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Synthesis of Syndiotactic Polystyrene (s-PS) Containing a Terminal Polar Group and Diblock Copolymers Containing s-PS and Polar Polymers

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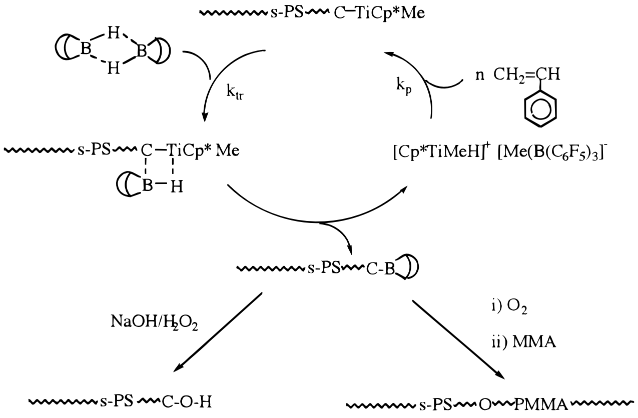
One of the major advantages of metallocene technology is in the preparation of syndiotactic polystyrene (s-PS),[1] which is a semicrystalline polymer with a high melting temperature (>270 °C). Despite the unique thermal properties, the s-PS polymer resembles regular atactic polystyrene (a-PS) prepared by free radical or anionic initiators in that it has a very poor impact strength and a 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 the functionalized s-PS polymer, including sulfonated s-PS[3] and hydroxylated s-PS[4] prepared via a poly(styrene-*co*-4-*tert*-butyldimethylsilyloxystyrene) precursor.

The in situ chain transfer reaction to the molecule containing the heteroatom during the transition metal coordination polymerization of α-olefins presents a very convenient method of preparing polyolefins containing a terminal polar group. A couple of years ago, Marks et al.[5] reported that some organosilanes having Si−H groups are effective chain transfer agents in metallocene-mediated polymerizations that result in silane-terminated polyolefins and copolymers. Recently, we reported a new organoborane chain transfer agent[6] containing a B−H group, such as a 9-borabicyclo[3.3.1]nonane (9-BBN), that can also effectively engage in chain transfer reaction during zirconocene-catalyzed ethylene polymerizations. The resulting borane-terminated polyethylene is a very versatile intermediate in the preparation of poly(ethylene-*b*-methyl methacrylate) diblock copolymer.

In this communication, we will explore this B−H chain transfer reaction in titanocene-catalyzed styrene polymerizations for the preparation of two new types functionalized s-PS polymers, including a s-PS having a terminal polar group and a diblock copolymer containing a s-PS and a polar polymer. The reaction scheme is illustrated in Scheme 1.

Scheme 1



With the appropriate choice of reaction conditions and catalyst systems to prevent potential side reactions, such as hydroboration of styrene and reaction between borane and cocatalyst, the ligand exchange reaction takes place between B−H and Ti−polymer chain during the syndiospecific styrene polymerization to obtain the borane-terminated syndiotactic polystyrene (s-PS-t-B). The borane terminal group can be easily interconverted to a hydroxy group under mild reaction conditions, or spontaneously transformed to a peroxide (B−O−O−C) speices by oxidation with oxygen. The B−O−O−C species formed will further decompose to a stable polymeric (C−O*) radical and a borinate radical (B−O*). The alkoxyl radical is active in initiating polymerization of functional monomers.[7] On the other hand, the borinate radical (B−O*) is too stable to initiate polymerization due to the back-donating of electrons to the empty p-orbital of boron. However, this “dormant” borinate radical may form a reversible bond with the radical at the growing chain end to prolong the lifetime of the propagating radical.[8] Overall, the reaction process resembles a transformation reaction from metallocene coordination polymerization to living free radical polymerization via a borane group at the polymer chain end. Since the reaction only involves one borane group per polymer chain, the whole reaction process provides an ultimate test for examining the effectiveness of borane chain transfer agents and the efficiency of the borane reagent in the chain extension process.

A metallocene polymerization with in situ chain transfer reaction was conducted in an autoclave reactor by mixing the designated quantities (shown in Table 1) of styrene, 9-BBN, toluene, and a $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$ complex, under rigorously anhydrous/anaerobic conditions. To minimize mass transfer and to maintain the constant 9-BBN/styrene ratio, the reactions were carried out by rapid mixing and with a short reaction time.

After 3 min of reaction time, the polymer solution was quenched with anhydrous/anaerobic MeOH, and the resulting borane-terminated s-PS (s-PS-t-B) was washed with anhydrous/anaerobic THF to remove excess 9-BBN. The s-PS-t-B was then dried at 50 °C on a high-vacuum line. Some of the s-PS-t-B polymer was oxidized by $NaOH/H_2O_2$ reagents at 40 °C for 6 h to form a hydroxy-terminated polymer (s-PS-t-OH). For the ^1H NMR study, the terminal hydroxy group was further reacted with $Cl-Si(CH_3)_3$ to form silane-terminated s-PS (s-PS-t-O−Si(CH$_3$)$_3$). Figure 1a shows the ^1H NMR spectra of a s-PS-t-O−Si(CH$_3$)$_3$ sample with a molecular weight of about 15 000.

There are two sets of major peaks at 1.45 and 2.10 ppm, corresponding to the C**H**$_2$ and C**H** protons in the s-PS backbone, and at 6.82 and 7.21 ppm, corresponding to the protons of the phenyl groups that have a syndiotactic arrangement. In addition, two minor peaks at 0.15 and 3.81 ppm correspond to the protons of the −O−Si-

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Table 1. Metallocene-Activated Styrene Syndiospecific Polymerization in the Presence of 9-BBN as Chain Transfer Agent[a]

run	amt of 9-BBN (μmol)	reacn time (min)	yield (g)	catalyst activity[b]	syn.[c] (%)	T_m (°C)	[η]	M_w[d]
1	25	3	1.3	2600	97.0	270	1.270	460 000
2	50	3	1.4	2800	96.2	271	0.806	240 000
3	100	3	1.3	2600	95.8	270	0.580	150 000
4	150	3	1.1	2200	95.2	271	0.373	80 000
5	200	3	0.8	1600	93.4	270	0.340	70 000
6	300	3	0.5	1000	94.7	272	0.188	30 000
7	400	3	0.3	600	95.0	270	0.116	15 000
8	500	3	0.1	200	93.2	270	0.087	10 000

[a] Styrene = 10 mL. Catalyst = $[Cp^*TiMe_2]^+[Me(B(C_6F_5)_3]^-$; catalyst concentration = 10 μmol. [b] Catalyst activity = kg of s-PS/mol of Ti·h. [c] Syndiotactic index was determined by ^{13}C NMR. [d] Molecular weight was determined from the intrinsic viscosity in *o*-dichlorobenzene at 135 °C: $[\eta] = 1.38 \times 10^{-4} M_w^{0.7}$.

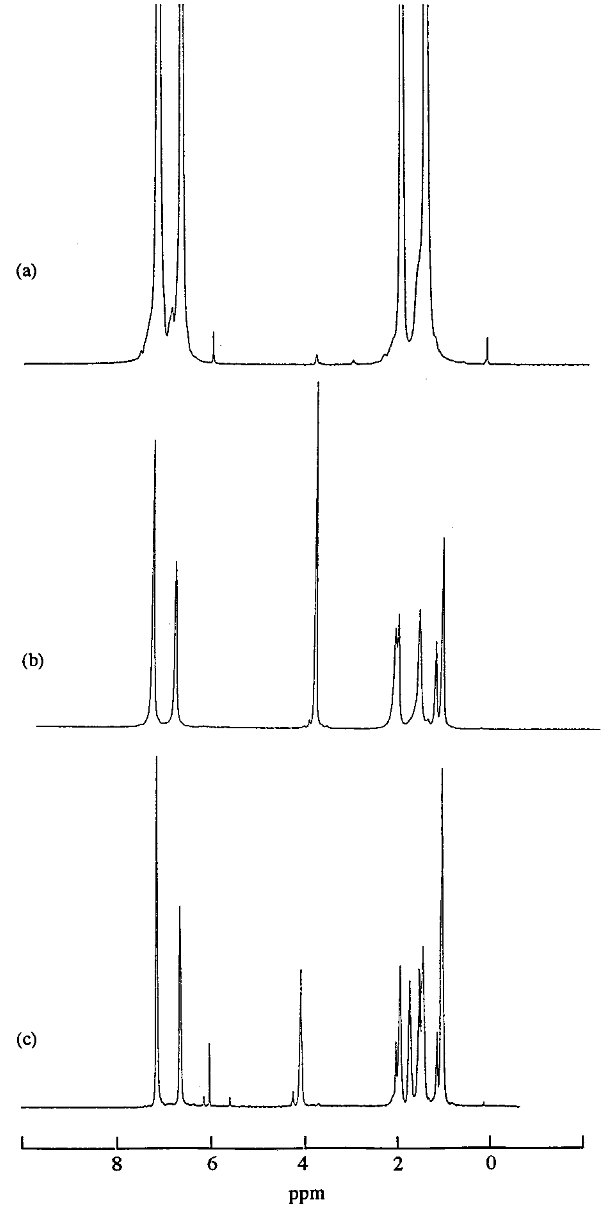

Figure 1. ^1H NMR spectrum of (a) s-PS-t-O−Si(CH$_3$)$_3$ and the corresponding diblock copolymers, (b) s-PS-*b*-PMMA and (c) s-PS-*b*-PBMA. (solvent, $C_2D_2Cl_4$; temperature, 110 °C).

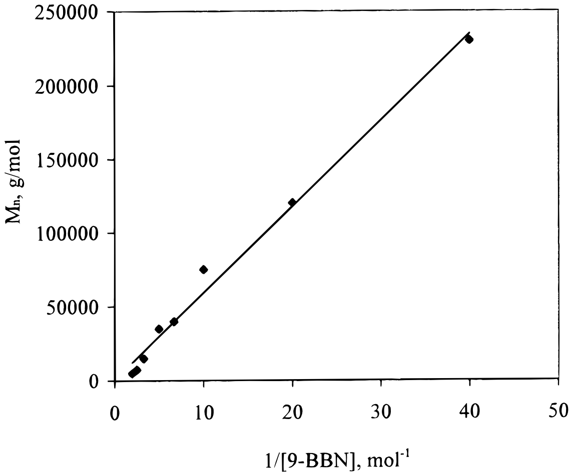

Figure 2. Plot of average molecular weight of s-PS-t-B vs 1/[9-BBN].

$(C\mathbf{H}_3)_3$ and $-C\mathbf{H}(Ph)-OSi(CH_3)_3$ groups, respectively. The combination of peak intensity ratio between silane and phenyl groups and the molecular weight of polymer indicates that most of the s-PS polymers contain a terminal silane group. The silane terminal group in each s-PS polymer implies the effective in situ chain transfer reaction as well as the oxidation and silation reactions, despite of the heterogeneous reaction conditions. Most of the borane and silane terminal groups are located in the amorphous phases, and are readily accessible for the reaction.

The effects of the chain transfer reaction are further revealed by the reduction of polymer molecular weight in the presence of 9-BBN. Figure 2 shows the plot of polymer molecular weight vs the 1/[9-BBN] for the comparative runs 1−8 in Table 1.

Basically, the higher the concentration of 9-BBN chain transfer agent used, the lower the molecular weight of the resulting polystyrene. The catalyst activity was somewhat depressed if a high concentration of 9-BBN was presented in the system, which may reflect the competitive coordination at the titanocene active sites between monomers and chain transfer agents. The polymer molecular weight is almost linearly proportional to 1/[9-BBN]. It is clear that the chain transfer reaction to 9-BBN is the dominant termination process. It is very interesting to note that all s-PS-t-B polymers have similar syndiotacticity and melting temperature (shown in Table 1) to those of s-PS polymer. The 9-BBN chain transfer agent did not interfere the regio- and stereoselective insertion process.

Most of the s-PS-t-B polymer was suspended in benzene and subjected to the oxidation reaction by oxygen in the presence of free radical polymerizable monomers, i.e., methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA). As illustrated in Scheme 1, the borane-terminated s-PS was selectively oxidized and transformed to a stable polymeric radical for polymerization of MMA and BMA. The resulting reaction mixture was carefully fractionated by Soxhlet extraction using boiling THF to remove any PMMA or PBMA homopolymers. In most cases, only a very small amount (about 10%) of homopolymer was present and which may have been initiated by the radical in a bicyclic ring, instead of a polymeric radical, due to the nonselective oxidation reaction of alkyl-9-BBN. The insoluble fraction is primarily s-PS-*b*-PMMA or s-PS-*b*-PBMA diblock copolymer. Parts b and c of Figure 1 show the ^1H NMR spectra of the s-PS-*b*-PMMA and s-PS-*b*-PBMA copolymers, respectively. The new peak at 3.78 ppm is

Table 2. Summary of SPS-*b*-PMMA and SPS-*b*-PBMA Diblock Copolymers

				polar monomer				polystyrene block		p-MMA block	
run	T (°C)	sPS-t-B (g)	O_2 (mL)	monomer	concn (M)	reacn time (h)	yield (g)	$10^{-3}M_n$	M_w/M_n	$10^{-3}M_n{}^a$	unit ratio
1	25	5	1.9	MMA	1.87	3	5.43	15.0	2.2		
2	25	5	1.9	MMA	1.87	6	6.25	15.0	2.2	2.0	100:14
3	25	5	1.9	MMA	1.87	12	7.56	15.0	2.2	5.0	100:35
4	25	5	1.9	MMA	1.87	24	9.98	15.0	2.2	14.0	100:97
5	25	3	1.5	MMA	1.87	6	4.25	10.0	2.4	1.7	100:18
6	40	3	1.5	MMA	1.87	12	5.56	10.0	2.4	4.1	100:43
7	60	3	1.5	MMA	1.87	24	7.23	10.0	2.4	10.5	100:109
8	25	7	2.4	MMA	1.87	6	7.56	70.0	2.1	3.0	100:4.5
9	25	7	2.4	MMA	1.87	12	8.13	70.0	2.1	8.0	100:12
10	25	7	2.4	MMA	1.87	24	8.98	70.0	2.1	17.0	100:25
11	25	5	1.9	BMA	1.87	10	6.72	15.0	2.2	7.1	100:35
12	25	5	1.9	BMA	1.87	20	7.56	15.0	2.2	15.0	100:72
13	25	5	1.9	BMA	1.87	24	8.94	15.0	2.2	18.3	100:89

[a] Determined by ^{1}H NMR with reference to M_n values of the initial polystyrene.

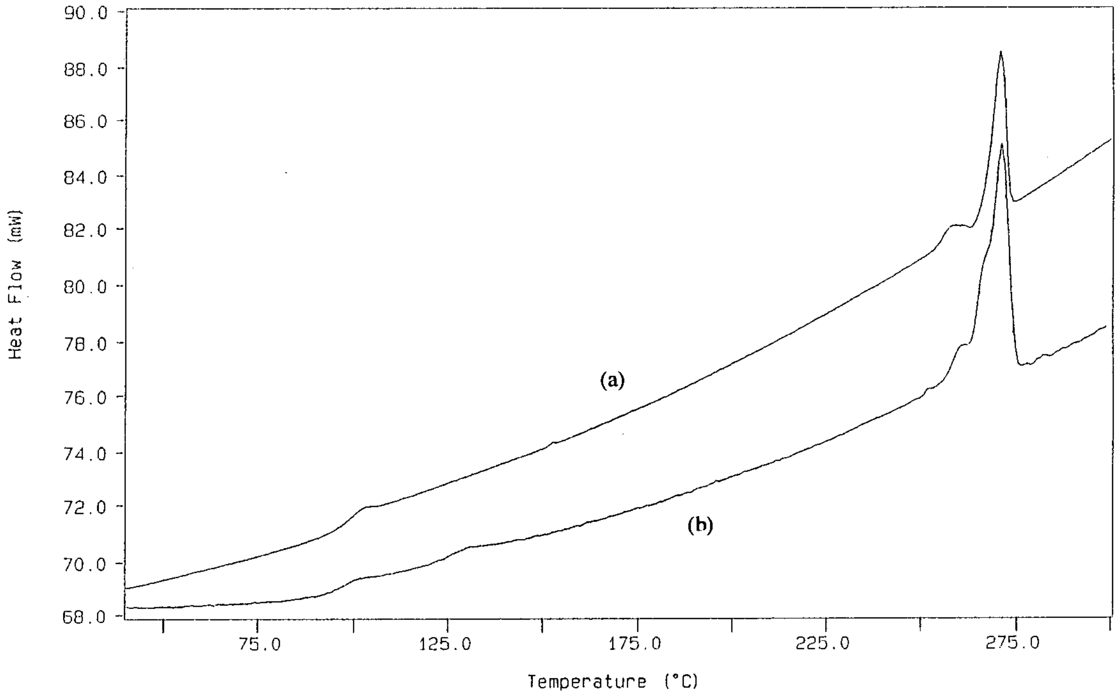

Figure 3. DSC curve comparison between (a) s-PS-t-OH polymer and (b) the corresponding s-PS-*b*-PMMA.

assigned to the methoxyl groups (OC**H**$_3$) in the PMMA block, and the peak at 4.15 ppm is assigned to the methylene groups (OC**H**$_2$) in the PBMA block. Apparently, a very high concentration of polar polymer blocks can be incorporated in the s-PS diblock copolymers.

Table 2 summarizes the reaction conditions and results of the diblock copolymers.

In general, both PMMA and PBMA blocks increase with increased the reaction time, and chain extension reactions continue even after 12 h. Diblock copolymers with a nearly 1/1 mole ratio of [styrene]/[MMA] or [styrene]/[BMA] have been prepared, despite the heterogeneous reaction conditions. These effective and long-life chain extension reactions provide strong evidence of the borane group existence at the s-PS chain end and imply the living free radical chain extension process. Figure 3 compares two DSC curves of s-PS-t-B (run 7 in Table 1) and the corresponding s-PS-*b*-PMMA (run 4 in Table 2).

Two identical thermal transition temperatures, including a T_m near 270 °C and a T_g near 100 °C for the s-PS polymer, were observed in both samples. A clear new T_g at about 130 °C (corresponding to the high molecular weight PMMA polymer[7]) was shown in Figure 3b. Both polymer segments in the s-PS-*b*-PMMA copolymer must have long consecutive (undisturbed) sequences to form separate domains.

In summary, this research clearly demonstrates a novel method that can be used to prepare new functionalized s-PS polymers, namely s-PS containing a terminal polar group and a s-PS diblock copolymer containing a s-PS and a polar polymer blocks. The in situ chain transfer reaction to borane (B−H) during titanocene-catalyzed styrene polymerization provides a convenient and effective route for preparing borane-terminated s-PS that is a very valuable intermediate for preparing functionalized s-PS with a polar end group or diblock copolymer containing a polyolefin and functional (polar) polymer segments.

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Supporting Information Available: Text giving experimental details for this work, including instrumentation and materials and syntheses. This material is available free of charge via the Internet at http://pubs.acs.org.

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