). Furthermore, this catalyst was found to be relatively insensitive to the reaction temperature, concentration, and the [Al]/[Ti] ratio.[21] With regard to this, we employed the (Ind)TiCl$_3$/MAO catalyst to determine the reactivity ratios of styrene (M$_1$) and TBDMSS (M$_2$). It has been reported that the r_1r_2 product in the copolymerization of styrene (M$_1$) with *p*-methoxystyrene (M$_2$) using the syndiospecific TiBz$_4$/MAO catalyst exhibited a very high value.[8b] Concerning this high value, the authors saw no evidence of random copolymerization of the two monomers.[8b] The (Ind)TiCl$_3$-catalyzed polymerization of TBDMSS, analogous to *p*-methoxystyrene, produced amorphous polymer under similar reaction conditions.[7] The major goal for this copolymerization was to modify the physical properties of syndiotactic polystyrene by incorporating a functional group into the polymer backbone through the copolymerization of styrene with its analogues. The reactivity ratio is very important in controlling the copolymer composition, e.g., the degree of incorporation of functional group in the copolymerization. The copolymerization conditions and results are summarized in Table 2. Highly incorporated TBDMSS played the major role in decreasing not only the stereoregularity of the copolymers determined by melting point as shown in Figure 4 but also the production yields. Specifically, the yield of copolymer 1 was in fairly good agreement with the literature value,[8b] but the production yield of copolymer 4 decreased markedly to ca. 12% of that of copolymer 1. The molecular weight of the formed copolymer exhibited a dependency on the TBDMSS as shown in Figure 5. The negative refractive index in the SECs from the high-temperature GPC analysis shown in Figure 5 typically implies the existence of an amorphous fraction in the copolymer composition. Especially, the decrease of the production yield in the cases of copolymers 1−4 would result from more kinetically

Table 2. Copolymerization Conditions and the Characterization Results of the Products[a]

copolym.	styrene/ TBDMSS[b] (mL/mL)	activity[c]	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$	T_m (°C)	ΔH (J/g)
1	46.5/1	78	12.0	2.2	261	24.8
2	22.4/1	22.7	12.0	2.1	245	21.8
3	14.8/1	10.5	9.0	2.4	232	20.9
4	11.4/1	6.3	8.0	2.7	227	17.1
5	2.28/5	26.5	11.0[d]	1.7	-	-
6	1.37/5	46.8	14.0[d]	1.8	-	-

[a] Catalyst; (Ind)TiCl$_3$ (1.0 × 10^{-5} mol), MAO (2.0 × 10^{-2} mol) in 50 mL toluene at 50°C for 1 h. [b] The feed ratio of styrene to TBDMSS in copolymerization. [c] The copolymer yield produced for 1 h in kilogram per mole of Ti. [d] The number-average molecular weight of the copolymer obtained from SEC analysis using the room-temperature GPC instrument using THF as the eluent.

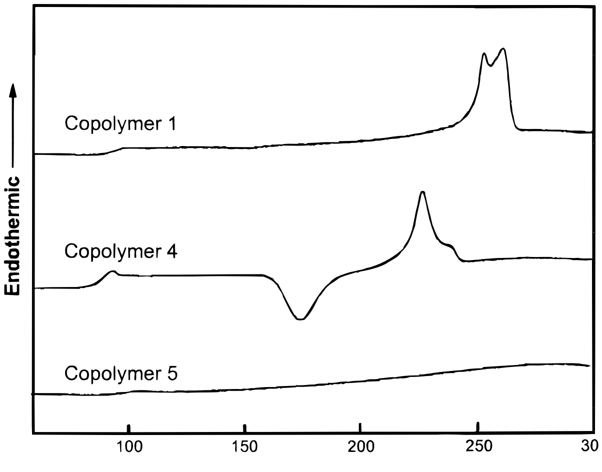


Figure 4. Comparison of DSC thermograms of the copolymers in Table 2.

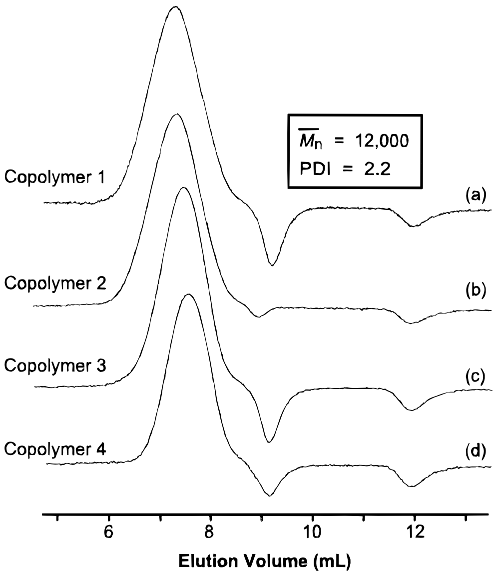


Figure 5. Comparison of SECs of the copolymers listed in Table 2: (a) copolymer 1, (b) copolymer 2, (c) copolymer 3, (d) copolymer 4, using a high-temperature GPC instrument.

controlled incorporation of styrene after a fast insertion of TBDMSS within a limited conversion. However, the copolymers 5 and 6 synthesized at the 50/50 and 30/70 feed ratios of TBDMSS to styrene arise from a relatively fast reaction rate of TBDMSS. This gives rises to the higher production yields shown in Table 2 compared to those in the medium feed range (97/3 to 96/4, mol/mol) under the same reaction conditions. The SEC results were obtained on common HPLC equipment using THF as the eluent at 30 °C as shown in Figure 6. Under the same reaction conditions, their molecular weights (copolymers 5 and 6) were somewhat higher than that of copolymer 4, as shown in Figure 6 and Table 2. Presumably, it is due to the higher local concentration of the TBDMSS around the active metal center, but the yields are still lower compared with that of styrene.[8b] This also indicates that this copolymerization is the kinetically controlled reaction arising from the steric hindrance effect as already described. It will be discussed in more detail later. Although a critical feed ratio changing from a crystalline copolymer to amorphous copolymer was not determined in these experiments, the TBDMSS must cause a great inhibition to the copolymerization due to both electronic and steric effects of the silyloxy group. This results in a decrease in the catalytic activity in a certain range of comonomer mole ratio when the comonomer has a polar group with a negative Hammett σ value.

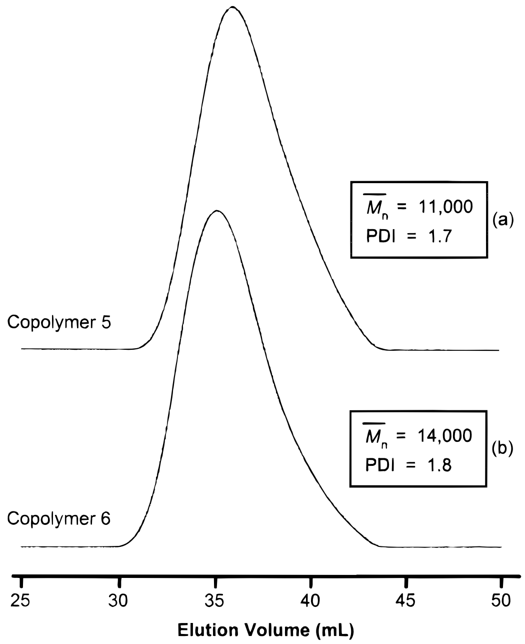


Figure 6. Comparison of SECs of the copolymers in Table 2: (a) copolymer 5 and (b) copolymer 6, using a common GPC instrument eluted with THF at 30 °C.

It is very important that the titanocene-catalyzed copolymerizations of styrene with the TBDMSS can successfully produce the precursor of hydroxyl-functionalized syndiotactic polystyrene. In this respect, the reactivity ratios, i.e., r_1 and r_2, of styrene (M$_1$) and the TBDMSS (M$_2$) will be important controlling the physical properties of the precursors related to their melting points, as shown in Figure 4. The reactivity ratios between styrene and substituted styrenes using homogeneous Ti-catalyzed copolymerizations had mostly been determined by ^{1}H-decoupled ^{13}C NMR spectroscopic analysis (inverse gated decoupling).[8] However, the copolymer compositions were readily determined by ^{1}H NMR spectroscopic analysis without adding an internal standard such as hexamethyldisiloxane, as shown in Figure 7. The chemical shift at $\delta = 0.2$ ppm is clearly assigned to the protons on the methyl group adjacent to the Si atom ($-$OSi(t-C$_4$H$_9$)(CH_3)$_2$) for the determination of the incorporated TBDMSS fraction. The sharp

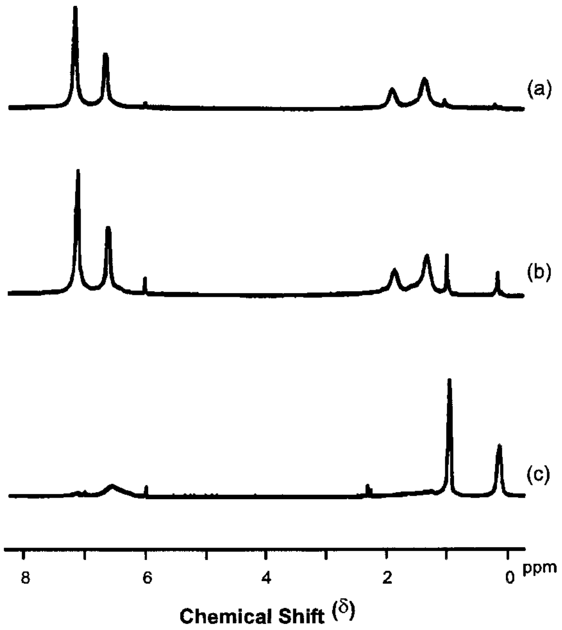


Figure 7. Comparison of ^{1}H NMR spectra of the copolymers in Table 2: (a) copolymer 1, (b) copolymer 4, and (c) copolymer 5.

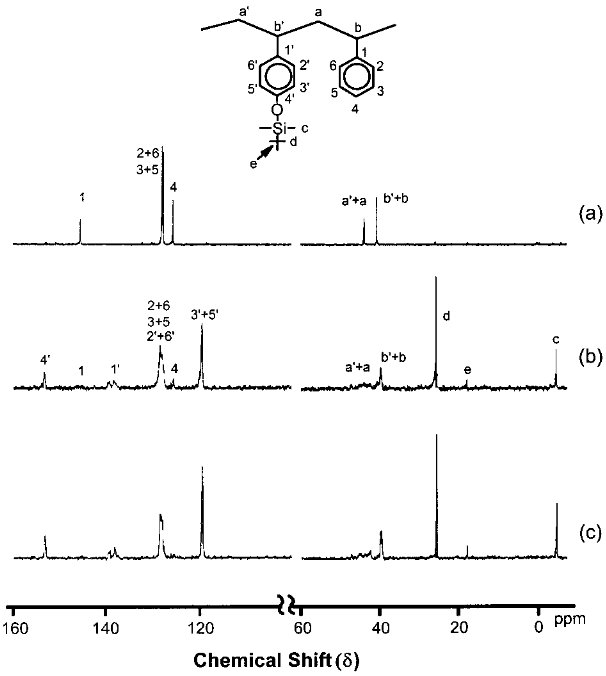


Figure 8. Comparison of ^{13}C NMR spectra of the copolymers in Table 2: (a) copolymer 1, (b) copolymer 4, and (c) copolymer 5.

absorption bands in the aromatic range of $\delta = 6-8$ ppm corresponding to the protons on the phenyl ring indicate indirectly that the formed copolymers include the crystalline phases shown in Figure 7a,b, whereas copolymer 5 exhibits chemical shifts similar to that of amorphous polystyrene. On the basis of the results for the DSC thermograms, copolymer 4 must include a crystalline phase as shown in Figure 4b. The ^{13}C NMR spectra for copolymers 1, 4, and 5 are compared in Figure 8. As shown in Figure 8a, the very sharp absorption at $\delta = 145$ ppm corresponding to the C-1 atom on the phenyl ring of styrene and its area reveal the degree of the racemic pentad (*rrrr*) configuration of the formed polymer.[2b] The increase of incorporation of TBDMSS leads to the reduction of the fraction of the pentad configuration, resulting in the decrease of its intensity and the broadened peak shown in Figure 8b. Furthermore, the chemical shifts in the aliphatic region at $\delta = 40-50$ ppm corresponding to the methylene (a + a′) and the methine carbon (b + b′) also lose sharpness and were broadened with incorporated TBDMSS. This behavior, analogous to that of poly(*p*-methoxystyrene) synthesized by homogeneous Ti-based catalysts, indicates a great loss of crystallinity in the formed copolymer. This means that the TBDMSS retains no stereoselectivity even on use of stereospecific catalysts. Presumably, this arises from a nonbonding interaction between the silyloxy group and the cationlike metal leading to the loss of stereoregularity.

In this experiment, it was difficult in practice to figure out the configurations of the copolymers simply by using ^{1}H NMR and ^{13}C NMR spectra.[21] On the basis of the results for Raman spectroscopic analysis,[22] in the cases of unannealed samples, the conformations of all of the copolymers exhibit structures similar to that of syndiotactic polystyrene. Interestingly, long all-trans sequences was rather dominant compared with less well-defined trans/gauche conformations of the copolymer backbones observed after the samples (copolymers 1−4 in Table 2) were annealed. With regard to this, a reduction of the melting temperature arising from the decrease of crystallinity by incorporation of a few units of the TBDMSS may be mainly affected not by conformational changes but by a looser packing effect because of the bulky silyloxy group.

The reactivity ratio in this copolymerization system gives rise to very useful information for the production of the functionalized copolymers retaining the syndiospecific property. To obtain the reactivity ratios of the comonomers in Table 2, all the results are rewritten in Table 3 on the basis of ^{1}H NMR spectroscopic analysis. The reactivity ratios can be obtained from the plot of $(1 - F)/f$ versus F/f^2 as shown in eq 1, which is the original Finemann and Ross equation modified from the "copolymer composition" equation,[9] where F is the mole fraction of styrene to comonomer in the composition of the copolymer and f represents the mole fraction of styrene in the feed composition.

$$\frac{1-F}{f} = r_2 \frac{F}{f^2} - r_1 \tag{1}$$

As shown in Figure 9, the reactivity ratios, r_1 and r_2, of styrene (M_1) and TBDMSS (M_2) were 0.997 and 7.27, respectively. In addition, the relative reactivity in the copolymerization of α-methylstyrene (M_1) with substituted styrene (M_2) correlated by the Hammett $\sigma-\rho$ relationship can be expressed as shown in eq 2.[23]

$$\log\left(\frac{1}{r_1}\right) = \rho\sigma \tag{2}$$

It is well-known that the plot of the $\log(1/r_1)$ value against the σ-substituent constant should yield a straight line with slope of ρ.[23] For instance, if $1/r_1$ is increased by electron-donating substituents for a negative ρ value, the copolymerization occurs via a cationic mechanism.[23] Furthermore, homogeneous Ti-catalyzed copolymerizations of styrene with styrene analogues having electron-donating substituents yielded a negative straight line ($\rho = -1.17$).[8a] With regard to the negative value, the authors suggested that the copolymerization proceeded

Table 3. Values for Evaluation of the Finmann and Ross Plot

copolym.	styrene/TBDMSS[a] (mol %/mol %)	*P* (TBDMSS)[b] (mol %)	f[c]	F[d]	F/f^2	$(1 - F)/f$
1	99/1	0.96	99.00	103.66	0.011	−1.037
2	98/2	2.27	49.00	43.10	0.018	−0.859
3	97/3	3.56	32.33	27.10	0.026	−0.807
4	96/4	5.00	24.00	19.01	0.033	−0.750
5	50/50	82.10	1.00	0.218	0.218	0.782
6	30/70	92.42	0.43	0.082	0.443	2.135

[a] The mole feed ratio of styrene to TBDMSS. [b] The mole fraction of the TBDMSS incorporated into the copolymer backbone. [c] The molar feed ratio of styrene to TBDMSS. [d] The molar composition ratio of styrene to TBDMSS in the copolymer.

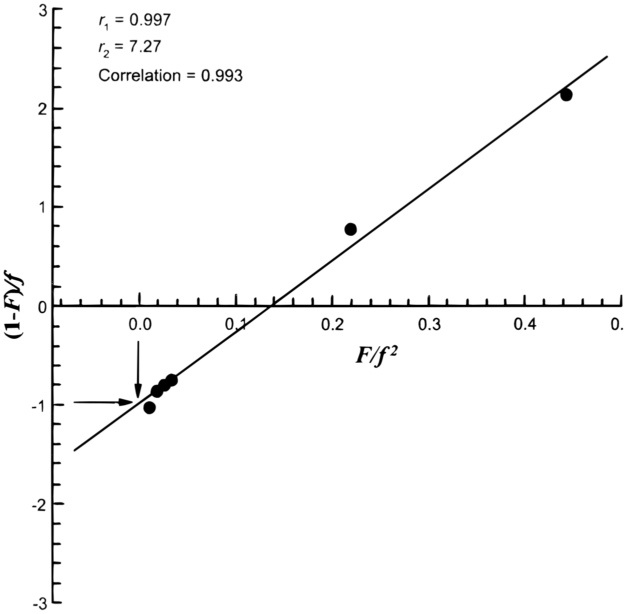


Figure 9. The Finemann and Ross plot of copolymerization of styrene with TBDMSS catalyzed by the (Ind)TiCl$_3$ in the presence of MAO.

via a cationic mechanism.[2b,8a] The silyloxy group, analogous to the *p*-methoxy group, is also expected to exhibit a negative σ value ($\sigma = -0.22^{23}$ and -0.32^{24} for *p*-OCH$_3$). As expected, r_2 has a much higher value (7.27) compared with r_1 (0.997). This indicates that the TBDMSS should retain a reaction rate faster than that of styrene in this copolymerization system. In addition, on the basis of r_1r_2 product value (7.25), our copolymerization system deviated greatly from the ideal copolymerization ($r_1r_2 \approx 1.0$). On the basis of these results, our copolymerization system in the higher TBDMSS feed range presumably produces not only a blocky type of copolymer (not confirmed) but also amorphous copolymer even when using syndiospecific homogeneous Ti catalysts in the presence of MAO. However, the homopolymerization rate of the TBDMSS is expected to be slower than that of styrene using the same half-sandwich titanocenes because this reaction is the kinetically controlled by both steric and the electronic effects of the *tert*-butyldimethylsilyloxy group. In this respect, to synthesize the precursors as hydroxyl-functionalized syndiotactic polystyrenes without a great loss of physical property, the feed ratio and a proper choice of the catalytic system should be optimized.

Conclusion

The Ti(OBu)$_4$-catalyzed copolymerization gives rise to much higher incorporation of the TBDMSS compared with those by the half-sandwich titanocenes, even though a lower yield was observed. The Ti(OBu)$_4$/MAO system may ultimately produce different active centers by adding TBDMSS on the basis of its SEC result. The rationale is due to different compositions of polymer chains produced by different active centers with different reactivities. In the cases of half-sandwich titanocene-based catalysts, the stronger electron-donating substituent on the cyclopentadienyl ring led to a decrease in the catalytic activity, unlike the syndiospecific polymerization of styrene. The addition of TBDMSS into the CpTiCl$_3$/MAO catalytic system leads to the hypsochromic shift (blueshift) of the UV/visible spectrum of the growing active species due to the localization of π-electrons around the metal center. Another rationale is due to a $\eta^5 \rightarrow \eta^3$ or $\eta^5 \rightarrow \eta^1$ cyclopentadienyl ring slippage (not confirmed) resulting from a full-electron saturation with respect to the 14-electron structure of the catalytic complex by a nonbonding interaction of the electron-donating silyloxy group leading to a great loss of $\pi \rightarrow \pi^*$ excitation. The reactivity ratios, r_1 and r_2, of styrene (M$_1$) and of TBDMSS (M$_2$) by evaluation of a Finemann and Ross plot were 0.997 and 7.27 in the (Ind)TiCl$_3$-catalyzed copolymerization, respectively. On the basis of the r_1r_2 product value (7.25), this copolymerization deviated greatly from an ideal copolymerization producing random copolymer, resulting in a block type of copolymer at a relatively high TBDMSS feed range. In the 98/2 to 97/3 range of the mole ratio of styrene to the TBDMSS, useful precursors as hydroxyl-functionalized syndiotactic polystyrenes without a great loss of the physical properties seem to be obtained.

References and Notes

(1) (a) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986,** *19*, 2464−2465. (b) Chien, J. C. W.; Salajka, Z. *J. Polym. Sci., Part A.: Polym. Chem.* **1991,** *29*, 1253−1263. (c) Pellicchia, C.; Proto, A.; Zambelli, A. *Macromolecules* **1992,** *25*, 4450−4452. (d) Kaminsky, W.; Lenk, S. *Macromol. Chem. Phys.* **1994,** *195*, 2093-2105. (e) Nishida, H.; Uozumi, T.; Arai, T.; Soga, K. *Macromol. Rapid Commun.* **1995,** *16*, 821−830. (f) Grassi, A.; Lamberti, C.; Zambelli, A.; Mingozzi, I. *Macromolecules* **1997,** *30*, 1884−1889.

(2) (a) Ishihara, N. *Macromol. Symp.* **1995,** *89*, 553−562. (b) Tomotsu, N.; Ishihara, N.; Newman, T. H.; Malanga, M. T. *J. Mol. Catal. A: Chem.* **1998,** *128*, 167−190.

(3) Kellar, E. J. C.; Galiotis, C.; Andrews, E. H. *Macromolecules* **1996,** *29*, 3515−3520.

(4) Su, Z.; Li, X.; Hsu, S. L. *Macromolecules* **1994,** *27*, 2635−2637.

(5) Bruce Orler, E.; Yontz, D. J.; Moore, R. B. *Macromolecules* **1993,** *26*, 5157−5160.

(6) Bruce Orler, E.; Moore, R. B. *Macromolecules* **1994**, *27*, 4774−4780.

(7) Kim, K. H.; Jo, W. H.; Kwak, S.; Kim, K. U.; Kim, J. *Macromol. Rapid Commun.* **1999,** *20*, 175−178.

(8) (a) Soga, K.; Nakatani, H.; Monoi, T. *Macromolecules* **1990,** *23*, 953−957. (b) Grassi, A.; Longo, P.; Proto, A.; Zambelli, A. *Macromolecules* **1989,** *22*, 104−108. (c) Oliva, L.; Mazza, S.; Longo, P. *Macromol. Chem. Phys.* **1996,** *197*, 3115−3122. (d) Thomann, R.; Sernetz, F. G.; Heinemann, J.; Steimann, S.; Mulhaupt, R. *Macromolecules* **1997,** *30*, 8401−8409.

(9) Finemann, M.; Ross, S. D. *J. Polym. Sci.* **1950,** *5*, 259−265.

(10) (a) Soga, K. Monoi, T. *Macromolecules* **1989,** *22,* 3823−3824. (b) Pellecchia, C.; Pappalardo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996,** *29,* 1158−1162.

(11) Kim, J.; Kim, K. H.; Cho, J. C.; Kwak, S.; Kim, K. U.; Jo, W. H.; Yoon, H. S.; Lim, D. *J. Polym. Sci., Part A.: Polym. Chem.* **1998,** *36,* 1733−1741.

(12) (a) Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972,** *94,* 2549−2550. (b) Pine, S. H.; Shen, G. S.; Hoang, H. *Synthesis* **1990,** 165−167. (c) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978,** *100,* 3611−3613. (d) Kim, J.; Kwak, S.; Kim, K. U.; Kim, K. H.; Cho, J. C.; Jo, W. H.; Lim. D.; Kim, D. *Macromol. Chem. Phys.* **1998,** *199,* 2185−2191.

(13) (a) Chen, X.; Jankova, K.; Kops, J.; Batsberg, W. *J. Polym. Sci., Part A.: Polym. Chem.* **1999,** *37,* 627−633. (b) Zhao, J. Q.; Pearce, E. M.; Kwei, T. K.; Jeon, H. S.; Kesani, P. K.; Balsara, N. P. *Macromolecules* **1995,** *28,* 1972−1978.

(14) (a) Weidmann, B.; Seebach, D, *Angew. Chem., Int. Ed. Engl.* **1983,** *22,* 31−45. (b) Reetz, M. T.; Kyung, S. H.; Hullmann, M. *Tetrahedron* **1986,** *42,* 2931−2935. (c) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992,** *92,* 807−832.

(15) (a) Casey, C. P.; O'Connor, J. P. *Organometallics* **1985,** *4,* 384−388. (b) Simanko, W.; Tesch, W.; Sapunov, V. N.; Mereiter, K.; Schmid, R.; Kirchner, K.; Coddington, J.; Wherland, S. *Organometallics* **1998,** *17,* 5674−5688. (c) Lee, S.; Cooper, N. J. *J. Am. Chem. Soc.* **1991,** *113,* 716−717.

(16) Endo, K.; Senoo, K. *Macromol. Rapid Commun.* **1998,** *19,* 563−566.

(17) Kim, J.; Kim, K. H., to be published.

(18) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem.* **1992,** *192,* 223−231.

(19) (a) Grubbs, R. H. Coates, G. W. *Acc. Chem. Res.* **1996,** *29,* 85−93. (b) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990,** *112,* 1566−1577.

(20) Hsieh, H. L.; Glaze, W. H. *Rubber Chem. Technol.* **1970,** *43,* 22−73.

(21) Ready, T. E.; Day, R. O.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1993,** *26,* 5822−5823.

(22) Raman spectroscopy is a useful and nondestructive method to assess polymer crystallinity arising from conformational changes of trans and gauche states of the polymer backbone; for syndiotactic polystyrene, a long all-trans sequences gives rise to a peak at ∼773 cm^{-1}, whereas less well-defined trans/gauche conformations exhibit separately a peak at ∼798 cm^{-1}. In our experiment, the spectra were obtained by using the samples preparing as follows: the samples were polymerized and annealed at 120 °C for 5 h. See: Kellar, E. J. C.; Evans, A. M.; Knowles, J.; Galiotos, C.; Andrews, E. H. *Macromolecules* **1997,** *30,* 2400−2407.

(23) Overberger, C. G.; Arend, L. H.; Tanner, D.; Tayler, J. J.; Alfrey, T., Jr. *J. Am. Chem. Soc.* **1952**, *74,* 4848−4853.

(24) *Lange's Handbook of Chemistry;* Dean, J. A., Ed.; McGraw-Hill: New York, 1985; p 3−137.

MA991036I