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Syntheses of *syndiotactic*-Polystyrene-*graft*-poly(methyl methacrylate), *syndiotactic*-Polystyrene-*graft*-poly(methyl acrylate), and *syndiotactic*-Polystyrene-*graft*-*atactic*-polystyrene with Defined Structures by Atom Transfer Radical Polymerization

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ABSTRACT: Syndiotactic polystyrene graft copolymers, *syndiotactic*-polystyrene-*graft*-poly(methyl methacrylate), *syndiotactic*-polystyrene-*graft*-poly(methyl acrylate), and *syndiotactic*-polystyrene-*graft*-polystyrene, were synthesized by atom transfer radical polymerization using brominated syndiotactic polystyrene as initiator and CuBr combined with pentamethyldiethylenetriamine as catalyst. Both the graft density and the molecular weight of the graft segments were controlled by changing the bromine content of syndiotactic polystyrene and the amount of monomer used in the grafting reaction. The atom transfer radical polymerization mechanism for grafting was supported by NMR analysis of the end groups. The melting point behavior of *syndiotactic*-polystyrene-*graft*-poly(methyl methacrylate) depends on both graft density and graft length.

Introduction

Syndiotactic polystyrene (*s*PS) has been prepared by metallocene catalysts activated by methyaluminoxane (MAO).[1] Due to its stereoregularity, *s*PS is crystalline with a melting point greater than 255 °C. This, along with its good chemical resistance, low water absorbability, and enhanced mechanical properties, makes *s*PS an attractive engineering thermoplastic. However, its inherent brittleness and poor impact and tear resistance significantly limit some end uses.

Recently, attempts have been made to improve the physical properties and processability of *s*PS through several procedures. One involves the addition of a second monomer, in particular ethylene, during polymerization to produce a styrene/olefin copolymer.[2] Depending on the polymerization condition and the metallocene catalyst used, different microstructures, such as random, block, and alternating, are produced.[2−4] Physical blending with other polymers is a versatile and economical possibility for producing a material that combines properties of the two blended polymers.[5−7] Indeed, blending with elastomers and fibers may extend the commercial utility of *s*PS.[8] However, since *s*PS lacks functionalities capable of interacting with the second polymer, blending sPS with other polymers usually leads to phase separation. This problem can be solved with new graft or block compatibilizers that incorporate *s*PS and the second polymeric component.

In this paper, we report an efficient method for the synthesis of sPS graft copolymers with defined structures by atom transfer radical polymerization (ATRP).[9] Such polymeric materials cannot be synthesized by other routes due to the inability of a single catalyst/initiator to effect the syndiotactic polymerization of styrene and the polymerization of the second monomer.

Experimental Section

Characterization. NMR spectra were recorded at 130 °C on a Bruker FX-300 spectrometer using 1,1,2,2-tetrachloroethane-d_2 as the solvent. The chemical shifts were referenced to the solvent. Thermal analyses of polymers were conducted on a Perkin-Elmer DSC-7 operating from 25 to 300 °C with a heating rate of 20 °C/min. Thermal history differences were erased by reheating samples and recording a second DSC scan.

Materials. Styrene (99%), methyl acrylate (MA, 99%) and methyl methacrylate (MMA, 99%) were vacuum distilled from CaH_2 and stored under N_2. CCl_4 (99+ %), anisole (99%), CuBr (98%), and pentamethyldiethylenetriamine (PMDETA, 99%) were obtained from Aldrich and used without further purification. Methylaluminoxane (MAO) was supplied by Ethyl Co. as a 30 wt % solution in toluene.

Synthesis of *s*PS. In a N_2-filled glovebox, a 500 mL flask with a magnetic stirring bar was charged with toluene (100 mL), MAO (25 mmol), and $CpTiCl_3$ (50 μmol). The flask was sealed with a rubber septum, removed from the glovebox, and placed in an oil bath at 50 °C. Styrene (0.3 mol) was then added. The polymerization was stopped after 2 h by the addition of acidified methanol. The resulting polymer was washed with 500 mL of methanol and dried under vacuum for 24 h, affording 15.3 g of polystyrene. The crude product was extracted with boiling methylethyl ketone (MEK) and 14.6 g MEK-insoluble solid was obtained. Yield of *s*PS: 46.8%. The syndiotactic index of *s*PS used in this work was more than 99%, as determined by ^{13}C NMR spectroscopy.[1a] $^{13}C\{^1H\}$ NMR (1,1,2,2-$C_2D_2Cl_4$, ppm): 41.1, 44.5, 125.0, 128.0, 146. M_w = 135 000; M_w/M_n = 2.1.

Bromination of *s*PS. In a typical experiment, *N*-bromosuccinimide (NBS, 0.96 g) and AIBN (0.13 g) were added to a suspension of *s*PS (5 g) in CCl_4(200 mL) in a 500 mL round-bottomed flask with a magnetic stirring bar. After refluxing at 90 °C for 5 h, the reaction mixture was filtered and washed well with acetone and then dried overnight under vacuum at ambient temperature. Yield: 5.20 g. Elemental analysis by Galbraith Laboratories revealed a bromine content of 6.3%. The ^1H NMR spectrum (1,1,2,2-$C_2D_2Cl_4$) of the sample is shown in Figure 1b.

Synthesis of *s*PS-*graft*-PMMA (Table 2, Entry 2). In a typical experiment, a dry round-bottomed flask was charged with anisole (10 mL), CuBr (0.45 mmol), PMDETA (0.45 mmol), MMA (0.02 mol), and brominated *s*PS (0.5 g, 6.3 mol % Br). The flask was sealed and two cycles of freeze−pump−thaw were performed to remove O_2. Then the flask was filled with purified N_2. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath at 90 °C for 4.5 h. The reaction was terminated by pouring

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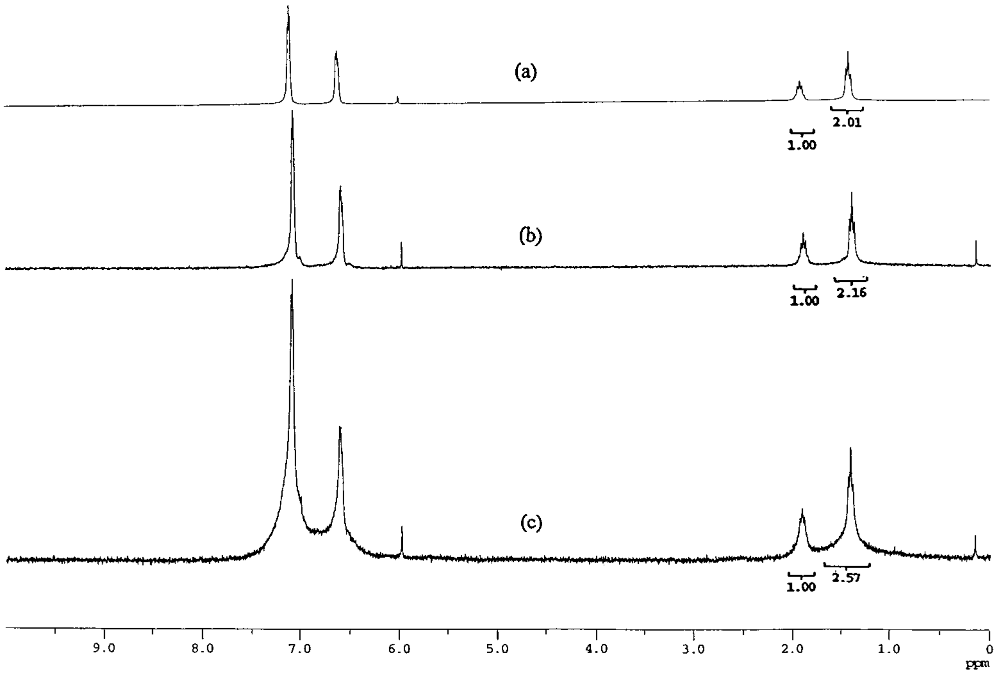


Figure 1. ^{1}H NMR spectra of (a) *s*PS, (b) brominated *s*PS (6.3 mol % Br), and (c) brominated *s*PS (18.9 mol % Br).

Table 1. Bromination of *s*PS[a]

run	*s*PS (mmol)	[NBS]/*s*PS (mol/mol)	[AIBN]/[NBS] (mol/mol)	Br content[b] (mol %)	graft density (graft/1000C)
1	38.4	0.01	0.25	1.1	5
2	48.1	0.03	0.14	2.8	14
3	48.1	0.05	0.13	3.2	16
4	48.1	0.11	0.15	6.3	32
5	48.1	0.33	0.14	18.9	95

[a] Conditions: 90 °C; 200 mL of CCl_4. [b] Determined by elemental analysis.

the contents of the flask into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 1.41 g. The ^{1}H NMR spectrum (1,1,2,2-$C_2D_2Cl_4$) of the sample is shown in Figure 2.

Synthesis of *s*PS-*graft*-PMA (Table 4, Entries 1 and 2). The above procedure was used except MA was the monomer and the reaction temperature was 110 or 120 °C. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$, ppm): 1.4 (CH_2, S); 1.8 (CH_2, MA); 1.9 (CH, S); 2.5 (CH, MA); 3.7 ($COOCH_3$, MA), 6.6−7.1 (phenyl, S).

Synthesis of *s*PS-*graft*-*atactic*-PS (Table 2, Entries 3 and 4). The above procedure was used except styrene was the monomer and the reaction temperature was 110 or 130 °C. The ^{1}H NMR spectrum (1,1,2,2-$C_2D_2Cl_4$) of a sample is shown in Figure 3.

Results and Discussion

Organic halides (R−X) efficiently initiate atom transfer free radical polymerization (ATRP) in the presence of certain transition metal complexes, M_t^n.[9−11] In this polymerization, dormant polymer halide, R−(monomer)$_n$−X, is repeatedly activated by the transition metal compound to produce the growing radical, R−(monomer)$_n^\bullet$, and the oxidized transition metal species, M_t^{n+1}. The equilibrium between dormant and growing species is fast and reversible. The low concentration of radicals minimizes termination relative to propagation rate, and a controlled/living polymerization is achieved.

In this work, *s*PS was partially brominated at the benzylic positions using *N*-bromosuccinimide (NBS) to form a "poly" benzyl bromide. The brominated *s*PS was used as an organic halide initiator in the presence of CuBr combined with the ligand pentamethyldiethylenetriamine (PMDETA) as the catalyst, to graft poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), or atactic polystyrene (*a*PS). The overall procedure is summarized in Scheme 1.

Bromination of *s*PS. *s*PS powder was brominated using NBS and AIBN in CCl_4. Table 1 summarizes the experimental conditions and results of bromination. The degree of bromination increased with increasing amounts of NBS and AIBN. The bromination procedure is quite effective with the bromine content in the product reaching 18.9 mol %, despite of the insolubility of *s*PS in CCl_4.

Figure 1 shows the ^{1}H NMR spectra of starting *s*PS and the brominated products. The resonances at 1.9 and

Table 2. Syntheses of *s*PS-*graft*-PMMA by ATRP[a]

[MMA]/[C(Ph)Br] (molar ratio)	*s*PS−Br (mol % Br)	CuBr (mmol)	PMDETA[b] (mmol)	time (h)	yield (g)	graft density[c] (graft/1000C)	M_n of graft segment[d] (g/mol)	T_m (°C)
68.9	6.3	0.29	0.29	4.5	0.67	32	580	241.7
68.9	6.3	0.45	0.45	4.5	1.41	32	3180	no T_m
172	6.3	0.29	0.29	10.5	3.71	32	11070	no T_m
154	2.8	0.10	0.10	4.5	0.63	14	1000	241.2, 253.2
385	2.8	0.13	0.13	22	1.43	14	7150	251.0
110	18.9	0.32	0.32	5.0	0.80	95	1890	no T_m
110	18.9	0.48	0.48	5.0	1.47	95	3970	no T_m
110	18.9	0.64	0.64	5.0	1.34	95	3560	no T_m

[a] Conditions: 90 °C; 10 mL of anisole. [b] PMDETA = pentamethyldiethylenetriamine. [c] Graft density = [(mol % Br)/2] × 10. [d] M_n of graft segment = [(wt of graft copolymer − wt of starting *s*PS−Br)/mol of Br].

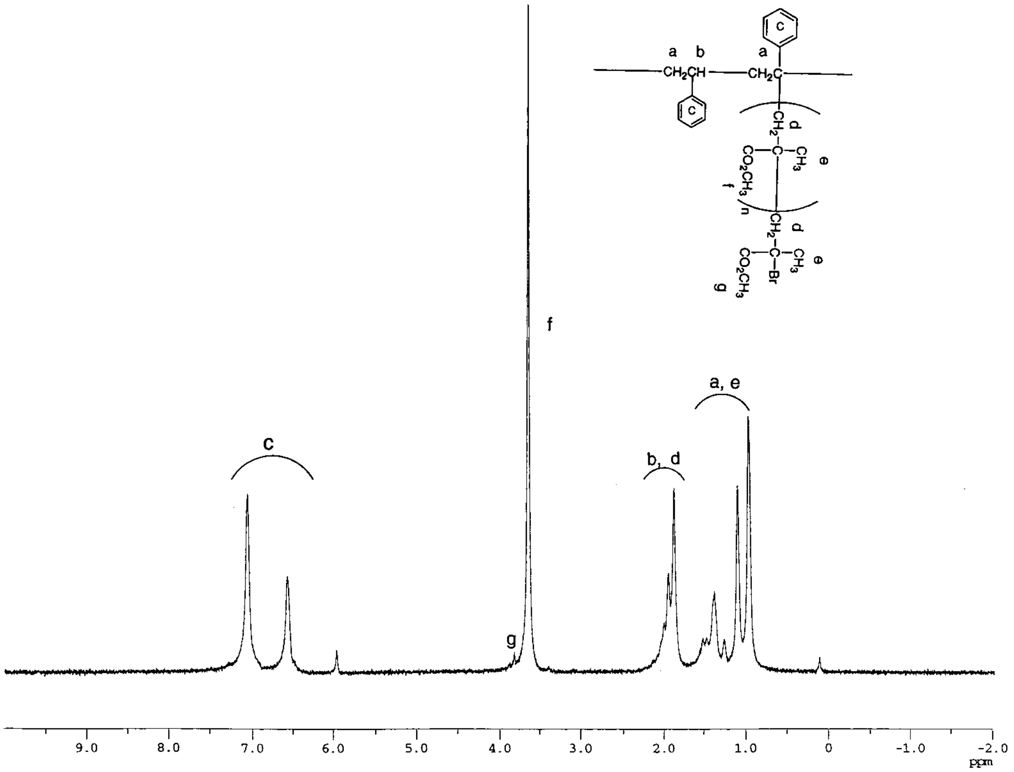


Figure 2. ^{1}H NMR spectrum of *s*PS-*graft*-PMMA.

Table 3. ATRP Grafting of MMA on to *s*PS as a Function of the Ligand[a]

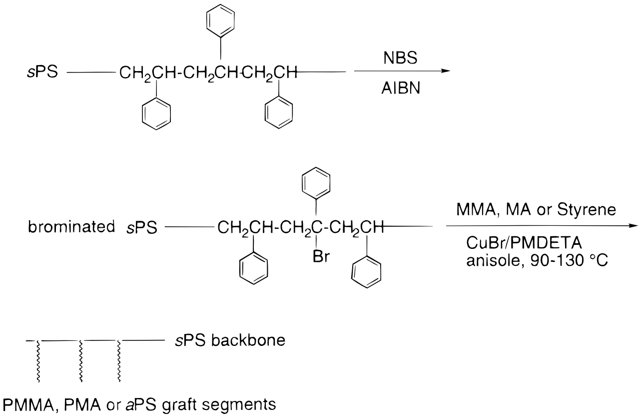
ligand	yield (%)
PMDETA	62.8
2,2′-dipyridyl	39.4
4,4′-diphenyl-2,2′-dipyridyl	34.3
diimine[b]	1.3

[a] Conditions: *s*PS−Br, 0.5 g (3.2 mol %); [MMA]/[C(Ph)Br] (molar ratio) = 208; CuBr, 0.23 mmol; ligand, 0.23 mmol; anisole, 5 mL; MMA, 0.03 mol; 90 °C, 5.5 h. [b] Diimine = 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine.

1.4 ppm are assigned to CH and CH_2 units, respectively, in the *s*PS backbone. After bromination, the intensity ratio of the CH_2 and CH resonances increased from 2 to 2.16 (Run 4, Table 1) and 2.57 (Run 5, Table 1), due to the decrease in peak intensity of the CH unit as a consequence of benzylic bromination. The bromine content of the resultant polymer, estimated from the above integration ratios (7.4 and 22.2 mol % for runs 4 and 5, respectively), are similar to elemental analysis values. This also confirms that the benzylic carbon is the predominant site of bromination. Considering the structure of *s*PS, the distribution of bromine atoms along the polymer backbone should be uniform.

Grafting Reaction. The grafting reaction with methyl methacrylate (MMA) was carried out using brominated *s*PS as initiator, CuBr as catalyst, and PMDETA as ligand. The C−Br groups will be the initiating sites for the ATRP grafts. If they are quantitatively converted to “living” free-radical centers,[9−11] the graft density should be similar to the density of bromine atoms in the *s*PS chains and the grafted side chains will be arranged regularly along the *s*PS backbone.

Scheme 1



Unlike the usual ATRP processes in which the organic halide initiator is soluble in the reaction medium, the brominated sPS was completely insoluble. Nevertheless, as shown in Table 2, the grafting reaction produced graft copolymers with different graft densities and graft

Table 4. Syntheses of *s*PS-*graft*-PMA and *s*PS-*graft*-*a*PS by ATRP[a]

run	CuBr (mmol)	PMDET (mmol)	comonomer (amt, g)	[comonomer]/ [C(Ph)Br] (molar ratio)	time (h)	temp (°C)	yield (%)
1	0.23	0.23	MA, 2.58	200	5.5	110	1.2
2	0.45	0.45	MA, 3.50	271	6.5	120	7.1
3	0.23	0.23	styrene, 3.12	200	5.5	110	6.4
4[b]	0.20	0.20	styrene, 2.66	197	5.5	130	43

[a] Conditions: *s*PS−Br (3.2 mol % Br), 0.5 g; anisole, 5 mL. [b] *s*PS−Br (2.8 mol % Br), 0.5 g.

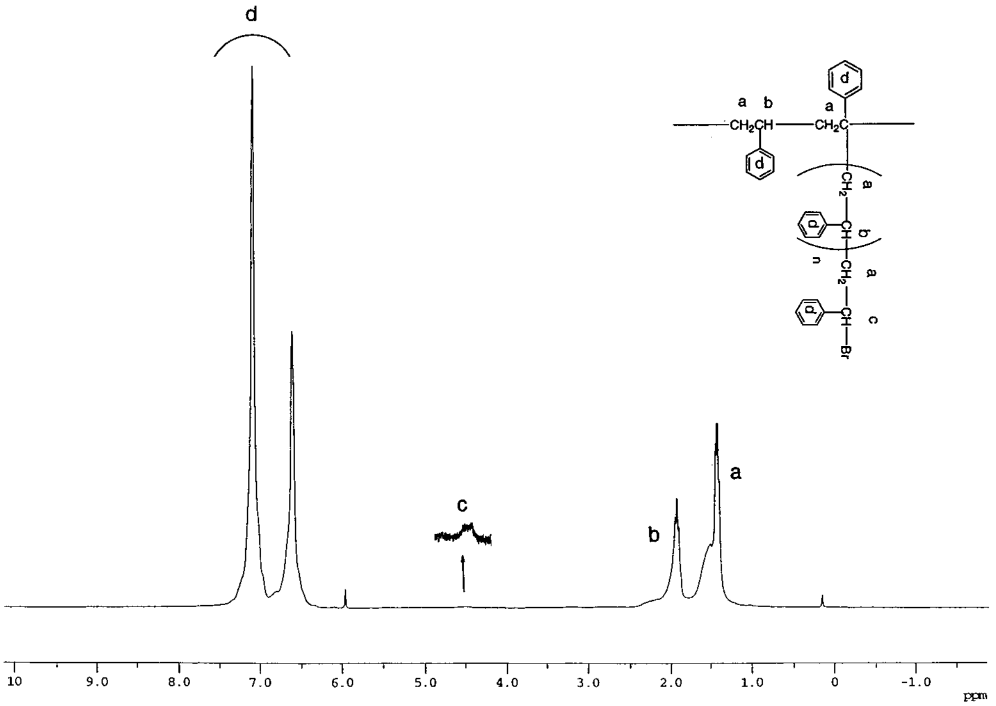


Figure 3. ^{1}H NMR spectrum of *s*PS-*graft*-*a*PS.

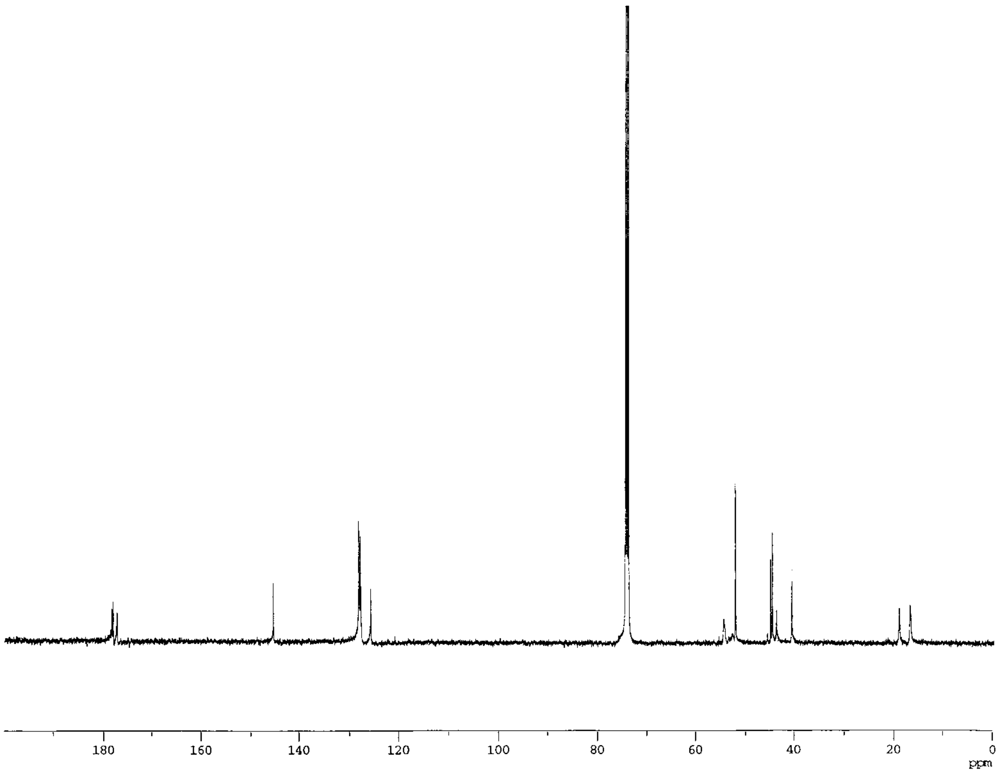


Figure 4. ^{13}C NMR spectrum of *s*PS-*graft*-PMMA.

lengths. Because of the "living" nature of ATRP, copolymers containing long grafted side chains were easily obtained by simply prolonging the reaction time. The optimum molar ratio of CuBr/PMDETA/C−Br for MMA graft copolymerization was 1.5:1.5:1.

The possibility that the grafting reactions resulted in the formation of a mixture of *s*PS and PMMA rather than *s*PS-*graft*-PMMA can be dispelled by the following observations. Under identical ATRP conditions, no PMMA was formed in the absence of brominated *s*PS. As shown in Figure 2, ^{1}H NMR analysis of the PMMA graft segments confirms that the chains are capped with halide on one end. The large resonances at 1.0 and 3.6 ppm are due to the $-CH_3$ and $-COOCH_3$ groups, respectively, on the PMMA backbone. The small peak at 3.82 ppm is ascribable to the terminal $-COOCH_3$ group. It is downfield from the internal $-COOCH_3$ because of the bromine atom.[11a] The ^{1}H NMR spectrum of *s*PS-*graft*-*a*PS showed a small peak at 4.52 ppm due to the end group, $CH(C_6H_5)(Br)$ (Figure 3). Overall, the ^{1}H NMR spectra of the copolymers are consistent with graft segments formed by ATRP.[11] Finally, two samples with identical graft density (32 grafts/1000 carbons) but with graft segments with M_n of 580 and 11070 respectively, were Soxhlet extracted with THF for 12 h. No detectable amount of the first sample was found in the THF-soluble fraction. On the other hand, almost all of the second sample was extracted by THF. Since *s*PS is THF-insoluble, whereas PMMA is completely soluble in THF, the solubility of *s*PS-*graft*-PMMA in THF for a given graft density increases with increasing graft length.

The ^{13}C NMR spectrum of *s*PS-*graft*-PMMA is shown in Figure 4. In addition to *s*PS resonances, five sets of new resonances were observed at 18.0 and 19.6, 45.4 and 45.7, 51.6, 54.4, and 177 and 178 ppm, which are ascribed to $-CH_3$, $-C-$, $-OCH_3$, $-CH_2-$, and $C{=}O$, respectively. The two peaks at 18.0 and 19.6 ppm and the quartet peaks around 177 ppm suggest the atactic structure of PMMA.[13]

The efficacy of different ligands added to CuBr on the graft polymerization of MMA is shown in Table 3. Of these, PMDETA was the best. Although the role of the ligand in ATRP is complex, one possible reason for the high efficiency of PMDETA is its remarkable ability to solubilize CuBr.[10e]

Our strategy for grafting polymers onto *s*PS is quite general, and Table 4 summarizes our results from the synthesis of *s*PS-*graft*-PMA and *s*PS-*graft*-*a*PS. ATRP grafting using methyl acrylate (MA) and styrene is much less efficient than MMA and requires higher reaction temperatures. *s*PS-*graft*-*a*PS is interesting in that it has a syndiotactic backbone and atactic side chains. Few polymers containing different stereoregularities in one macromolecule have been reported.[12]

Thermal Properties. The *s*PS-*graft*-PMMA copolymers were analyzed by DSC (see Table 2). The parent *s*PS melts at 257.5 °C (T_m). The melting behavior of *s*PS-*graft*-PMMA depends on both graft density and the molecular weight of the graft segments. No T_m was detected for samples with high graft density (95 grafts/1000 carbons). However, copolymers with low graft density (14 grafts/1000 carbons) showed crystalline melting even with graft segments with M_n of 7150. The melting behavior of copolymers with intermediate graft densities (32 grafts/1000 carbons) depended on the molecular weight of the graft segments. For example, a T_m of 241.7 °C was observed for the copolymer with graft segments with M_n of 580; however, no melting point was observed for copolymers with graft segments with M_n values of 3180 and 11070.

For many applications, copolymers with low graft densities are preferred in order to preserve the high melting point and crystallinity of *s*PS. *s*PS-based blends also require copolymers with low graft densities as compatibilizers to ensure efficient cocrystallization with bulk *s*PS.

Conclusion

We have described the efficient synthesis of *s*PS graft copolymers, *s*PS-*graft*-PMMA, *s*PS-*graft*-PMA, and *s*PS-*graft*-PS, by ATRP. The grafting was performed using brominated *s*PS as initiator and CuBr combined with pentamethyldiethylenetriamine (PMDETA) as catalyst. Both the graft density and the molecular weight of the graft segments were controlled by changing the bromine content of *s*PS and the amount of monomer used in the grafting reaction. The ATRP mechanism for grafting was supported by NMR analysis of end groups. This method of preparation of *s*PS graft copolymers is attractive because of the relatively wide scope of monomers that can be employed, the stability of the catalyst, the simple polymerization procedure, and the good control of graft structure. The melting point behavior of *s*PS-*graft*-PMMA depends on both graft density and graft length.

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