

Articles

Syndiospecific Synthesis of Longer *p-n*-Alkyl-Substituted Polystyrenes Using Monocyclopentadienyl-Type Titanium Catalysts

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ABSTRACT: Substituted styrenes with linear alkyl substituents (C_6 to C_{12}) at the para position on the ring were synthesized and polymerized using the $(Me)_5CpTi(OMe)_3/MAO$ catalytic system. Increased polymerization activities were observed for longer alkyl group ($>C_6$) substituted styrenes; all resulting polymers were highly syndiospecific ($>99\%$ rr) regardless of alkyl chain lengths. Syndiotactic poly(*p*-alkylstyrene)s were characterized by SEC, 1H and ^{13}C NMR, DSC, and X-ray diffraction. No melting transition was observed for polymers prepared from *p*-methyl-, *p-n*-hexyl-, and *p-n*-octylstyrenes. Side-chain-induced crystallization was observed for linear C_{10} and C_{12} alkyl-substituted polystyrenes ($T_m \approx 90$ °C). The T_g decreased with an increase in the length of alkyl side chain up to C_8 length; above C_{10} side-chain length, the T_g slightly increased. The T_g 's of syndiotactic poly(*p-n*-alkylstyrene)s were significantly higher than those reported for the corresponding nontactic analogues.

Introduction

Since Ishihara et al.¹ first synthesized syndiotactic polystyrene using transition-metal catalysts in 1986, analogous syndiospecific polymerization of a number of substituted styrenes has been investigated. Although many mechanistic aspects of syndiospecific styrene polymerizations have been elucidated,² the effects of para-substituted alkyl groups on these polymerizations are contradictory. Ishihara and co-workers³ reported that *m*- and *p*-methylstyrene and *tert*-butylstyrene undergo syndiospecific polymerization with $\eta-C_5H_5TiCl_3$ /methylaluminoxane in toluene. Much lower rates of conversion were observed for ring-substituted styrenes with electron-withdrawing groups (F, Cl, Br). Soga and co-workers⁴ reported that the Hammett rho (ρ) value was -1.2 for copolymerization of styrene with substituted styrenes using the syndiospecific catalyst system composed of $Ti(OMentyl)_4$ and methylaluminoxane in toluene. In contrast to the syndiospecific polymerizations of halogen-substituted styrenes reported by Ishihara et al.,³ Soga and co-workers⁴ reported that nontactic polymers were obtained for halogen-substituted styrenes as well as for *p*-methoxystyrene. Soga and co-workers⁵ investigated the syndiospecific polymerizations of several 4-*n*-alkyl-substituted styrenes using the syndiospecific catalyst system of $\eta-C_5(CH_3)_5TiCl_3$ /methylaluminoxane. They reported that nontactic polymers were obtained from *p*-ethyl-, *p-n*-propyl-, and *p-n*-butylstyrenes, whereas highly syndiospecific polymers were obtained for styrene and *p*-methylstyrene. In contrast, Mülhaupt and co-workers⁶ reported that *p-n*-butylstyrene was polymerized with high syndiospecificity using the catalyst system of $\eta-C_5H_5TiCl_3$ /methylaluminoxane in toluene as was used by Ishihara et al.³ The groups of both Soga⁵ and Mülhaupt⁶ reported that the molecular weights were significantly lower for poly(*p-n*-butylstyrene) compared to polystyrene. Furthermore, Soga et al.⁵ reported that the rates of polymerization decreased

as the size of the *p-n*-alkyl group increased, while Mülhaupt et al.⁶ reported that the activity was 3 times higher for *p-n*-butylstyrene compared to styrene. However, few investigations of such polymerizations with longer alkyl-substituted styrenes have been reported, presumably because of the lack of available monomers.

Since alkyl groups at the para position of a benzene ring exhibit negative Hammett sigma (σ) values,⁷ decreased reactivity of higher alkyl-substituted styrenes is not consistent with the cationic $Ti(III)$ complex⁸ that has been proposed for these polymerizations and the negative Hammett ρ value^{2,4} reported for these polymerizations. Therefore, it was of interest to carefully investigate the effect of alkyl group substituents, especially long-chain alkyl groups, on the reactivity of styrenes with syndiospecific polymerization catalysts.

A related subject was the effect of long-chain alkyl groups on the crystallinity of syndiotactic poly(*p-n*-alkylstyrene)s and their glass transition temperatures.^{3–6} The linear alkyl side chains in a variety of polymers are known to easily disrupt the backbone crystal structure and to affect the free volume through their rotations and mobility affects, analogous to the interaction with diluents.^{9–11} Therefore, thermal properties of the resulting polymers should be easily controlled by varying the substituents on the phenyl ring. In addition, if longer *p-n*-alkyl-substituted styrenes are polymerized in highly syndiospecific manner, regularly alkyl-branched syndiotactic polystyrenes can be obtained.

In this study, substituted styrenes with linear (C_6 to C_{12}) alkyl groups at the para position on the phenyl ring have been prepared using a recently described synthesis and purification procedure.¹² Herein are reported the results of an investigation of the syndiospecific polymerization of *p-n*-alkylstyrenes using the $(Me)_5CpTi(OMe)_3/MAO$ catalytic system and characterization of the resulting polymers.

Table 1. Characterization of *p*-Alkyl-Substituted Styrenes

substituent	characterization
<i>n</i> -hexyl-	65% yield, colorless liquid; IR (neat): 3050 (C–H at sp ²), 2925, 2852 (C–H), 1629 cm ⁻¹ (C=C); ¹ H NMR (CDCl ₃): δ = 0.89 (t, 3H), 1.30 (m, 6H), 1.61 (quintet, 2H), 2.60 (t, 2H), 5.20 (q, 1H), 5.70 (q, 1H), 6.71 (q, 1H) and 7.15 & 7.33 (q, 4H) ppm; ¹³ C NMR (CDCl ₃): δ = 14.60, 23.21, 29.55, 31.90, 32.27, 36.25, 113.01, 126.41, 128.80, 135.35, 137.10, and 143.01 ppm
<i>n</i> -octyl-	83% yield, colorless liquid; IR (neat): 3054 (C–H at sp ²), 2928, 2859 (C–H), 1632 cm ⁻¹ (C=C); ¹ H NMR(CDCl ₃): δ = 0.89 (t, 3H), 1.29 (m, 10H), 1.59 (quintet, 2H), 2.59 (t, 2H), 5.20 (q, 1H), 5.72 (q, 1H), 6.70 (q, 1H) and 7.15 & 7.32 (q, 4H) ppm; ¹³ C NMR (CDCl ₃): δ = 14.60, 23.10, 29.72, 29.90, 31.90, 32.29, 36.15, 113.21, 126.31, 128.71, 135.21, 137.10, and 143.01 ppm
<i>n</i> -decyl-	88% yield, colorless liquid; IR (neat): 3050 (C–H at sp ²), 2923, 2855 (C–H), 1629 cm ⁻¹ (C=C); ¹ H NMR (CDCl ₃): δ = 0.88 (t, 3H), 1.28 (m, 14H), 1.57 (quintet, 2H), 2.55 (t, 2H), 5.15 (q, 1H), 5.68 (q, 1H), 6.67 (q, 1H) and 7.10 & 7.29 (q, 4H) ppm; ¹³ C NMR (CDCl ₃): δ = 14.64, 23.22, 29.90, 31.96, 32.42, 36.19, 112.99, 126.39, 128.82, 135.29, 137.02, and 142.94 ppm
<i>n</i> -dodecyl-	92% yield, colorless liquid; IR (neat): 3050 (C–H at sp ²), 2926, 2855 (C–H), 1629 cm ⁻¹ (C=C); ¹ H NMR (CDCl ₃): δ = 0.89 (t, 3H), 1.30 (m, 18H), 1.61 (quintet, 2H), 2.60 (t, 2H), 5.18 (q, 1H), 5.69 (q, 1H), 6.71 (q, 1H) and 7.15 & 7.33 (q, 4H) ppm; ¹³ C NMR (CDCl ₃): δ = 14.42, 23.00, 29.62, 29.90, 31.76, 32.24, 36.00, 112.99, 126.38, 128.83, 135.30, 137.03, and 143.00 ppm

Experimental Section

Materials. All materials were handled in a Schlenk line, in a high-vacuum apparatus, or in a drybox.^{13,14} Styrene (Aldrich, >99%) and *p*-methylstyrene (Aldrich, 96%) were dried over calcium hydride for 2 days and distilled under high vacuum before use. Toluene (Fisher, reagent grade) was dried over calcium hydride for 2 days and sodium/benzophenone for 2 days and then distilled under high vacuum before use. Cyclopentadienyltitanium trichloride (CpTiCl₃, 97%, Aldrich) and pentamethylcyclopentadienyltitanium trimethoxide [(Me)₅CpTi(OMe)₃, 95%, Aldrich] were used as received. Methylaluminoxane (MAO, 30 wt % in toluene, Albemarle) was evacuated under high vacuum for 3 days to remove toluene and free methylaluminum and then stored in a drybox under an argon atmosphere and used as a white granular solid.¹⁵ An empirical formula of C_{5.5}H_{17.5}Al₄O₄ for the solid sample which approximately corresponds to the tetramer structure of MAO¹⁵ was obtained from elemental analysis done by Galbraith Laboratories Inc.¹⁶

Synthesis of *p*-Alkyl-Substituted Styrene Derivatives. The synthetic route was based on Wang's work.¹² Acetic anhydride (89.8 g, 0.88 mol in 100 mL of CH₂Cl₂) was added to a stirred mixture of AlCl₃ (227 g, 1.76 mol) in CH₂Cl₂ (800 mL) at 0 °C over 30 min. After stirring for 15 min at 0 °C, a solution of alkylbenzene (0.4 mol) in CH₂Cl₂ (100 mL) was slowly added over 30 min and stirred for 5 h at room temperature. Then, the reaction mixture was poured onto crushed ice (1500 mL). The separated organic layer was washed sequentially with 10% aqueous HCl solution (2 × 500 mL), saturated aqueous Na₂CO₃ (2 × 500 mL), and brine (2 × 500 mL), dried over anhydrous MgSO₄, and concentrated. The resulting *p*-alkylacetophenone was purified by crystallization from methanol.

To a stirred mixture of 0.3 mol of *p*-alkylacetophenone in 1000 mL of MeOH, 0.09 mol (3.4 g) of sodium borohydride was slowly (10 aliquots, 5 min) added at 0 °C. The mixture warmed to room temperature and was stirred for 2 h. After methanol was removed using a rotary evaporator, 1000 mL of *n*-hexane was added. The hexane solution was washed sequentially with 10% aqueous HCl solution (2 × 500 mL) and brine (2 × 500 mL), dried over anhydrous MgSO₄, filtered, concentrated, and crystallized at low temperature (~-20 °C) to obtain *p*-(alkylphenyl)methylcarbinol.

To a solution of 0.052 mol of (*p*-alkylphenyl)methylcarbinol in 500 mL of toluene in a flask equipped with a Dean–Stark trap was added 0.26 g (2 mol %) of *p*-toluenesulfonic acid monohydrate. The solution was heated to reflux, stirred for 2 h, allowed to cool to room temperature, washed with H₂O (500 mL), dried over anhydrous MgSO₄, and concentrated to a colorless liquid identified as *p*-alkylstyrene. The resulting product was purified by column chromatography using activated basic alumina as support and *n*-hexane as eluent. The substitution reactions were observed to occur exclusively at the para position on the phenyl ring as determined by the AB splitting patterns for the aromatic protons in ¹H NMR

spectra.¹⁷ The purity of the resulting styrene derivatives was >99% as determined by HPLC and TLC analyses. The characterization data for the synthesized *p*-alkyl-substituted styrenes are listed in Table 1.

Polymerizations. All polymerizations were performed using a 300 mL Büchi Mini-Clave glass reactor with a magnetic stirrer under a N₂ atmosphere. In a drybox, the fully dried glass reactor equipped with a thermocouple, and a catalyst injector was filled with toluene, styrene monomer, and powdered MAO as cocatalyst. The required amount of catalyst [(Me)₅CpTi(OMe)₃] and 5 mL of toluene were added into the catalyst injector. Then, the reactor was placed into a water bath preheated to 50 °C. When temperature was equilibrated, the catalyst solution was injected into the solution, stirred for 90 min, and then terminated by adding 5 mL of acidic methanol (10 vol % HCl). The resulting polymers were precipitated into 500 mL of acidic methanol, filtered, washed with methanol, and dried under vacuum at 60 °C for 12 h.

Characterization. ¹H NMR spectra of the *p*-alkyl-substituted styrenes were recorded on a Varian Mercury 300 spectrometer operating at 300 MHz with CDCl₃ solvent and TMS as reference at 30 °C. ¹³C NMR analyses of the alkyl-substituted styrenes and the resulting polymers were performed using a Varian Mercury 300 spectrometer operating at 75 MHz in CDCl₃ solvent at 30 °C and a Bruker DRX 500 spectrometer operating at 125 MHz in a solvent mixture of 1,2,4-trichlorobenzene (TCB) and C₆D₆ (7/3 w/w) at 120 °C. An inverse gated ¹H-decoupling mode and 10 s of pulse delay time were applied for the polymers in both ¹³C NMR experiments. FTIR spectra of neat synthesized monomer samples on a KBR window were obtained on a Mattson Genesis Series FTIR. HPLC chromatograms of the monomers were obtained using a Waters 501 HPLC with a Zorbax column and diode array detector at 30 °C in cyclohexane solvent. Thin-layer chromatography analyses were carried out on silica gel plates (Eastman Kodak silica gel chromatogram sheet 131811) with *n*-hexane as eluent. The molecular weights and molecular weight distributions of the polymers were measured with a Waters 150C GPC equipped with three Waters HR columns (Styragel HR1 100 Å, Styragel HR 4E 50–10⁴ Å, and Styragel HR SE 100–10⁶ Å) in THF at 30 °C and with a PL 210 GPC equipped with two PLgel 10 μm mixed-B columns in TCB solvent at 135 °C using calibration with polystyrene standards. Thermal properties (*T*_g and *T*_m) were measured using a Dupont DSC 2910 at 10 °C/min heating rate under a N₂ atmosphere. DSC thermograms were obtained during second heating. Wide-angle X-ray diffraction measurements for the as-polymerized samples were carried out using a Rigaku X-ray diffractometer with Cu Kα radiation at the ambient temperature.

Results and Discussion

As shown in Table 1, *p*-alkyl-substituted styrenes with different alkyl group lengths were synthesized in high purity and in relatively high yields. These mono-

Table 2. Polymerization Results of Different *p*-Alkyl-Substituted Styrenes^a

monomer	activity ^d	$M_n (X_n) \times 10^{-3}$	M_w/M_n	rr (%) ^g	T_g (°C) ^h
styrene ^b	190	70 ^e (0.7)	2.2 ^e	92	100
styrene ^c	580	340 ^e (3.3)	2.1 ^e	>99	100
<i>p</i> -methylstyrene ^c	820	450 ^e (3.8)	2.2 ^e	>99	110
<i>p</i> - <i>n</i> -hexylstyrene ^c	1500	530 ^f (2.8)	1.7 ^f	>99	-11/-27 ⁱ
<i>p</i> - <i>n</i> -octylstyrene ^c	1400	550 ^f (2.6)	1.7 ^f	>99	-28/-45 ⁱ
<i>p</i> - <i>n</i> -decylstyrene ^c	2900	830 ^f (3.4)	1.7 ^f	>99	-33/-65 ⁱ
<i>p</i> - <i>n</i> -dodecylstyrene ^c	2600	930 ^f (3.4)	2.5 ^f	>99	-27/-52 ⁱ

^a Polymerization conditions: [Ti] = 42.5 mmol/L, [Al]/[Ti] = 1,000, 0.5 mol/L monomer concentration, 50 °C, toluene solvent, 50 mL volume, 90 min. ^b CpTiCl₃/MAO catalytic system. ^c (Me)₅CpTi(OMe)₃/MAO catalytic system. ^d kg of PS/(mol of Ti [M] h). ^e PL210 GPC, 135 °C, TCB solvent, PL mixed column (×2), PS standard calibration. ^f Waters 150 C GPC, 30 °C, THF solvent, Waters HR column (×3), Universal calibration. ^g Determined using the areas of the methylene carbon resonance peaks from ¹³C NMR spectra.²⁰ ^h Measured by a Dupont DSC 2910, 10 °C/min heating rate, second heating. ⁱ Data taken from the ref 23 using conventional radical polymerization.

mers were polymerized using the (Me)₅CpTi(OMe)₃/MAO initiating system; the results were compared with polymers prepared from commercially available styrene and *p*-methylstyrene using the same initiating system. The effect of the five methyl substituents on the Cp ligand (Cp*) of the above initiating system was also compared to the CpTiCl₃/MAO system for styrene polymerization. The polymerization results are summarized in Table 2.

The initiating system with the Cp* ligand showed a higher catalytic activity, a higher syndiospecificity, and a lower tendency for β -hydride elimination (higher molecular weights) compared to the results obtained with the nonsubstituted Cp titanium catalyst. These results correspond to the previously published effects by Ishihara et al.^{2,18} Significantly increased catalytic activities with longer alkyl-substituted styrenes (>C₆) using the (Me)₅CpTi(OMe)₃/MAO catalytic system were observed. Considering the cationic character of the catalytically active species as proposed by Zambelli et al.,⁸ styrenes substituted with electron-donating groups should have higher reactivities for these polymerizations assuming no significant steric effects. A more polarizable, electron-donating *p*-alkyl group promotes the coordination of the monomer with the electron-deficient Ti metal center. This electronic effect can lower the activation energy barrier for the four-centered transition state during the insertion process and accelerate the monomer insertion rate. However, it is very difficult to quantify differences in the electron-donating abilities of the longer alkyl substituents with the chain length.⁷ Soga et al.⁵ reported that the catalytic activity of the alkyl-substituted styrenes using the (Me)₅CpTiCl₃/MAO catalytic system in the absence of solvent decreased with increasing size of the substituents from methyl to the *p*-*n*-butyl group; however, *p*-methylstyrene was more reactive than styrene. Although a similar increase in the catalytic activity with *p*-methylstyrene compared to styrene was observed, the above retarding effect with longer linear-alkyl groups (C₆ to C₁₂) was not observed in this study. In contrast to a retarding effect, all longer *p*-*n*-alkyl-substituted styrenes were more reactive than *p*-methylstyrene, as shown in Table 2. This discrepancy could result from the different polymerization conditions [higher [MAO]/[Ti] ratio (2200 vs 1000) and no solvent use in Soga et al.⁵], monomer purity, purification of MAO solution, etc. The purity of the synthesized *p*-*n*-alkylstyrenes investigated in this study was observed to be >99% by HPLC and TLC experiments. Also, a clear AB splitting pattern of the aromatic ring protons for these monomers from ¹H NMR spectra was observed, which means that the substitution reaction occurs exclusively at the para position on the phenyl ring.¹⁷ The results reported herein are consistent with the

proposed electron-deficient cationic active species⁸ and the negative Hammett rho (ρ) value^{2,4} for this polymerization. This means that the insertion of styrene monomer to the Ti–C bond in this polymerization system would be largely determined by the electronic effects of *p*-alkyl substituents.

Another possible explanation for part of the observed higher catalytic activities for longer *p*-alkyl-substituted styrenes might be due to the ease of diffusion of the monomers to catalytic sites. This may result from the increased solubility of syndiotactic poly(*p*-alkylstyrene)s in toluene as polymerization solvent compared to syndiotactic polystyrene, for which significant gelation was observed during polymerization.

The molecular weights of the polymers appeared to increase with increasing the size of the alkyl substituents; however, the degree of polymerization (X_n) did not show a clear trend as seen in Table 2. Analogous to the results reported by Soga et al.,⁵ Mülhaupt et al.⁶ reported that a decreased molecular weight was observed for syndiotactic poly(*p*-*n*-butylstyrene) prepared using the less reactive CpTiCl₃/MAO initiating system in toluene. They suggested that the formation of a more stable π -complex due to the increased electron density by *p*-*n*-butylstyrene would lead to a slower insertion of the monomer and an increased β -hydride elimination resulting in a lower molecular weight. In this study, no evidence for an increased tendency toward chain transfer was observed. This discrepancy might be ascribed to a higher β -hydride elimination tendency of the nonsubstituted Cp-type procatalyst or the presence of free trimethylammonium (TMA) in their MAO solution. They used an MAO/toluene solution as received. The MAO solution reported herein was filtered and evacuated to remove toluene and free TMA. It is known that free TMA can act as a chain transfer agent and leads to a lower conversion.² Molecular weight distributions of the resulting polymers were not much different from theoretical predictions for a homogeneous catalyst system ($M_w/M_n \rightarrow 2$).¹⁹

Among the ¹³C NMR resonances of polystyrene, the ipso carbon (C1) on the phenyl ring and the methylene carbon on the backbone are highly sensitive to the backbone configuration; a sharp single peak in these resonance regions means that the backbone configuration is highly stereospecific.^{1,20} In Figure 1, the ¹³C NMR spectrum of the syndiotactic poly(*p*-*n*-dodecylstyrene) synthesized in this study shows a clear single peak for both the C1 carbon ($\delta = 142.5$ ppm) and the methylene carbon ($\delta = 44.2$ ppm). It is noteworthy that Wang¹² observed broad ¹³C NMR resonance peaks for the C1 carbon and methylene carbon for nontactic poly(*p*-*n*-dodecylstyrene) ($M_n = 111 \times 10^3$ g/mol, $M_w/M_n = 1.04$) prepared using anionic polymerization.

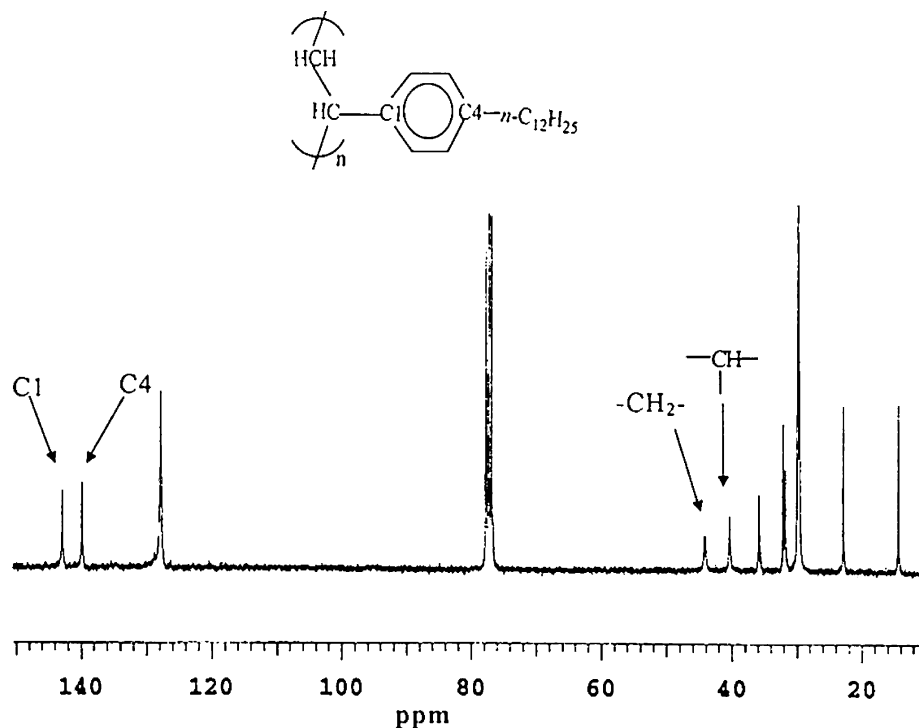


Figure 1. ^{13}C NMR spectra of syndiospecific poly(*p-n*-dodecylstyrene) measured using a Varian Mercury 300 spectrometer operating at 75 MHz at 27 °C in CDCl_3 solvent.

More interestingly, it was observed that, regardless of the alkyl substituents, all resulting polymers were highly syndiospecific as determined from the ^{13}C NMR resonances corresponding to the methylene carbon on the main chain and the ipso carbon on the phenyl ring.^{1,6} In Figure 2, the ^{13}C NMR spectra of syndiotactic poly(*p-n*-alkylstyrene)s with different alkyl group lengths are compared to the spectrum of syndiotactic PS made using the same catalyst system. Only sharp single resonance peaks for the C1 and methylene carbons are observed in these spectra, which means that the backbone configuration of all of these polymers is highly syndiospecific. The ipso carbon (C1) on the phenyl ring attached to the backbone for the linear alkyl-substituted syndiotactic polystyrenes was shielded ($\delta = 142.8$ ppm) and the other ipso carbon (C4) directly attached to the alkyl substituent was deshielded ($\delta = 139.8$ ppm) compared to those of unsubstituted syndiotactic polystyrene ($\delta_{\text{C1}} = 145.5$ ppm and $\delta_{\text{C4}} = 125.8$ ppm). This is the result of the electron-donating effect of the alkyl substituents corresponding to the observations for syndiotactic poly(*p-n*-butylstyrene) of Mülhaupt et al.⁶ The above findings indicate that the alkyl substituents at the para position do not have any significant effect on the backbone configuration and that the steric control of the chain end in this polymerization is mainly governed by the bulky phenyl ring. These results are in conflict with the results reported by Soga et al.⁵ in which the rr triad fractions were 32, 44, and 43% for *p*-ethyl-, *p*-propyl-, and *p-n*-butylstyrene, respectively.

The thermal properties of the *p*-alkyl-substituted styrene polymers were highly dependent on the length and bulkiness of the substituents.^{9–11} In linear *p*-alkyl-substituted polystyrenes with alkyl side chain lengths ≤ 6 , the alkyl side chain acts as diluent. Therefore, the crystallinity is not only disrupted, but also the free volume in the chain packing is increased by the inclusion of the side chain.

In Figure 3, the DSC thermograms of syndiotactic poly(*p*-alkylstyrene)s having different alkyl chain lengths synthesized in this study are compared. The crystalline melting peak of the SPS at 270 °C disappeared with alkyl substituents (C_6 , C_8 , C_{10} , and C_{12}) at the para position on the phenyl ring. Even syndiotactic poly(*p*-methylstyrene) did not show any melting transition. Ishihara et al.³ reported that syndiotactic poly(*p*-methylstyrene) showed a melting transition at 173 °C, whereas Soga et al.⁵ did not find any melting transition for this polymer by DSC. This inconsistency may result from the differences in sample preparation method, measurement conditions, etc. In this study, the purity of *p*-methylstyrene was 96%, and the other 4% corresponded to the meta isomer, which may cause a different melting behavior for this polymer. Despite the inconsistency in the crystallinity of the syndiotactic poly(*p*-methylstyrene), it was confirmed that the *p*-alkyl substituents have a profound effect on the crystallinity of syndiotactic polystyrene. Furthermore, a melting transition at around 90 °C for the linear C_{10} - and C_{12} -alkyl-substituted polystyrenes was found. These melting peaks can be attributed to a side-chain-induced crystallization.¹⁰ Wang¹² reported a side-chain crystallization peak for the nontactic poly(*p-n*-dodecylstyrene) at around -30 °C. Thus, this polymer exhibited a significantly lower T_m than that of the syndiotactic analogue. This implies that the observed high backbone stereoregularity for the syndiotactic poly(*p-n*-alkylstyrene)s can promote more side-chain crystallization. McIntosh¹⁶ reported a similar observation that there are large differences in the thermal properties between the nontactic poly(α -olefin)s and the corresponding isotactic analogues.

This side-chain-induced crystallization was investigated in more detail by X-ray diffraction experiments. Figure 4 shows the X-ray powder patterns of the as-polymerized samples. A sharp reflection was observed

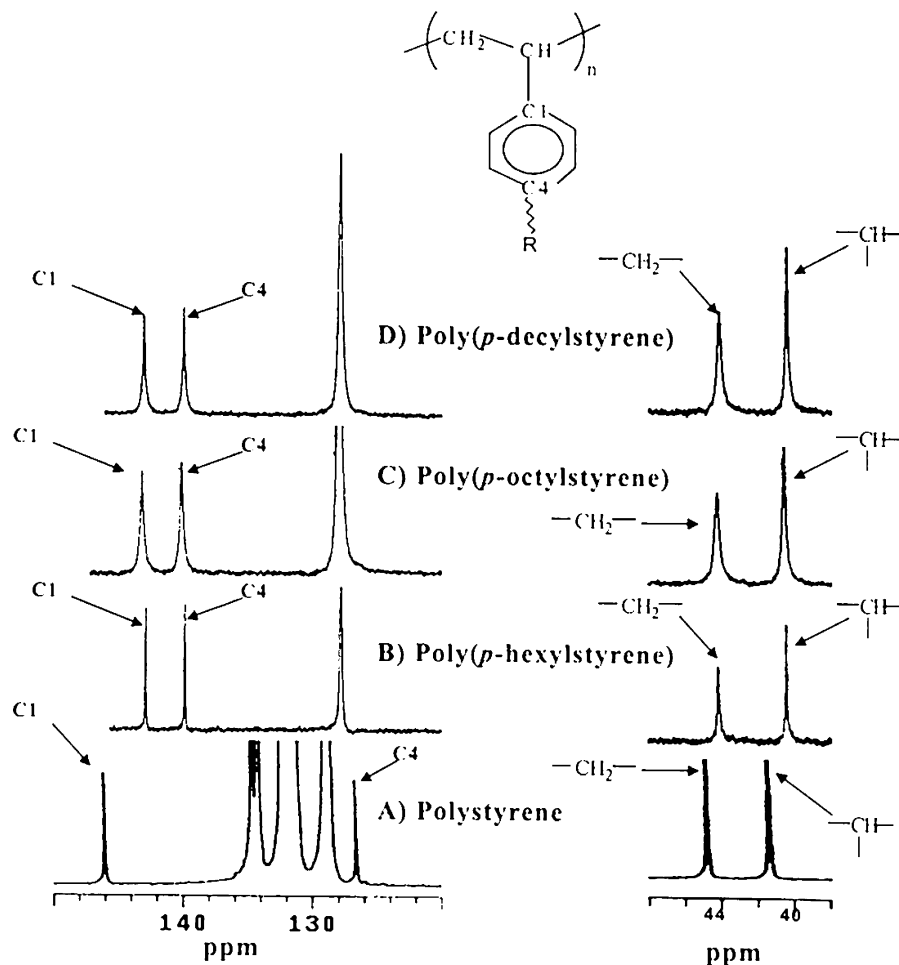


Figure 2. ^{13}C NMR spectra of syndiotactic poly(*p*-*n*-alkylstyrene)s: (a) measured using a Bruker DRX 500 spectrometer operating at 125 MHz at 120 °C in 1,2,4- $\text{TCB}/\text{C}_6\text{D}_6$ (7/3) solvent and (b–d) using a Varian Mercury 300 spectrometer operating at 75 MHz at 27 °C in CDCl_3 solvent.

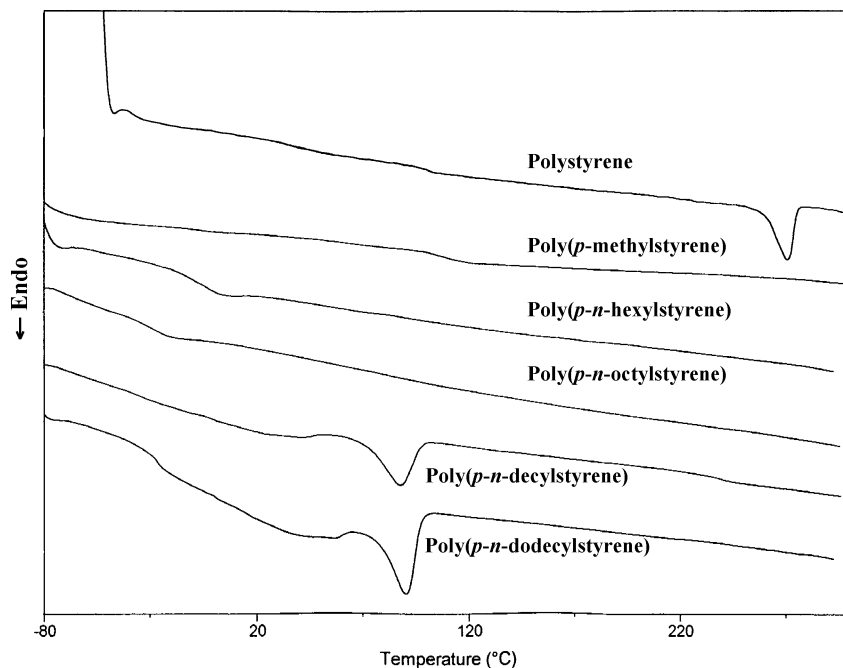


Figure 3. DSC thermograms of syndiotactic polystyrenes with different *p*-alkyl substituents measured using a Dupont 2910 DSC at heating rate 10 °C/min during second heating.

in the low angle region ($2\theta = 2.8^\circ$) of the powder pattern of syndiotactic poly(*p*-*n*-dodecylstyrene). In contrast, there was no significant reflection peak in the diffraction

pattern of syndiotactic poly(*p*-*n*-hexylstyrene). This corresponds to the results reported by Jones²¹ in which the C_6 side chain does not have a crystalline order.

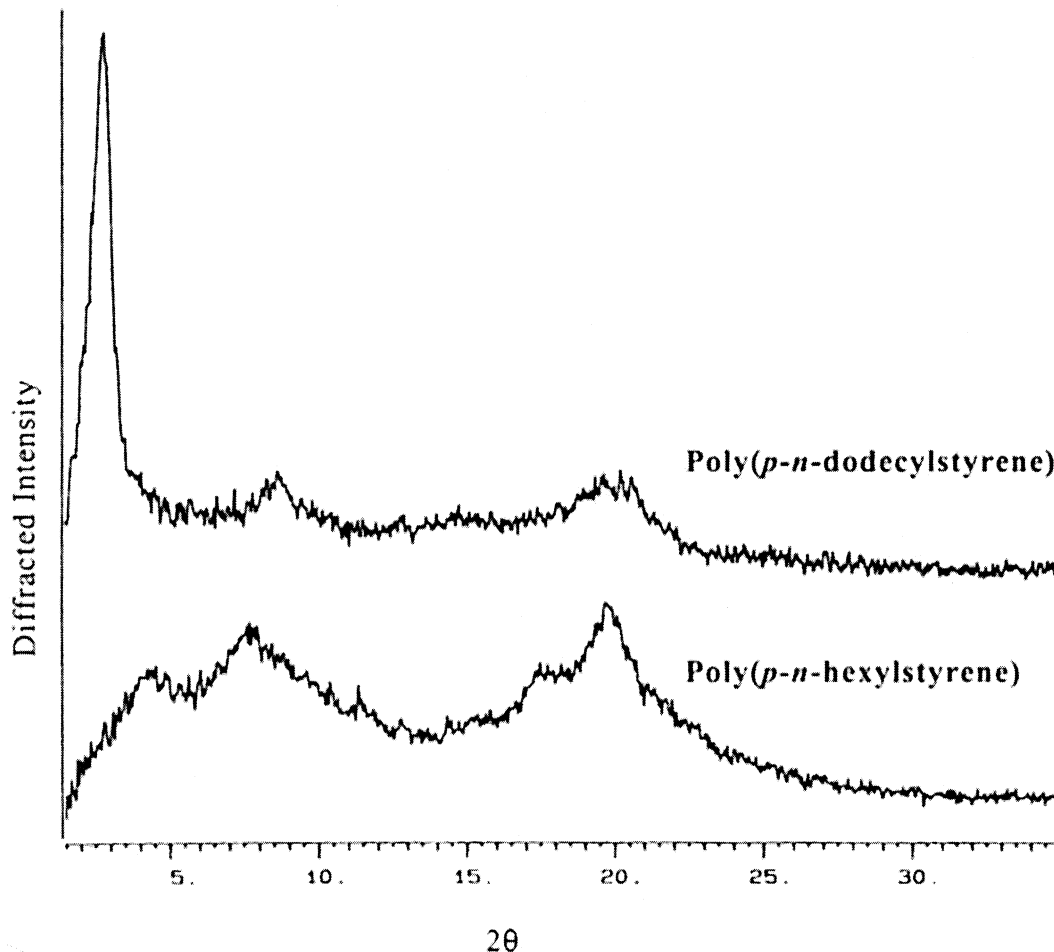


Figure 4. X-ray diffraction patterns for as-polymerized samples of syndiotactic poly(*p-n*-hexylstyrene) and poly(*p-n*-dodecylstyrene) measured using a Rigaku X-ray diffractometer with a Cu K α radiation at a scan rate of 10 °C/min and at ambient temperature.

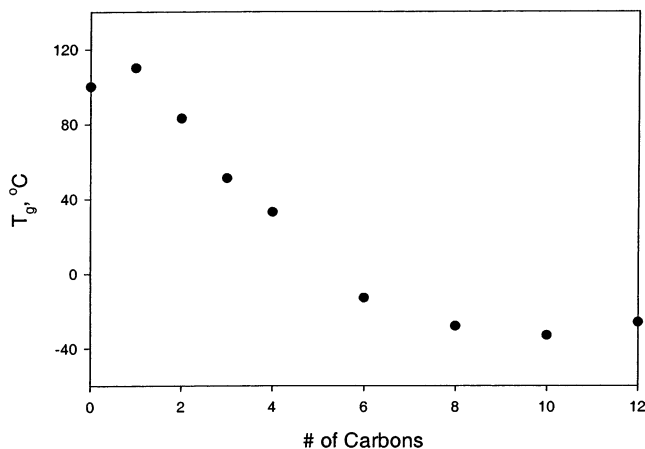


Figure 5. Effect of chain length of linear *p*-alkyl substituents on T_g 's of syndiotactic poly(*p-n*-alkylstyrene)s. (Data points of C₂, C₃, and C₄ substituents were taken from ref 6.)

The T_g 's of the syndiotactic poly(*p-n*-alkylstyrene)s as shown in Table 2 and Figure 5 also varied with the alkyl group size. As the length of the alkyl substituent increased, the T_g decreased linearly up to a certain length (C₈). This can be easily explained by the increased free volume in the packing of the chains caused by the increased length of the side chains.⁹ Interestingly, above a side-chain length of C₁₀, the T_g did not decrease further, which can be explained by the effect of the crystallization induced by the side chain above a certain alkyl chain length. This crystallinity ties down the

crystalline regions so that the flexibility of the chains in the amorphous regions decreases.⁹ As a result, the free volume would not increase further or may even decrease. Considering that the T_g of nontactic poly(*p-n*-dodecylstyrene) was found to be at -45 °C by Wang,¹² there is a significant difference in the T_g 's between the syndiotactic poly(*p-n*-dodecylstyrene) and the nontactic analogue. Overberger et al.²² reported the T_g 's of a series of nontactic poly(*p-n*-alkylstyrene)s synthesized using conventional radical polymerization (see Table 2). They found that there was a minimum in T_g at C₁₀ alkyl chain length followed by an increase in which the T_g 's of poly(*p-n*-decylstyrene) and poly(*p-n*-dodecylstyrene) were -65 and -52 °C, respectively. The higher T_g 's for the syndiotactic analogues (-33 °C for C₁₀ and -27 °C for C₁₂) observed in this study would be expected because of the higher side-chain crystallinity as discussed above.⁹

Summary

Substituted styrenes with linear alkyl substituents (C₆ to C₁₂) at the para position on the ring were synthesized and purified. The polymerizations of these monomers using the (Me)₅CpTi(OMe)₃/MAO catalytic system were mainly governed by electronic effects, not by steric factors from the alkyl-substituents. All resulting polymers were observed to be highly syndiospecific (>99% *rr*) as determined by ¹³C NMR analysis of the ipso carbon (C1) resonances on the phenyl ring. As the chain length of the alkyl substituents increased, the

catalytic activities increased. An increased tendency toward chain transfer was not observed, and the molecular weight distributions (M_w/M_n) of all resulting homopolymers were close to 2. Also, the thermal properties (T_g and T_m) of the resulting polymers were highly dependent on the length bulkiness of the substituents. Interestingly, side-chain-induced crystallization behavior ($T_m \approx 90$ °C) was found in syndiotactic poly(*p*-*n*-decylstyrene) and poly(*p*-*n*-dodecylstyrene) as determined by DSC and X-ray diffraction experiments; this crystallinity affected the T_g of these polymers. The T_g 's of the synthesized poly(*p*-*n*-alkylstyrene)s were higher than those reported for the corresponding non-tactic analogues.

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