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Synthesis of Poly(methylene-*b*-styrene) by Sequential Living Polymerization

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Introduction

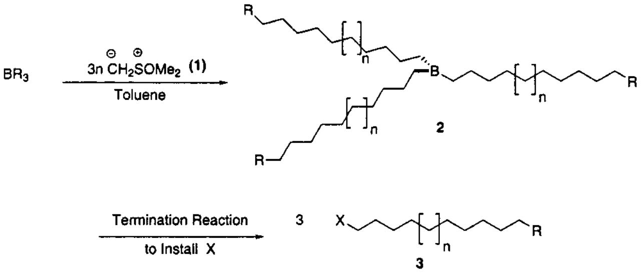
We have recently developed a synthesis of telechelic polymethylene.[1] Organoboranes serve as the initiator and dimethylsulfoxonium methylide (**1**) functions as the monomer. The carbon chain is built up one carbon at a time by repetitive homologation (polyhomologation) of alkyl substituents (Scheme 1). The living nature of the polyhomologation reaction permits control of the molecular weight as well as functionality at either end of the polymer chain.[2]

We are utilizing polyhomologation chemistry to develop general methods for the synthesis of well-defined copolymers of polymethylene and the major commodity polyolefins. These block copolymers can act as compatibilizers for blends of immiscible homopolymers such as polyethylene (PE) and polystyrene (PS).[3,4] PS and PE are both commercial plastics used in large quantities. PS is a typical brittle polymer with very low elongation and impact strength. PE, on the other hand, is commercially attractive for its toughness and low-temperature impact performance. It is very useful and profitable to toughen PS using PE;[5−7] however, PS/PE blends exhibit very poor mechanical properties compared with the individual constituents, which results from the weak interfacial adhesion and inferior stability of the phase dispersion.[5,8−10] The use of graft and block copolymers as emulsifiers and interfacial compatibilizers is an established technique to improve polymer properties and performance in polymer blends by reducing the domain size and increasing the interaction between domains.[3,4] This paper reports a method for preparing well-defined poly(methylene-*b*-styrene) (PE-*b*-PS). While considerable effort has been devoted to preparing of poly(ethylene-*co*-styrene)s (PE-*co*-PS), their syntheses are difficult, and molecular weight control of the PE block is challenging.[11−17]

Results and Discussion

A procedure for the synthesis of poly(methylene-*b*-styrene) is outlined in Scheme 2. The strategy unites two living polymerizations, resulting in control of the average DP (degree of polymerization) of both blocks. The polystyrene block is installed first via the TEMPO-mediated free radical polymerization of styrene.[18] The TEMPO polystyrene initiator **5**[19] was prepared from tetramethylpiperidinyloxy ethane (**4**) which was synthesized by reaction of benzoyl peroxide with an excess of styrene in the presence of TEMPO at 80−90 °C. Saponification of **4** with aqueous NaOH gave the hydroxyl derivative **5** in 83% yield from **4**. Polymerization of styrene with **5** at 130 °C for 72 h gave the hydroxyl-terminated polystyrene **6**. Although TEMPO-mediated polymerization of styrene has been used to prepare high molecular weight polystyrene, small blocks of PS were prepared to facilitate complete characterization. The NMR results clearly show the TEMPO unit attached to the PS blocks;[20,21] however, the MALDI-TOF characterization shows molecular ions corresponding to loss of the TEMPO group possibly due to its lability resulting in dissociation during the ion generation process. The results are summarized in Table 1. Both results are consistent with a controlled free radical polymerization. Polystyrene **6** was then allylated by reaction with sodium hydride followed by addition of allyl bromide in refluxing THF to give allyl-terminated polystyrene **7**.

Scheme 1. Polyhomologation Reaction



The allyl-teminated PS oligomer was hydroborated by reacting 3.1 equiv of **7** with $BH_3{\cdot}S(Me)_2$ at 0 °C in THF for 3 h to give borane **8**. The calculated concentration of borane **8** was based on the assumption of quantitative hydroboration; borane was used as the limiting reagent. The polyhomologation reaction was carried out in toluene with a known amount of dimethylsulfoxonium methylide to give the block copolymers **9** with different polymethylene lengths. The THF solution of borane **8** was quickly added to the preheated ylide solution in toluene. The course of polyhomologation was monitored by consumption of the ylide, which was found to be completed in approximately 5 min. Following alkaline peroxide oxidation, the copolymer product **9** was precipitated from excess methanol and then further extracted with acetone in a Soxhlet extractor for 24 h to remove remaining free PS. The copolymer, which was isolated in >90% yield, was characterized by both solution NMR and GPC analysis. The results are summarized in Table 1.

GPC analysis showed a unimodal distribution and very low polydispersity for all copolymers. Since borane **8** was prepared in situ from the polymer **7**, the concentration is not known exactly. However, changing the mole ratio of ylide to borane **8** gave the anticipated proportional increase in $\overline{\mathrm{DP}}$ (average degree of polymerization) between sample runs. Both findings are consistent with the living nature of the polyhomologation reaction. Thus, we demonstrated that this combined procedure allows molecular weight control of both blocks.

To establish the fate of the TEMPO linkage during the polyhomologation reaction and subsequent oxidative cleavage with hydrogen peroxide, polymer **12** and compound **13** were prepared as show in Scheme 3. Both products were analyzed by NMR. The results are also summarized in Table 1.

The ^{1}H NMR spectra of **13** reveals that the protons H$_a$, H$_b$, and H$_c$ derived from the styrene unit of compound **5** are also present in polymer **12** (Figure 1). The ^{13}C NMR spectra reveal the same chemical shift for the C1 and C2 carbons in both compounds (Figure

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Scheme 2. Procedure for the Synthesis of Poly(methylene-*b*-styrene)

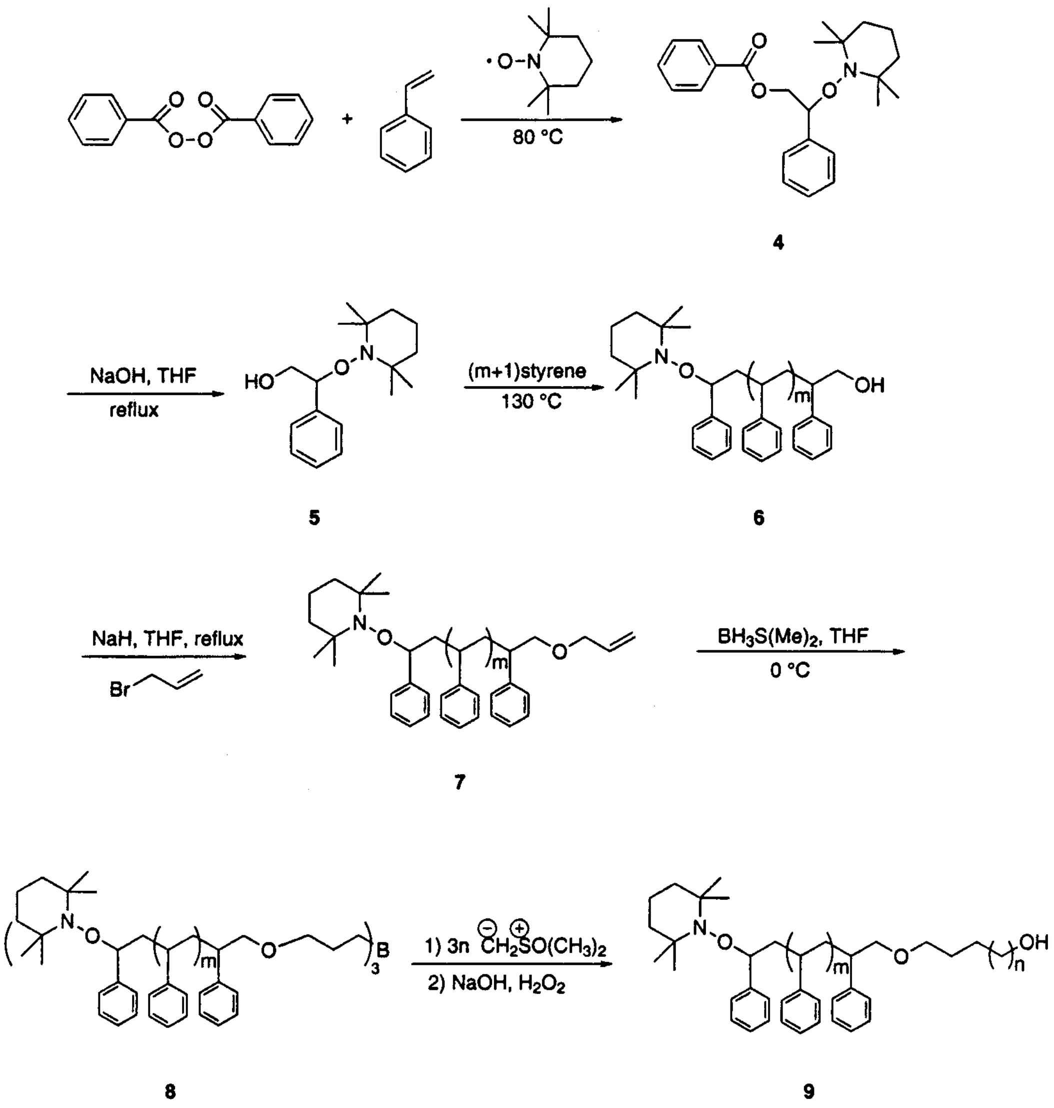


Table 1. Synthesis of PS−PM Block Copolymers

	entry	theor $\overline{DP}_n$ of PS	exptl $\overline{DP}_n$ of PS	theor $\overline{DP}_n$ of PE	exptl $\overline{DP}_n$ of PE	PDI	DSC[g] (°C) PE, T_m, (PS, T_g)
polystyrene **6**	A	10	10[a]			1.06[a]	
	B	20	17[a]			1.05[a]	
PS−PM (from entry A) **9**	C			50[b]	108[c]	1.03[d]	95.6, (−)
	D	10	10[a]	70[b]	132[c]	1.03[d]	97.5, (−)
	E			100[b]	184[c]	1.03[d]	105.2, (−)
PS−PM (from entry B) **9**	F			100[b]	254[c]	1.04[d]	119.7, (67.1)
	G	20	17[a]	150[b]	410[c]	1.06[d]	121.0, (64.3)
	H			200[b]	500[c]	1.05[d]	121.0, (62.7)
TEMPO-terminated PM **12**	I			20[e]	43[f]		
	J			50[e]	69[f]		
	K			100[e]	120[f]		

[a] MALDI-TOF results. [b] Theoretical $\overline{DP}_n$ of PE = (mol of ylide)/[(mol of borane **8**) × 3]. [c] ^{1}H NMR was obtained in 1,1,2,2-tetrachloroethane-d_2 at 100 °C. $\overline{DP}_n$ = [(sum of the areas 2.0−1.0 ppm − (sum of areas 7.3−6.5 ppm) × 0.6)] × 2.5 × ($\overline{DP}_n$ of PS + 1)/(sum of areas 7.3−6.5 ppm). [d] GPC analysis was performed at 100 °C in *o*-xylene with a flow rate of 1.0 mL/min. Four Ultrastyragel (5 μm particle size) columns were used in series: (500 Å × 2), (100 Å × 2). Calibration curves were made with polyethylene standards. The calibration curve has an $R^2 = 0.999\ 78$. [e] Theoretical $\overline{DP}_n$ of PE = (mol of ylide)/[(mol of borane **11**) × 3]. [f] ^{1}H NMR was carried out in toluene-d_8 at 60 °C. $\overline{DP}_n$ = (sum of methylene areas at 1.55−1.13)/[(methine areas at 4.96 ppm) × 2]. [g] Differential scanning calorimetry (DSC) measurements were recorded at a 10 °C/min heating rate under N_2. Aluminum oxide was used as the reference.

1), which is consistent with ^{1}H NMR. The peaks labeled 3 and 4 in the ^{13}C NMR spectra arise from the TEMPO group are present in both spectra. These results are consistent with the retention of the TEMPO group as one chain end in the copolymer. This group can be employed in a subsequent step as a macromolecular initiator to synthesize triblock copolymers.

The thermal properties of the copolymer were determined by differential scanning calorimetry (DSC). The results show an endothermic peak associated with the

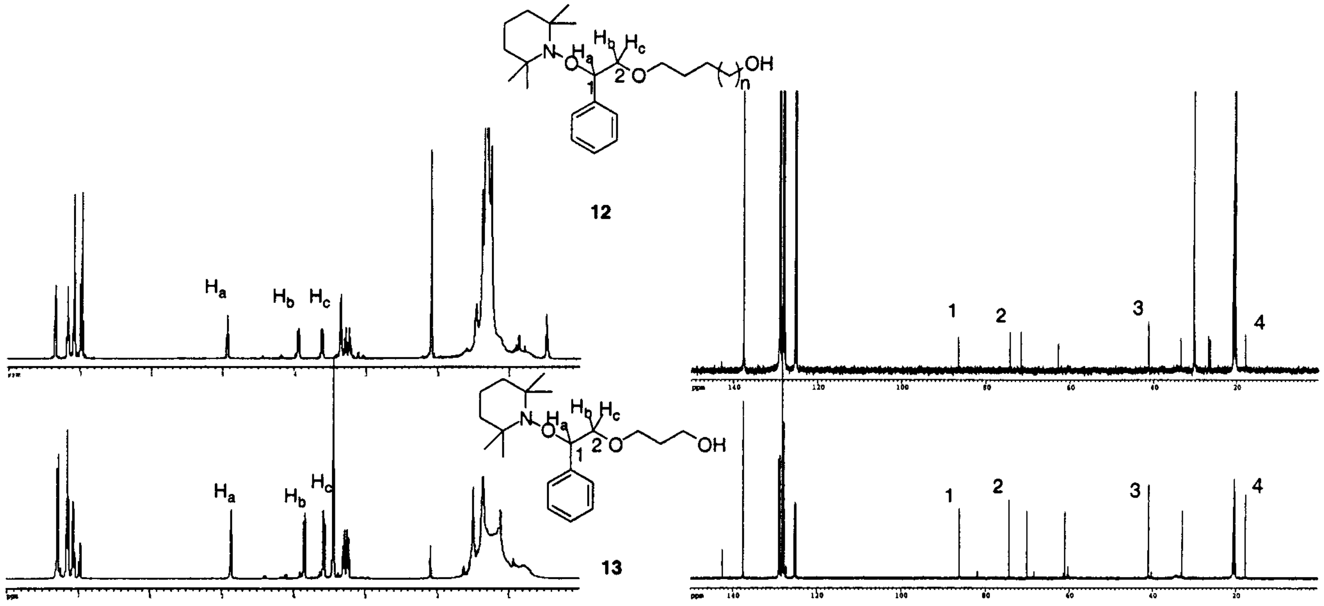
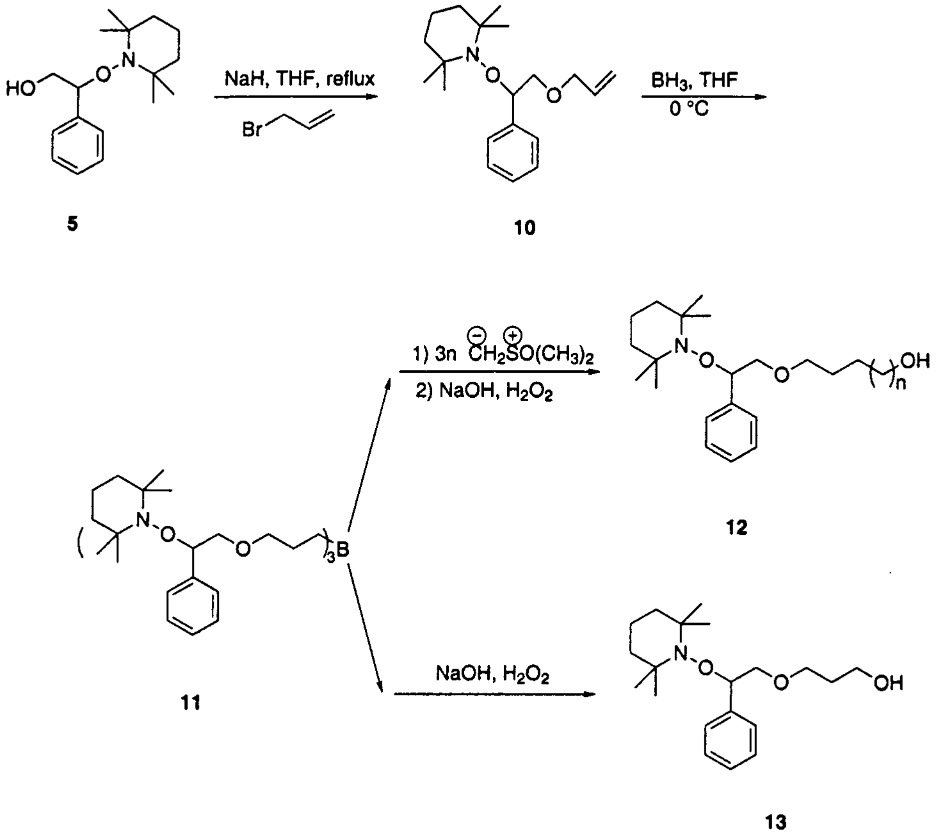


Figure 1. Comparison of the ^{1}H NMR and ^{13}C NMR spectra of polymer **12** and compound **13** which is run in toluene-d_8 at 60 °C.

Scheme 3. Synthesis of Compound 13 and Polymer 12



melting point of crystalline PE. As the PE block length increases, the melting point of PE only increases slightly (Table 1). With the high molecular weight PS block (Table 1, entries F, G, H), the glass transition temperature of the PS block was also observed. This transition temperature was not observed for the low molecular weight PS block (Table 1, entries C, D, E).

In conclusion, we have demonstrated the utility of the polyhomologation reaction for the synthesis of poly(methylene-*b*-styrene) block copolymers. A series of block copolymers were prepared by the hydroboration–polyhomologation protocol. Control over the chain length of the polymethylene block was achieved by adjusting the initial molar ratio of ylide to organoborane.

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Supporting Information Available: Details of experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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