Synthesis of Syndiotactic Polystyrene Derivatives Containing Amino Groups

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ABSTRACT: This paper discusses a new family of syndiotactic polystyrene (s-PS) derivatives containing the amino group, including poly(4-aminostyrene), poly(4-aminomethylstyrene), and poly(4-aminoethylstyrene). These semicrystalline polymers exhibit high melting temperatures (∼350 °C) and relatively fast crystallization rates. These functional syndiotactic polymers are prepared in two steps. Syndiospecific polymerization of a styrene derivative containing a masking *N*,*N*-bis(trimethylsilyl)amino group is achieved by using a half-sandwich titanocene/perfluoroborane catalyst system. This study focused on the catalyst system (catalyst and cocatalyst) that can polymerize functional monomers with high catalyst activity and syndiotacticity. Acid hydrolysis leads to the complete recovery of primary amino groups in s-PS derivatives.

Introduction

One of the most interesting features of metallocene catalysis is the preparation of syndiotactic polystyrene (s-PS) by half-sandwich titanocene catalysts,[1] such as $CpTiCl_3$/MAO and [Cp*Ti$(CH_3)_3$/B$(C_6F_5)_3$]. The s-PS polymers with high crystallinity exhibit many unique properties, superior to traditional atactic polystyrene (a-PS) prepared by anionic or free radical initiators and isotactic polystyrene (i-PS) prepared by heterogeneous Ziegler−Natta catalyst. The combination of high melting temperature (∼270 °C) with relatively high crystallization rate, low dielectric constant, high chemical resistance, and low specific gravity makes s-PS an attractive material for many applications in the electronic, packaging, and automotive industries.

Despite some unique properties, s-PS polymer resembles a-PS polymer with poor impact strength and low surface energy. The absence of polar groups in hydrophobic polystyrene restricts their end uses, especially where adhesion to substrates (metals, ceramics, glass, etc.) and compatibility[2] with polar polymers are desired. So far, there are only few reports discussing functionalized s-PS copolymers, including sulfonated s-PS,[3] hydroxylated s-PS[4] prepared via poly(styrene-*co*-4-*tert*-butyldimethylsilyloxystyrene) precursor, and s-PS-*b*-PMMA prepared via borane-terminated s-PS.[5]

It has been a long-standing scientific challenge and industrially interesting subject to prepare poly(α-olefin)s containing functional (polar) groups,[6] such as alcohol, amine, ether, ester, etc., by Ziegler−Natta (Z−N) polymerization. The facile acid−base interaction between catalytic sites (Lewis acid) and functional groups (Lewis base) usually prohibits the polymerization reaction. Two general approaches of preventing catalyst poisoning include the protection of functional groups by bulky substituents[7] (masking groups) and precomplexization of the functional group with Lewis acids, such as the alkylaluminum cocatalyst.[8] Many attempts in conventional Ziegler−Natta systems, containing group III or IV transition metal halides and alkylaluminum cocatalysts, showed only very limited success. Most of these efforts were in the copolymerization reactions of α-olefins with a small amount of protected functional comonomers.

Recently, interest in the functionalization approach has been renewed by using metallocene catalysts. Zirconocene/methylaluminoxane (MAO) catalysts were used in copolymerization[9] of ethylene and propylene with a small amount of comonomers that have large spacers between the olefin and the functional group, including 1-hydroxy-10-undecene,[9] 1-chloro-10-undecene,[10] *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene,[11] and *o*-heptenylphenol.[12] It is believed that MAO (in large excess) may serve as an in-situ protection agent to prevent catalyst deactivation. In fact, the pretreatment of functional monomer with MAO before initiation significantly increases the catalyst activity. Similar pretreatment using trimethylaluminum (TMA)[13] also showed good copolymerization results between α-olefins and hydroxy- and amino-containing monomers using zirconocene/MAO catalysts. It is interesting to note that the benefit of TMA-protected functional monomers in the copolymerizations[15] is also extended to the less oxophilic late transition metal catalysts.

Waymouth et al.[14] reported the advantage of perfluoroborane cocatalysts (replacing MAO in the metallocene catalyst) that were compatible with the protected functional groups. They successfully demonstrated the homopolymerization of several masked monomers, i.e., 5-(*N*,*N*-diisopropylamino)-1-pentene and 4-trimethylsiloxy-1,6-heptadiene, in good yields using zirconocene/perfluoroborane catalysts. However, stereospecific polymerization of functional olefin monomers with metallocene catalysts, especially titanocene systems, is an open research area. Detailed experimental results are needed to understand the effects of protected functional group on catalyst activity, stereoselectivity, and polymer molecular weight.

Results and Discussion

In this paper, we will discuss stereospecific homopolymerization of functional styrene derivatives, containing amino groups, using half-sandwich titanocene cata-

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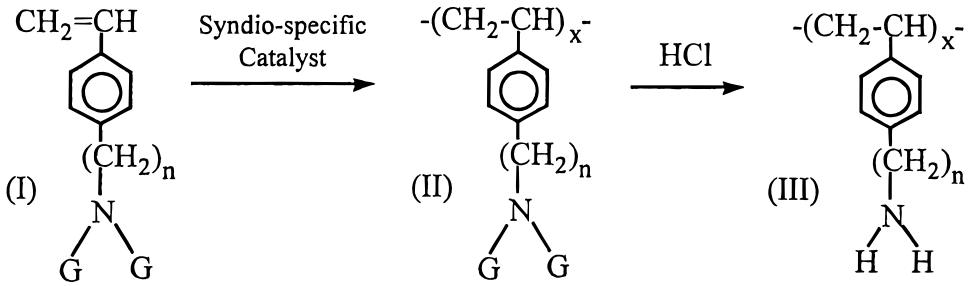
Scheme 1



n : 0, 1, and 2.

G: $Si(CH_3)_3$ masking group.

lysts. The chemistry affords a new family of functional s-PS homopolymers with high syndiotacticity, including syndiotactic poly(4-aminostyrene), poly(4-aminomethylstyrene), and poly(4-aminoethylstyrene). The research plan was formulated with several intriguing questions and objectives in mind. (i) Because the titanocene cation is generally more oxophilic than the corresponding zirconocene ion, is it still possible to homopolymerize the protected functional monomers in such an environment with high functional group concentration? (ii) How does the bulky protected functional group in the monomer affect the stereoselectivity of active site? (iii) Is it possible to manipulate active site with bulky ligands in the catalyst and/or cocatalyst to prevent acid−base complexation further and therefore enhance catalyst activity, polymer molecular weight, and syndiotacticity of the polymer? (iv) The resulting new syndiotactic functional s-PS homopolymers containing primary amino groups may be very interesting materials in terms of high surface energies, high melting temperatures, and fast crystallization rates due to strong hydrogen bonding.

The preparation of syndiotactic functional polystyrene homopolymers involves a two-step process as illustrated in Scheme 1. After polymerization of the styrene derivatives (**I**) containing the protected amino group, the resulting s-PS derivatives (**II**) were then deprotected by acid hydrolysis to recover primary amino groups along the polymer chain (**III**).

All polymers formed were analyzed by ^1H, ^{13}C NMR, DSC, GPC, and intrinsic viscosity to determine their molecular structures.

Syndiotactic Polystyrene Derivatives Containing Masked Amino Groups. As discussed, the polymerization study focused on suitable masking groups, initiators, and co-initiators that afford syndiotactic polystyrene derivatives with high syndiotacticity and catalyst activity. Two masking groups, including methyl and trimethylsily groups, were evaluated in the polymerization reaction along with several half-sandwich titanocene catalysts, including Cp^*TiMe_3, Cp^*TiCl_3, $IndTiMe_3$, [2-Me-Benz[*e*]Ind]$TiMe_3$, and [2-Ph-Phen[*e*]-Ind]$TiMe_3$, and co-initiators, including MAO, $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, and tris-(2,2′,2″-nonafluorobiphenyl)borane (PBB). In addition, a control polymerization of styrene was carried out under the same reaction conditions to understand the effect of the protected functional group on the polymerization reaction.

Figure 1 shows the ^1H NMR spectrum of three trimethylsilyl protected polymers prepared from 4-(*N*,*N*-bis(trimethylsilyl)amino)styrene, 4-(*N*,*N*-bis(trimethylsilyl)aminomethyl)styrene, and 4-(*N*,*N*-bis(trimethylsilyl)-aminoethyl)styrene monomers.

There are five common peaks in all three spectra, the peak at ∼0.15 ppm, corresponding to $Si(C\mathbf{H}_3)_3$ protons of the masking group, two aliphatic proton peaks at ∼1.5 and ∼2.0 ppm, corresponding to the C**H**$_2$ and C**H** protons in the polymer backbone, and two distinctive aromatic peaks around 7 ppm, corresponding to two sets of aromatic protons in the para-substituted phenyl groups that have a syndiotactic arrangement along the polymer chain. The detailed analysis of syndiotacticity will be discussed in further ^{13}C NMR studies. In

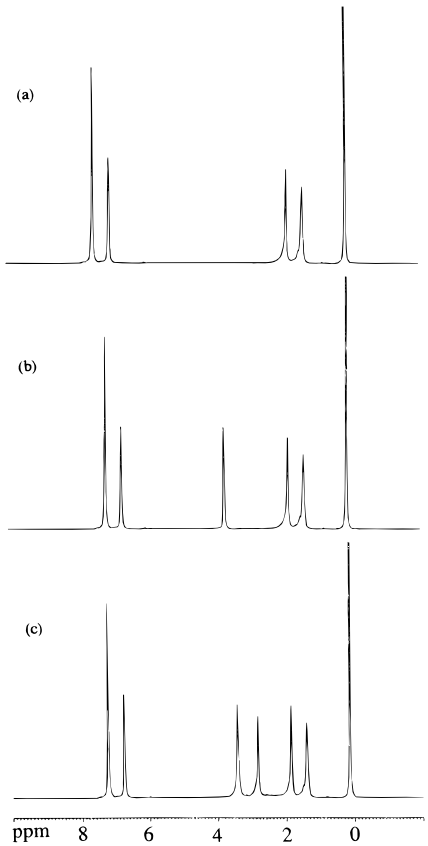
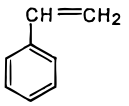
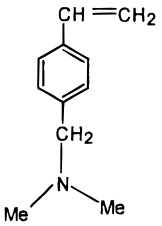
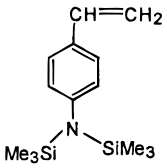
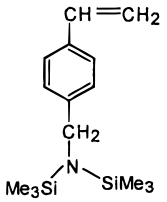
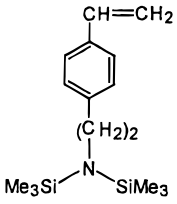


Figure 1. ^1H NMR spectra of (a) poly(4-(*N*,*N*-bis(trimethylsilyl)amino)styrene), (b) poly(4-(*N*,*N*-bis(trimethylsilyl)aminomethyl)styrene), and (c) poly(4-(*N*,*N*-bis(trimethylsilyl)-aminoethyl)styrene.

Table 1. Polymerization of Styrenic Monomers Using Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$ Catalyst[a]

monomer	[catalyst] (mM)	[monomer] (M)	conversion (wt %)	activity[b] ($\times 10^{-6}$)	syndiotactic[c] (%)	T_g[d] (°C)	T_m[d] (°C)	$[\eta]_{inh}$[e] (dL/g)
	0.6	1.28	96.5	11.15	97.1	100	270	0.75
	9.5	1.30	8.5	0.10	35.8	115	278 (weak)	0.04
	5.0	1.27	45.0	1.58	76.5	157	325	0.12
	5.0	1.30	80.2	2.97	85.2	152	330	0.29
	2.5	1.28	90.1	7.00	90.5	138	320	0.45

[a] Polymerization conditions: at 35 °C for 60 min, Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$ = 1, toluene solvent = 15 mL. [b] Activity in units of g of polymer/(mol of Ti)·(mol of monomer)·(h). [c] Portion of syndiotactic polymer, insoluble in 2-butanone and determined by ^{13}C NMR. [d] Determined by DSC at a heating rate of 10 °C/min. [e] Inherent viscosity, [η], determined in 1,2,4-trichlorobenzene at 130 °C.

addition, one peak at 3.75 ppm in Figure 1b is assigned to the protons of the ϕ-C**H**$_2$−N group and two peaks at 2.88 and 3.45 ppm in Figure 1c are assigned to the protons of the ϕ-C**H**$_2$−C**H**$_2$−N group. The good agreement between expected and measured peak intensity ratios for the protons in each group indicates, within the experimental error, that all three reaction products are clean.

Table 1 compares the polymerization results of styrene derivatives containing masked amino groups and styrene (control reaction) using Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$ catalyst under similar reaction conditions.

Homopolymerization of 4-(dimethylaminomethyl)styrene gave a very low polymer yield, with less than 1% of catalyst activity compared to that of styrene. The poor catalyst activity may due to the inadequate steric protection of the amino group by the two methyl groups. On the other hand, all three trimethylsilyl protected monomers, i.e., 4-(*N*,*N*-bis(trimethylsilyl)amino)styrene, 4-(*N*,*N*-bis(trimethylsilyl)aminomethyl)styrene, and 4-(*N*,*N*-bis(trimethylsilyl)aminoethyl)styrene, exhibited good catalyst activities. Especially, 4-(*N*,*N*-bis(trimethylsilyl)aminoethyl)styrene, having a spacer of two methylene groups between styrene and the protected amino group, showed close to 70% of the reactivity of styrene. A relatively weak interaction between the protected functional group and active sites may still exist, and locating the functional group further away from the olefin unit is clearly advantageous in minimizing the acid−base complexation.

The influence of the functional group on the polymerization reaction was also evident in the polymer structure. Both polymer molecular weight and syndiotacticity paralleled catalyst activity. About 90% of poly(4-(*N*,*N*-bis(trimethylsilyl)aminoethyl)styrene) obtained was syndiotactic polymer with high molecular weight (M_w = 10.5 × 10^4; M_n = 4.6 × 10^4 g/mol), determined by gel permeation chromatography (GPC). The narrow molecular distribution (M_w/M_n = 2.3), similar to s-PS homopolymer, strongly indicates the negligible effect of functional group on the catalytic site during the polymerization reaction.

Because the masking amino group in 4-(*N*,*N*-bis(trimethylsilyl)amino)styrene has some effects on the polymerization, it was very interesting to study this system further in terms of the nature of the catalytic site, especially the relationship between bulky ligands in the catalyst and/or cocatalyst and the catalyst activity and syndiotacticity of the resulting polymer. Table 2 summarizes the results for 4-(*N*,*N*-bis(trimethylsilyl)-amino)styrene using various half-sandwich titanocene catalyst systems.

Comparing the first four polymerization reactions, using the same Cp*TiMe$_3$ catalyst and four different borane cocatalysts, the bulky tris(2,2′,2″-nonafluorobiphenyl)borane (PBB) shows significantly higher catalyst

Table 2. Syndiospecific Polymerization of 4-(*N*,*N*-Bis(trimethylsilyl)amino)styrene with Titanocene Catalysts[a]

catalyst + cocatalyst	[catalyst] (mM)	[monomer] (M)	conversion (wt %)	activity[b] ($\times 10^6$)	syndiotactic[c] (%)	T_g (°C)[d]	T_m (°C)[d]	[η] (dL/g)[e]
$Cp^*TiMe_3 + B(C_6F_5)_3$	5.0	0.95	44	2.32	76.5	160	325	0.12
$Cp^*TiMe_3 + [Ph_3C]^+[B(C_6F_5)_4]^-$	5.0	0.95	65	3.42	78.2	158	325	0.14
$Cp^*TiMe_3 + [HNMe_2Ph]^+[B(C_6F_5)_4]^-$	5.0	0.96	40	2.11	67.8	157	324	0.07
Cp^*TiMe_3 + PBB	3.0	0.94	90	7.90	94.5	160	325	0.28
$IndTiMe_3 + B(C_6F_5)_3$	5.0	0.95	40	2.11	70.6	158	323	0.14
[2-Me-Benz[*e*]Ind]$TiMe_3 + B(C_6F_5)_3$	3.0	0.95	75	6.59	85.7	160	326	0.24
[2-Me-Cp[*l*]Phen]$TiMe_3 + B(C_6F_5)_3$	3.0	0.95	86	7.55	90.2	159	327	0.38
Cp^*TiMe_3 + MAO (100)	10.0	0.95	5	0.13				
Cp^*TiCl_3 + MAO (1000)	10.0	0.96	10	0.26	46.7	158	318	0.08

[a] Polymerization conditions: at 35 °C for 60 min, toluene = 10 mL, [catalyst]/[cocatalyst] = 1 except MAO cases. [b] Activity in units of g of polymer/(mol of Ti)·(mol of monomer)·(h). [c] Portion of syndiotactic polymer, insoluble in 2-butanone and determined by ^{13}C NMR. [d] Determined by DSC at a heating rate of 10 °C/min. [e] Inherent viscosity, [η], determined in 1,2,4-trichlorobenzene at 130 °C.

activity (more than 2−3 times higher than the others) and the highest content (94.5%) of syndiotactic polymer. The large $(PBB-CH_3)^-$ anion, associated with the half-sandwich titanocene cation, apparently prevents any acid−base interaction between the active sites and the silane-protected amino groups. In addition, it does not reduce the coordination capacity or insertion of α-olefin. In fact, both catalyst activity and syndiotactic polymer content surpasses the levels for 4-(*N*,*N*-bis(trimethylsilyl)aminoethy)styrene) as shown in Table 1. Similar steric effects were also observed in the catalyst itself. In a second set of comparative reactions, using various titanocene catalysts and the same $B(C_6F_5)_3$ cocatalyst, significantly higher catalyst activity and content of syndiotactic polymer were observed in the polymerization using ([2-Me-Cp[*l*]Phen]$TiMe_3/B(C_6F_5)_3$ catalyst with a bulky ligand. It is interesting to note that all catalyst systems using MAO cocatalyst produced very low yields of polymer, which may be associated with the interaction between MAO and the silane-protected functional group. Overall, the experimental results clearly show the advantages of combined protection mechanisms, including masking group, spacer, and bulky ligands in catalyst and cocatalyst. All of them appear to have no effect on the syndiospecific polymerization of styrene derivatives.

Syndiotactic Polystyrene Derivatives Containing Primary Amino Groups. The trimethylsilyl protected amino groups in polymer **II** were converted to primary amino groups by hydrolysis followed by neutralization. The complete removal of trimethylsilyl groups was evidenced by ^1H NMR spectra (Figure 2). Three resulting polymers, i.e., poly(4-aminostyrene), poly(4-methyleneaminostyrene), and poly(4-ethyleneaminostyrene), were prepared from the three corresponding protected polymers shown in Figure 1.

The silane groups, with a chemical shift near 0.15 ppm, were removed to beyond the detectable level in all samples. New chemical shifts appear at 3.95 ppm (Figure 2a) and 2.47 ppm (Figure 2b), corresponding to ϕ-N**H**$_2$ and ϕ-CH_2N**H**$_2$ in poly(4-aminostyrene) and poly(4-aminomethylstyrene), respectively. The chemical shift for ϕ-CH_2−CH_2N**H**$_2$ in poly(4-aminoethylstyrene) (Figure 2c) appears at 3.45 ppm, which almost overlaps with the peak at 3.40 ppm, corresponding to ϕ-CH_2−C**H**$_2$$NH_2$. The rest of resonances for aliphatic and aromatic protons remain unchanged, indicating a clean and selective deprotection reaction. It is very interesting to note that two sharp aromatic resonances, compared with those of the corresponding atactic polystyrene derivatives[16] prepared by living anionic polymerization, imply the steric regularity along the polymer chain.

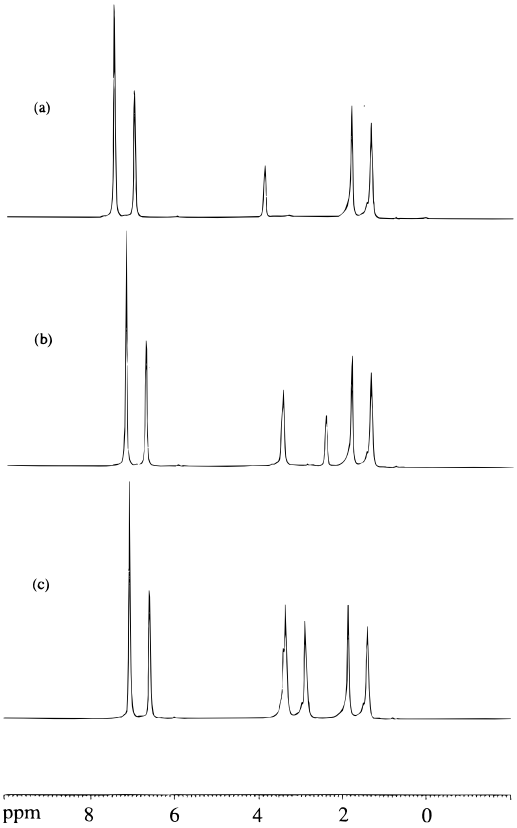
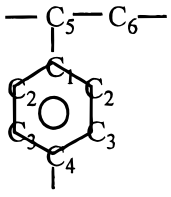


Figure 2. ^1H NMR spectra of (a) poly(4-aminostyrene), (b) poly(4-aminomethylstyrene), and (c) poly(4-aminoethylstyrene).

Stereostructure of polymer was further examined by ^{13}C NMR. Figure 3 shows ^{13}C NMR spectra of poly(4-aminostyrene), poly(4-aminomethylstyrene), and poly(4-aminoethylstyrene).

All peaks are sharp and assigned to the corresponding carbon atoms in the polymer structures. The presence of a single resonance for the quaternary C_1 carbon in phenyl groups (at 140.2 ppm in Figure 3a, 142.1 ppm in Figure 3b, and 142.5 ppp in Figure 3c) shows that these polymers are highly syndiotactic.



The same conclusion can be reached by considering two

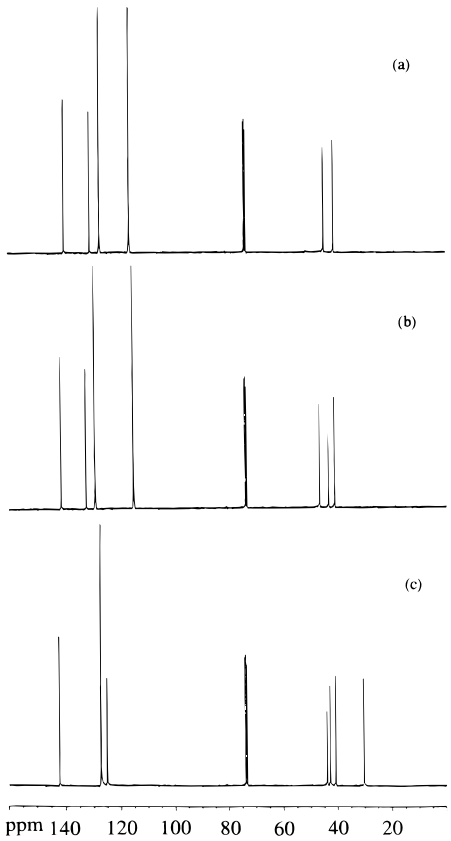


Figure 3. ^{13}C NMR spectra of (a) poly(4-aminostyrene), (b) poly(4-aminomethylstyrene), and (c) poly(4-aminoethylstyrene).

C_5 and C_6 aliphatic carbons in the polymer backbone. Figure 3a shows two sharp resonances at 45.0 and 41.5 ppm, corresponding to methine C_5 and methylene C_6 in a highly stereoregular environment. In Figure 3b, in addition to C_5 and C_6 carbons (peaks at 43.8 and 41.5 ppm, respectively), a new resonance at 47.0 ppm corresponds to the methylene carbon atom in the ϕ-$\mathbf{C}H_2-NH_2$ group. In Figure 3c, two C_5 and C_6 carbon resonances (peaks at 43.2 and 41.0 ppm, respectively) are accompanied by two new resonances at 44.4 and 30.2 ppm, corresponding to ϕ-$CH_2-\mathbf{C}H_2-NH_2$ and ϕ-$CH_2-\mathbf{C}H_2-NH_2$, respectively. It is interesting to note that the sharp resonance feature resembles those of syndiotactic polystyrene but is very different from several reported atactic polystyrene derivatives containing chloro and methoxy groups[17] prepared with other catalyst systems.

After deprotection, the molecular weight distribution of the polymer remains narrow ($M_w/M_n = 2.4$) with an expected reduction in polymer molecular weight ($M_w = 8.4 \times 10^4$; $M_n = 3.5 \times 10^4$ g/mol), estimated by standard polystyrene calibration.

DSC Studies. Differential scanning calorimetry (DSC) was used to measure the melting temperature of new polymers. Figures 4 and 5 show DSC curves of two sets of samples studied in Figures 1 and 2, respectively.

All samples were measured under the same thermal treatment, and the curves were recorded in the second heating cycle. In general, every sample shows a melting endotherm, indicative of semicrystalline morphology. Their melting temperatures are significantly higher than that of s-PS (~270 °C). In Figure 4, three silane-protected polymers show melting points around 320 °C. In Figure 5, after deprotection the melting point increases to about 340 °C for poly(4-aminomethylstyrene) and poly(4-aminoethylstyrene) and about 360 °C for poly(4-aminostyrene). It is very interesting to note that the endothermic peak becomes very sharp in all three NH_2-containing polymers, implying well-organized and uniform crystalline structure. The hydrogen bonding between NH_2 groups may also enhance the crystallization rate.

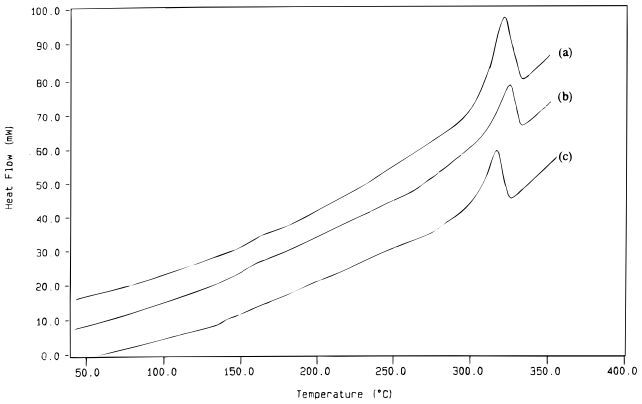


Figure 4. DSC curves of (a) poly(4-(*N*,*N*-bis(trimethylsilyl)-amino)styrene), (b) poly(4-(*N*,*N*-bis(trimethylsilyl)aminomethyl)styrene), and (c) poly(4-(*N*,*N*-bis(trimethylsilyl)aminoethyl)-styrene.

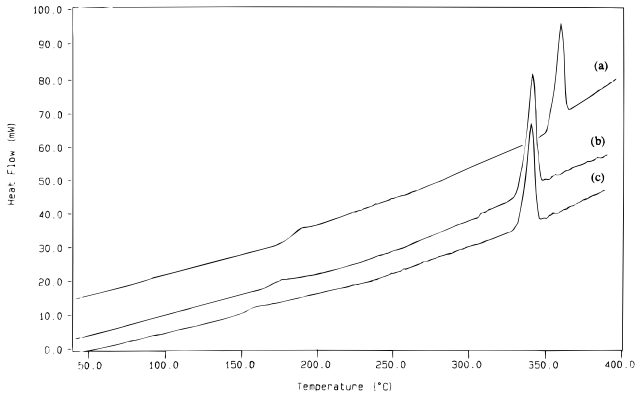


Figure 5. DSC curves of (a) poly(4-aminostyrene), (b) poly-(4-aminomethylstyrene), and (c) poly(4-aminoethylstyrene).

Experimental Section

All manipulations of air- and moisture-sensitive chemicals were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high-vacuum (10^{-6} Torr) line or in a argon-filled glovebox with a high-capacity recirculator (<1 ppm of O_2).

Materials. Anhydrous hexane, tetrahydrofuran (THF), heptane, pentane, diethyl ether, and toluene were purified by refluxing over Na−K alloy/benzophenone ketyl under nitrogen for at least a week followed by distillation. Styrene, 4-aminostyrene, 4-chlorostyrene, *N*-(4-vinylbenzyl)-*N*,*N*-dimethylamine, and 4-vinylbenzyl chloride were purchased from Aldrich or Fisher Scientific and dried over calcium hydride for 5 h at room temperature and distilled under reduced pressure prior to use. Trimethylsilyl chloride (Aldrich) was distilled from CaH_2 and degassed before use. Cp*$TiCl_3$ (Cp* = η^5-C_5Me_5), Ind$TiCl_3$, $B(C_6F_5)_3$, Cp_2ZrMe_2, $Cp^*_2ZrMe_2$ hexamethyldisilazane, ethylmagnesium bromide, benzylmagnesium chloride, lithium bis(trimethylsilyl)amide, and chloromethyl methyl ether were purchased from Aldrich and used without further purification. (2-Methylbenz[*e*]indenyl)trichlorotitanium ([2-Me-Benz[*e*]Ind]$TiCl_3$),[18] 2-methylcyclopenta-[*l*]-phenanthrene titanium trichloride ([2-Me-Cp[*l*]Phen]$TiCl_3$),[19]

$[Ph_3C]^+[B(C_6F_5)_4]^-$,[20] $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$,[21] Cp*$TiMe_3$,[22] tris(2,2′,2″-nonafluorobiphenyl)borane (PBB),[23] *N*,*N*-bis(trimethylsilyl)methoxymethylamine,[24] 4-(*N*,*N*-bis(trimethylsilyl)-amino)styrene,[25] 4-[*N*,*N*-bis(trimethylsilyl)aminomethyl]styrene,[26] and 4-[2-*N*,*N*-bis(trimethylsilyl)amino]ethyl]styrene[26] were prepared according to literature procedures.

Synthesis of IndTiMe$_3$. $IndTiCl_3$ (0.93 g, 3.46 mmol) was mixed with 40 mL of hexane in a 100 mL Schlenk tube in a drybox. The flask, equipped with a septum and a stir bar, was removed from the drybox, cooled to −78 °C, and allowed to stir for 10 min. Three equivalents of MeLi was added as a 1.6 M solution in diethyl ether (6.5 mL, 10.4 mmol). The resultant red/orange solution was allowed to stir at this reduced temperature for 30 min before it was warmed to room temperature and allowed to stir for 4 h. The reaction mixture became a yellow suspension. Upon filtration of LiCl through a medium glass frit packed with Celite and elimination of the solvent under reduced pressure, 0.68 g (90% yield) of yellow $IndTiMe_3$ was obtained as a microcrystalline solid. Recrystallization from pentane at −78 °C gave the product as yellow prisms that were sensitive to moisture and air. ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 2H, arom H), 7.52 (m, 2H, arom H), 7.15 (d, 2H, CpH), 7.10 (t, 1H, CpH), 0.68 (s, 9H, Ti-Me).

Synthesis of [2-Me-Benz[*e*]Ind]TiMe$_3$ and [2-Me-Cp[*l*]-Phen]TiMe$_3$. Similar procedures (in the previous section) were followed for the addition of 3 equiv of MeLi to [2-Me-Benz[*e*]Ind]$TiCl_3$ (1.05 g, 3.14 mmol) solution to yield a orange solution. After stirring the solution overnight at room temperature, a white/yellow suspension was observed. Filtration and crystallization produced 0.73 g (85% yield) of yellow/beige microcrystalline [2-Me-Benz[*e*]Ind]$TiMe_3$ solid. The structure was confirmed by ^{1}H NMR ($CDCl_3$): δ 8.20−8.25 (m, 1H, arom H), 7.55−7.82 (m, 5H, arom H), 7.45 (d, 1H, CpH), 7.10 (d, 1H, CpH), 2.65 (s, 3H, CH_3), 0.75 (s, 9H, Ti−Me).

In the preparation of [2-Me-Cp[*l*]Phen]$TiMe_3$, MeMgCl (8.7 mmol) in THF was added to [2-Me-Cp[*l*]Phen]$TiCl_3$ solution. The resulting red/orange solution turned yellow after stirring overnight at room temperature. Filtration and crystallization produced 0.42 g (49% yield) of a yellow [2-Me-Cp[*l*]Phen]$TiMe_3$ powder. The structure was confirmed by ^{1}H NMR ($CDCl_3$): δ 8.55 (d, 2H, arom H), 8.17 (d, 2H, arom H), 7.70−7.60 (m, 4H, arom H), 7.45 (s, 2H, CpH), 2.75 (s, 3H, CH_3), 0.77 (s, 9H, Ti−Me).

Polymerization. A 100 mL glass reactor equipped with a magnetic stirrer was attached to a high-vacuum line and then sealed under nitrogen. The reactor was then placed in a bath at the desired temperature. Freshly distilled anhydrous/anaerobic toluene was introduced through a syringe, followed by addition of anhydrous/anaerobic styrene monomers. A prescribed amount of the mixture of catalyst and cocatalyst in toluene was then quickly syringed into the rapidly stirred reaction system through an Ar-purged gastight syringe. After a measured time interval, the reaction was quenched with 10% HCl in methanol, filtered, and dried overnight in a vacuum oven at 80 °C. The polymer was then extracted with 2-butanone for 48 h in a Soxhlet extractor to remove any atactic polymer. The percent of syndiotactic polymer was determined as the amount of polymer insoluble in 2-butanone and confirmed by the ^{13}C NMR spectra.

Deprotection of Amino-Functionalized Syndiotactic Polystyrenes. Syndiotactic poly[4-(*N*,*N*-bis(trimethylsilyl)-amino)]styrene (2.0 g) was dissolved in *o*-dichlorobenzene (50 mL) at 110 °C and then cooled to 80 °C. To this solution was added dropwise 2 N methanolic hydrogen chloride solution. The mixture was stirred for 2.5 h at 80 °C, and the pH of the system was controlled between 3 and 5 during the reaction. The reaction mixture was then added slowly to 1 N methanolic KOH solution. The neutralized poly(4-aminostyrene) was collected and washed with 1 M aqueous ammonia and water under a nitrogen atmosphere. After the solution was removed, the polymer was dried overnight at 40 °C in a vacuum. The polymer yield was quantitative. Similarly, both syndiotactic poly(4-aminomethylstyrene) and poly(4-aminoethylstyrene) were obtained in almost quantitative yields.

Measurements. The inherent viscosity of the polymers was determined in 1,2,4-trichlorobenzene solutions at 135 °C. DSC curves were recorded with a Perkin-Elmer DSC-7 system at a heating rate of 10 °C/min. The melting temperature of the polymers was determined from the second heating scan. Both ^{1}N NMR and ^{13}C NMR spectra were recorded in 1,1,2,2-tetrachloroethane-d_2 at 110 °C on a Bruker PX-300 spectrometer. The molecular weight and molecular weight distribution of polymers were determined by gel permeation chromatography (GPC) using a Waters 150 C instrument with a refractive index (RI) detector and a set of u-Styragel HT columns of 10^6, 10^5, 10^4, and 10^3 pore size in series. The measurements were taken at 140 °C using 1,2,4-trichlorobenzene (TCB) as solvent and mobile phase at a flow rate of 0.7 mL/min. Polystyrene samples were used as standards for calibration.

Conclusion

In this work, a new family of syndiotactic styrenic polymers containing primary amino groups, including poly(4-aminostyrene), poly(4-aminomethylstyrene), and poly(4-aminoethylstyrene), has been described. With the combination of trimethylsilane masking group and a selective catalyst system, the styrene derivatives containing amino groups were homopolymerized to high polymers with high catalyst activity and high syndiotactic polymer content (similar to s-PS). The effective removal of the masking group affords the desired polymers with high melting temperature and relatively fast crystallization rate.

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