Synthesis and Characterization of Neutral/Ionic Block Copolymers of Various Architectures

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Received November 14, 2001; Revised Manuscript Received February 25, 2002

ABSTRACT: Near-monodisperse diblock, triblock, and multiarm star-block copolymers of polystyrene (PS) and poly(4-*tert*-butylstyrene) (P*t*BS) were synthesized using anionic polymerization techniques. Selective sulfonation of PS blocks by using the complex of sulfur trioxide (SO_3) and triethyl phosphate (TEP) in 1,2-dichloroethane (DCE), followed by neutralization with sodium methoxide, was performed to yield the corresponding well-defined neutral/ionic block copolymers of sodium poly(styrenesulfonate) (NaPSS) and P*t*BS. A number of techniques including matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI/TOF/MS), Fourier transform infrared spectroscopy (FT-IR), and nuclear magnetic resonance spectroscopy (NMR) were employed to characterize these materials.

Introduction

There has been increasing interest in ionic/neutral block copolymers since the pioneering work of Selb and Gallot,[1,2] continuing in more recent years with work by Eisenberg and co-workers[3,4] and Webber et al.[5−8] Such materials, when the ionic block is relatively long and highly charged, imparting water solubility ("block polyelectrolytes"), offer great potential for stabilization of aqueous dispersions and for development of aqueous controlled release vehicles as well as other potential applications. The vast majority of work with ionic/neutral block copolymers has been carried out on diblocks; there are relatively few reports on synthesis and properties of nonlinear architectures in the literature.[1,2,9−11]

Recently, Guenoun, Tirrell, and Mays, along with their collaborators, have studied adsorption and micellization of diblock copolymers, consisting of long sodium poly(styrenesulfonate) (NaPSS) hydrophilic segments and short poly(4-*tert*-butylstyrene) (P*t*BS) or poly(ethylene-*alt*-propylene) (PEP) hydrophobic segments, in aqueous media.[12−22] To be able to extend these physical studies to architectures more complex than diblocks, this work reports the synthesis and characterization of well-defined, narrow molecular weight distribution (MWD) star-block and symmetric and asymmetric triblock architectures of NaPSS and P*t*BS. The synthesis of diblock and symmetric triblock copolymers based on NaPSS and P*t*BS was first reported by Valint and Bock.[23] Their basic strategy was to synthesize block copolymers of styrene and 4-*tert*-butylstyrene (*t*BS) by sequential anionic polymerization followed by selective sulfonation of the polystyrene (PS) block and neutralization. We extend this strategy to more complex architectures having narrow MWD. The use of PS/P*t*BS precursor polymers offers a high level of control over molecular weight, block sequencing, and architecture. Selective sulfonation of the PS blocks makes it possible to synthesize a wide range of controlled architecture amphiphilic polymers with narrow MWD.

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Experimental Section

Materials. Styrene (Fisher, 99%), divinylbenzene (DVB, Aldrich, 55%), and *t*BS (Scientific Polymer Products, 95%) were purified on a high-vacuum line by rigorous degassing and sequential exposure to and distillation from freshly ground calcium hydride (Aldrich, 95%) and dibutylmagnesium (Aldrich, 1.0 M heptane solution). Desired quantities were then distilled into evacuated ampules equipped with break-seals.[24] DVB was diluted in vacuo with purified benzene prior to ampulization in order to prevent polymerization on storage. It is also crucial to store highly purified styrenic monomers in a darkened freezer to prevent polymerization. α,α′-Dibromo-*p*-xylene (Aldrich, 97%) was thoroughly pumped on the vacuum line, diluted with purified benzene, and sealed in evacuated ampules. Benzene (Fisher, 99.9%) was purified[24] by exposure to concentrated sulfuric acid for 2 weeks, followed by vacuum line degassing and purification over calcium hydride and sodium dispersion (prepared from dry sodium sticks, Aldrich, A.C.S. reagent). The pure benzene was stored on the vacuum line over red poly(styryllithium) oligomers until used. *sec*-Butyllithium was made by reacting *sec*-butyl chloride (Aldrich, 99%) with excess lithium metal powder (Aldrich, 99%) under vacuum, followed by dilution with purified hexanes and ampulization.[24] Sulfur trioxide (SO_3, Aldrich, 99%), triethyl phosphate (TEP, Aldrich, 99%), sodium methoxide (Aldrich, 95%), and 1,2-dichloroethane (DCE, Aldrich, 99%) were used as received. Methanol (Fisher, 99.8%), for use in terminating polymerizations, was degassed on the vacuum line and distilled into ampules equipped with break-seals.

Polymerization. Polymerizations were conducted in sealed all-glass reactors using break-seal techniques as previously described.[24] A brief procedure for diblock copolymers of styrene and *t*BS follows: After the polymerization apparatus was thoroughly purged (purge reagent, 2 mL of 1.6 M butyllithium in hexanes), about 250 mL of benzene was slowly distilled into the main reactor flask from the purge section. The purge section of the apparatus was removed using a torch.[24] The initiator (about 0.5 mmol of *sec*-BuLi in 2.8 mL of hexanes) was introduced into the reactor. After a homogeneous mixture of *sec*-BuLi and benzene was obtained, 18.3 mL of styrene was introduced into the reactor. The colorless solvent turned red within seconds. After 24 h, 0.95 mL of *t*BS was introduced into the reactor. After 12 h, the polymerization was terminated by adding methanol.

Triblock copolymers were synthesized the same way except third additions of monomer were employed. For star-block and symmetric triblock copolymers, transfer ampules were used to transfer the living diblock copolymer anions into flasks for cross-linking or coupling reaction. Cross-linking reagent (DVB)

10.1021/ma011992b CCC: $22.00
Published on Web 03/28/2002

Table 1. Molecular Characteristics of Diblock, Triblock, and Star-Block Copolymers

samples[a]	P*t*BS (wt %)	structure and DP[b]	M_w[c] × 10^{-5}	M_w/M_n[d]	M_n[e] × 10^{-5}	DVB/Li[f]	f[g]	sulfonation degree[h] (%)
DB678/38	8.0	PS/P*t*BS (678/38)	0.835	1.09	0.766			86
SB678/38a	8.0	star-PS/P*t*BS	12.2	1.09	11.2	5	14.6	95
SB678/38b	8.0	star-PS/P*t*BS	11.4	1.10	10.4	6	13.7	89
SB678/38c	8.0	star-PS/P*t*BS	14.0	1.09	12.8	11	16.8	97
TB38/1356/38	8.0	P*t*BS/PS/P*t*BS	1.84					100
DB307/10	4.8	PS/P*t*BS (307/10)	0.342	1.02	0.335			95
SB10/307a	4.8	star-P*t*BS/PS	3.40	1.12	3.04	4	9.9	95
SB10/307b	4.8	star-P*t*BS/PS	6.39	1.12	5.71	12	18.7	92
TB427/23/204	5.4	PS/P*t*BS/PS (427/23/204)	0.707	1.02	0.693			100

[a] Samples SB678/38 series are star-block copolymers made by linking living anions P*t*BS-*b*-PS$^-$ using divinylbenzene as linking reagent. Thus, formed star-block copolymers have P*t*BS blocks on the outside and PS blocks on the inside of the stars. A portion of the living P*t*BS-*b*-PS polymer was terminated using methanol before linking reaction, and this material is presented here as sample DB678/38. Sample TB38/1356/38 is P*t*BS-*b*-PS-*b*-P*t*BS triblock copolymer made by linking P*t*BS-*b*-PS$^-$ living anions using α,α′-dibromo-*p*-xylene as coupling agent. Samples SB10/307 series are star-block polymers made the same way, except living anions PS-*b*-P*t*BS$^-$ were used. Thus, they have PS blocks on the outside with P*t*BS blocks on the inside of the stars. A portion of the living PS-*b*-P*t*BS$^-$ was terminated before linking reaction, and they are DB307/10. Sample TB427/23/204 is PS-*b*-P*t*BS-*b*-PS triblock polymer made by sequential addition of styrene, *tert*-butylstyrene, and styrene during anionic polymerization. [b] Polymerization degrees of each block are presented in brackets in the order of the blocks expressed in structure. [c] Obtained by multiangle laser light scattering. [d] Obtained from SEC. [e] Calculated from M_w and M_w/M_n. [f] Ratio of DVB to living chain end. [g] Star functionality based on M_w of the stars and M_w of the diblock. [h] Sulfonation degree is calculated from the elemental analysis data on sulfur.

or coupling reagent (*p*,*p*-dibromo-*p*-xylene, 1:2 mole ratio of coupling agent to initiator) was introduced into the living anion solution with stirring to make corresponding star-block or symmetric triblock copolymers. All polymers were isolated by precipitation into methanol followed by vacuum-drying at 70−80 °C overnight. The final isolated yield of polymer is about 95%.

The molecular characteristics of the polymers are presented in Table 1. These block copolymers were named so as to reflect their structures and degree of polymerization of each block. DB, TB, and SB represent diblock, triblock, and star-block, respectively. The degrees of polymerization of blocks are given in the order of their block sequence. For star-block copolymers, the degrees of polymerization of blocks in arm are given in the block sequence from inside to outside of the star. To differentiate star-block copolymers with the same length and composition of arms but different number of arms, lower case letters a, b, and c are used at the end of their names. In the case of diblocks and triblocks, the measured molecular weights are within 10% of the values predicted from stoichiometry.

Fractionation. Fractionation of the PS/P*t*BS block copolymers was done via the solvent/nonsolvent method. Methanol was added to dilute polymer solutions (2 g of polymer in 200 mL of toluene) until turbidity was established; the solution was gently heated to achieve homogeneity and was transferred to a warm separatory funnel. The funnel and its contents were allowed to cool to room temperature, and the phase separation was allowed to take place over periods ranging from overnight to days. The separated lower layer was collected by using a custom constructed long transfer pipet, and it was dissolved in 200 mL of toluene again and the fractionation was repeated. The final viscous polymer layer obtained was dissolved in about 20 mL of toluene and was precipitated in methanol. The obtained polymer was dried in a vacuum. The SEC chromatograph of sample SB10/307a prior to and after fractionation is shown in Figure 2.

Sulfonation and Neutralization. Sulfonation was conducted using the method of Valint and Bock.[23] TEP (0.2 equiv) in DCE (2 g of TEP per 100 mL of DCE) was placed in a flask equipped with two addition funnels, a thermometer, and a mechanical stirrer and was cooled to below 0 °C using an salt ice bath. Copolymer (1.0 equiv based on PS content only) was dissolved in DCE (<5% w/v depending on molecular weight) and placed in one addition funnel. SO_3 in DCE (1.1 equiv) was placed in the other addition funnel. SO_3 solution was added first at about 1−2 drops per second. Polymer solution was added a few seconds later at the same rate with stirring, while keeping the solution below 0 °C. The sulfonated polymer precipitated from solution and was purified by washing with pentane. It was neutralized by dissolving the polyacid in methanol and adding sodium methoxide until a pH of 7 was achieved. The polymers were freed of low molecular weight impurities by dialysis in a dialysis tube (MW cutoff 3500 g/mol, Spectrum Lab, Laguna, CA) against 8 L of fresh deionized

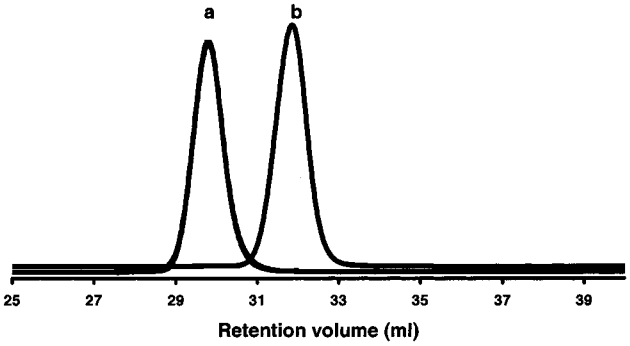


Figure 1. Typical SEC elugrams of (a) triblock (TB427/23/204) and (b) diblock (DB307/10) copolymers.

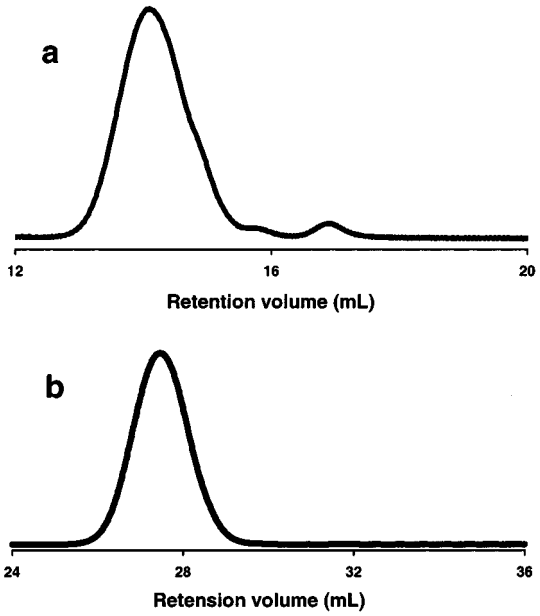


Figure 2. Typical SEC elugrams of DVB-linked star-block copolymer sample SB10/307a (a) prior to and (b) after the fractionation. (Two Waters Styragel columns HT3 and HT6E were used for the elugram a).

water for at least 3 days (every 8 h the water was changed). The dialyzed polymers were freeze-dried.

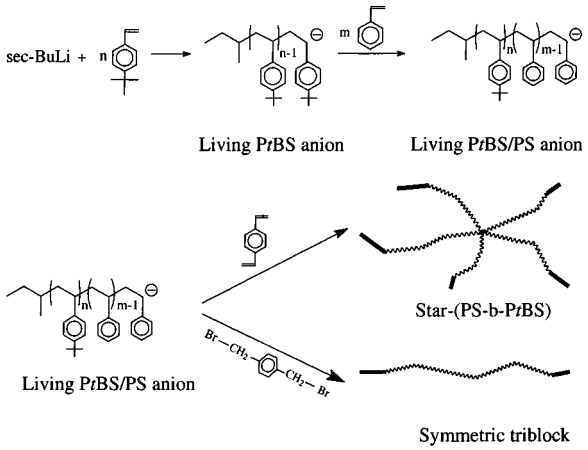
Characterization of PS/P*t*BS and NaPSS/P*t*BS Copolymers. Polydispersities, molecular weights, and MWDs of PS/P*t*BS were measured using a combination of size exclusion chromatography (SEC), light scattering (LS), and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF-MS). The SEC unit was a Waters Alliance System employing three Waters Styragel columns (one HT3 column and two HT6E columns in series, 10 μm particle size, 7.8 mm i.d. × 300 mm) with tetrahydrofuran (THF, Fisher, certified) as the mobile phase at 1.00 mL/min at 24 °C except notified elsewhere. The differential refractive index detector was a Waters 2410 unit. The weight-average molecular weights (M_w) of all PS/P*t*BS block copolymers were measured online via SEC/LS measurements (Wyatt DAWN DSP, laser light wavelength 633 nm) in chloroform using two columns (Polymer Labs 5 μm MIXED-D, 7.5 mm i.d. × 300 mm) at flow rate 1.00 mL/min at 24 °C. At least two measurements were conducted for each sample. The M_w values for each sample agreed within 2.8%. The average M_w values of two measurements are listed in Table 1. Some samples were also measured by SEC/LS with the three Waters columns (described above) in THF. The obtained values agreed with those obtained in chloroform (differences less than 5.8%). The refractive index increments (dn/dc) for PS/P*t*BS block copolymers were calculated the same time with SEC/LS measurements from injected sample mass (assuming 100% mass recovery). The dn/dc values in chloroform fall in the range 0.131−0.138 mL/g for all linear block copolymers and 0.133−0.142 mL/g for all star-shaped block copolymers. The average dn/dc values of 0.135 and 0.137 mL/g were used for linear and star-shaped block copolymers, respectively. In THF the average dn/dc value was 0.173 ± 0.02 mL/g, determined in the same fashion.

MALDI−TOF-MS was performed using a Voyager Elite DE system (PerSeptive Biosystems, Framingham, MA) and was used to measure molecular weight and MWD of a relatively low molecular weight specimen to check for possible degradation or other deleterious side reactions that might occur during sulfonation. Details of our MALDI−TOF-MS experiments on PS/P*t*BS and NaPSS/PtBS have been previously reported.[25] Two kinds of matrices were used in the analyses. For neutral polymer precursors, *trans,trans*-1,4-diphenyl-1,3-butadiene was used. For ion containing polymers, 3,5-dimethoxy-4-hydroxycinnamic acid (sinapinic acid) was used. A brief description follows: For PS/P*t*BS neutral block copolymers, the matrix solution was prepared by mixing 10 mg of *trans,trans*-1,4-diphenyl-1,3-butadiene and 0.5 mL of THF (purified by CaH_2 and Na/K alloy) together and vortexing for 30 s. The THF used was purified by exposure to CaH_2, and Na/K alloy, sequentially, under vacuum conditions. A trace amount of silver acetate was added to this matrix solution. For NaPSS/P*t*BS diblock copolymers, the matrix solution was prepared by mixing 10 mg of sinapinic acid, 0.7 mL of 0.1% trifluoroacetic acid, and 0.3 mL of acetonitrile together, vortexing for 1 min, and centrifuging for 20 s. The polymer solution (0.1 wt % in THF for PS/P*t*BS or 0.1 wt % in water [Milli-Q] for NaPSS/P*t*BS) and matrix solution were mixed together at polymer matrix solution volumetric ratios ranging typically from 1:1 to 1:100. After vortexing the polymer−matrix solution for 30 s, about 3 μL of solution was deposited and crystallized on the sample plate by repeating the deposition−evaporation cycle three times. The extent of sulfonation of the NaPSS/P*t*BS was determined by elemental analysis (Atlantic Microlabs, Norcross, GA).

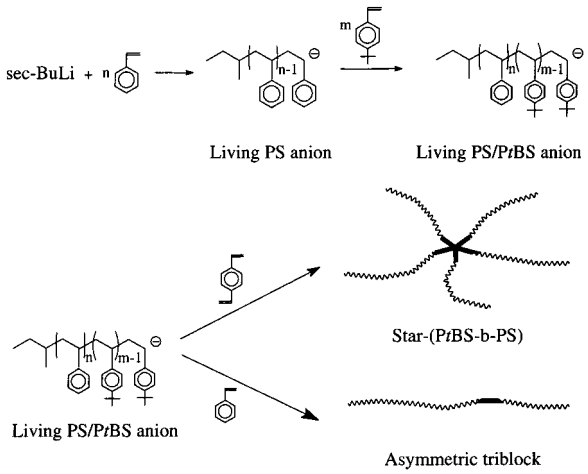
The copolymers were also structurally characterized using NMR and FT-IR. The NMR measurements were conducted on Bruker DRX-400 and ARX-300 spectrometers. PS/P*t*BS block copolymers were dissolved in deuterated chloroform ($CDCl_3$, Aldrich, 99.8 atom % D). NaPSS/P*t*BS block copolymers were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6, 99.9 atom % D, Cambridge Isotope Lab, Andover, MA). Mixtures of DMSO-d_6 and $CDCl_3$ up to 8:2 by volume were used sometimes for better dissolution of polymers. About 5% polymer concentration (0.6 mL of solution) was used. PS/P*t*BS samples were analyzed at 298 K, while NaPSS/P*t*BS samples were analyzed at 358 K. Spectra were referenced to residual solvent peaks; the probe temperature was calibrated using neat ethylene glycol.

FT-IR spectra of polymer samples were obtained with a Bruker Vector 22 spectrometer. Dilute polymer solutions (5 mg per mL of solvent) were prepared in solvent (THF or water) and were deposited on a germanium IR window. They formed thin films upon evaporation of solvent using a tungsten lamp. Further drying of solvent was conducted in a vacuum oven at room temperature overnight. All FT-IR spectra represent an average of 256 scans with a frequency resolution of 2 cm^{-1} and frequency range of 4000−600 cm^{-1}.

Scheme 1. Synthesis of Model Block Copolymer with P*t*BS as Outer Block Segments



Scheme 2. Synthesis of Model Block Copolymer with PS as Outer Block Segments

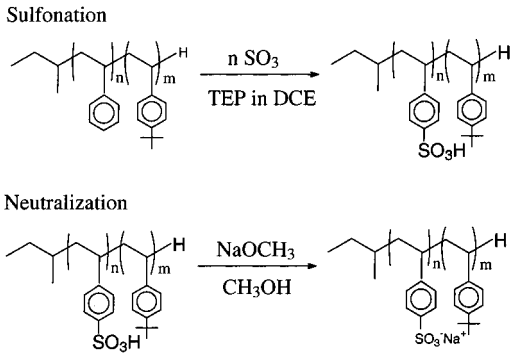


Results and Discussion

As precursors to more complex architectures, diblock copolymers of PS and P*t*BS were synthesized by sequential addition of the monomers to *sec*-BuLi in benzene (Schemes 1 and 2). Because of the rapid crossover reactions from poly(styryllithium) to poly(4-*tert*-butylstyryllithium), and vice versa, narrow MWD diblocks can be obtained regardless of the sequence of monomer addition. This is in contrast to the usual situation in anionic synthesis of precursors to ionic/neutral block copolymers, where order of addition of monomers is crucial (e.g., styrene−acrylic and styrene−vinylpyridine monomer pairs). Typical SEC chromatograms are given in Figure 1.

Once the P*t*BS-*b*-PS^- or PS-*b*-$PtBS^-$ living anions were obtained, addition of DVB resulted in the forma-

Scheme 3. Sulfonation and Neutralization of Polystyrene and Poly(4-*tert*-butylstyrene) Block Copolymer (Diblock Copolymer Shown Here)



tion of star polymers having P*t*BS outer segments (Scheme 1) or PS outer segments (Scheme 2). Residual active centers were deactivated with methanol. A typical SEC chromatogram for such a DVB-linked star-block is shown in Figure 2. Clearly, the star-block copolymer exhibits a somewhat broader MWD, with some residual arm and what appears to be coupled product present. These are typical results for linking PS type anions with DVB.[26] Fractionation was used to free the star-block copolymers of low molecular weight contaminants, resulting in materials with polydispersity ratios (ratio of weight-average to number-average molecular weights, M_w/M_n) of 1.09−1.12. The amount of DVB per active center could be varied to exercise some control over the number of arms (*f*) in the star. Weight-average numbers of arms (*f* values) were determined by the ratio of absolute M_w for the purified star to that of its arm. Molecular characteristics of the star-block copolymers and their linear diblock precursors are summarized in Table 1. Notice that in all cases the weight percent of P*t*BS in the PS/P*t*BS diblock was kept low (4.8−8.0%). This was done to ensure solubility of the sulfonation products in pure water. At higher hydrophobic content solubilization in pure water becomes difficult. The choice of DVB as a linking agent rather than chlorosilanes also requires explanation. Whereas chlorosilanes yield greater control over arm number and polydispersity,[27] the DVB-linked materials are more robust and survive the sulfonation reaction to yield NaPSS without cleavage of arms from the star.[28]

Two different methods were used to synthesize triblock copolymers. The coupling reagent α,α′-dibromo-*p*-xylene was used to make symmetric P*t*BS-*b*-PS-*b*-P*t*BS triblock (Scheme 1). Residual arm, due to use of a slight excess of arms in coupling, was removed by fractionation. This coupling approach ensures that the two end blocks are identical in length and polydispersity. It is also feasible to prepare PS-*b*-P*t*BS-*b*-PS symmetrical triblocks by reversing the sequence of monomer addition. The choice of coupling agent was dictated, as above, by the desire to avoid use of chlorosilanes due to potential degradation during sulfonation. After fractionating the P*t*BS-*b*-PS-*b*-P*t*BS triblock to remove residual arm, SEC indicated the presence of a small (about 4 wt %) peak at lower elution volume. This might be due to an impurity in the coupling agent; also, the reaction of alkyllithium species with bromomethyl groups in hydrocarbon solvents can be influenced by lithium−halogen exchange reactions.[29] Molecular characteristics of this triblock are summarized in Table 1.

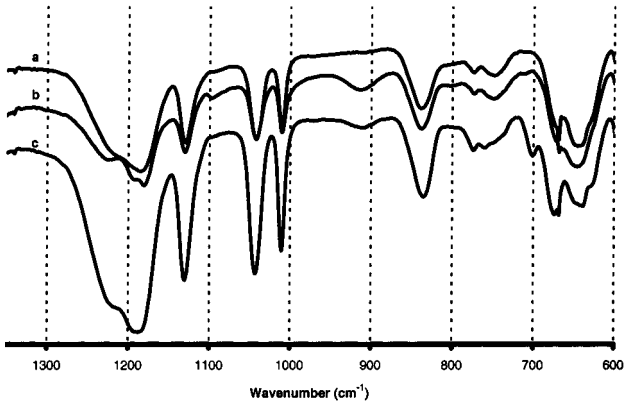


Figure 3. FT-IR spectrum of sulfonated block copolymer samples (a) SB10/307b, (b) TB427/23/204, and (c) DB678/38 in the frequency range 1350−600 cm^{-1}.

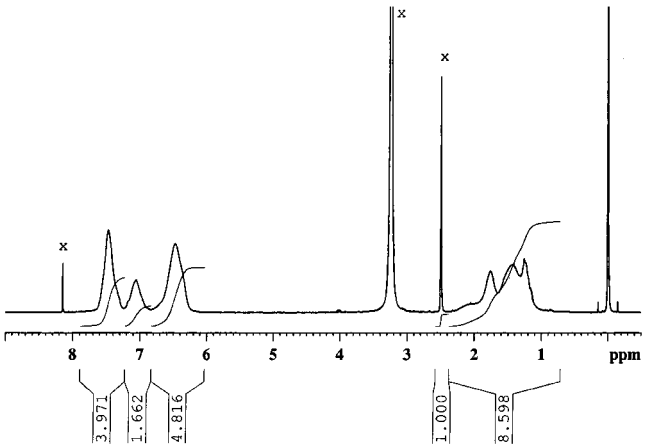


Figure 4. ^{1}H NMR spectrum of sulfonated diblock copolymer sample DB678/38.

We used simple three-step monomer addition, previously used by Valint and Bock to make asymmetrical triblocks, to synthesize a PS-*b*-P*t*BS-*b*-PS triblock having one PS end block twice as long as the other PS end block. The polydispersity of this asymmetric triblock is 1.02 (Table 1 and Figure 2), suggesting that multiblocks could also be synthesized by further monomer additions. This synthesis highlights two of the advantages of this chemistry in synthesis of precursors to ionic/neutral block copolymers: (1) The use of all hydrocarbon monomers and polymerization in benzene at room temperatures allows optimum control of the polymerization. (2) The favorable rate of crossover from PS to P*t*BS type ions, and vice versa, facilitates synthesis of more complex architectures.

Ideally, the method of Valint and Bock will selectively sulfonate only the PS aromatic rings, leaving P*t*BS unsulfonated, since the preferred sulfonation position (para) is already substituted with *tert*-butyl groups,[23] as shown in Scheme 3. Based on this assumption, elemental analysis for sulfur gives degrees of sulfonation ranging from 86 to 100% (Table 1). We found no evidence by NMR or IR for sulfonation of PtBS units. There seems to be little effect of architecture on sulfonation degree although, coincidentally we believe, both triblocks underwent 100% sulfonation, while lower levels were observed for other species.

All of the sulfonated polymers were readily soluble in water except the star-blocks having P*t*BS blocks at the chain ends. Clear, colorless gels with air bubbles

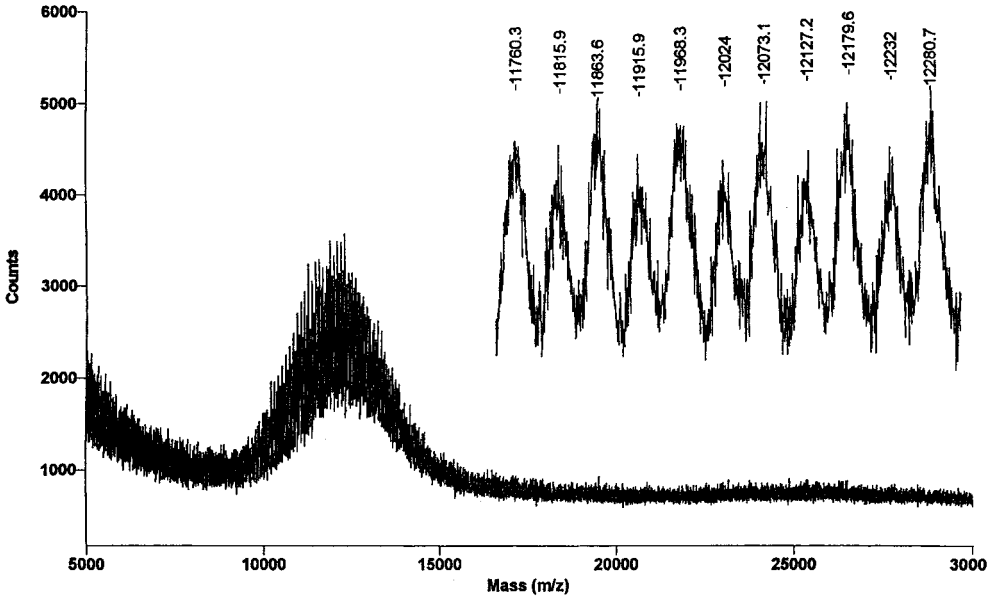


Figure 5. MALDI−TOF-MS of PS-*b*-P*t*BS block copolymer (M_n = 12 000 g/mol, M_w/M_n = 1.03) (positive ion mode). The inset is an expansion of some oligomer peaks.

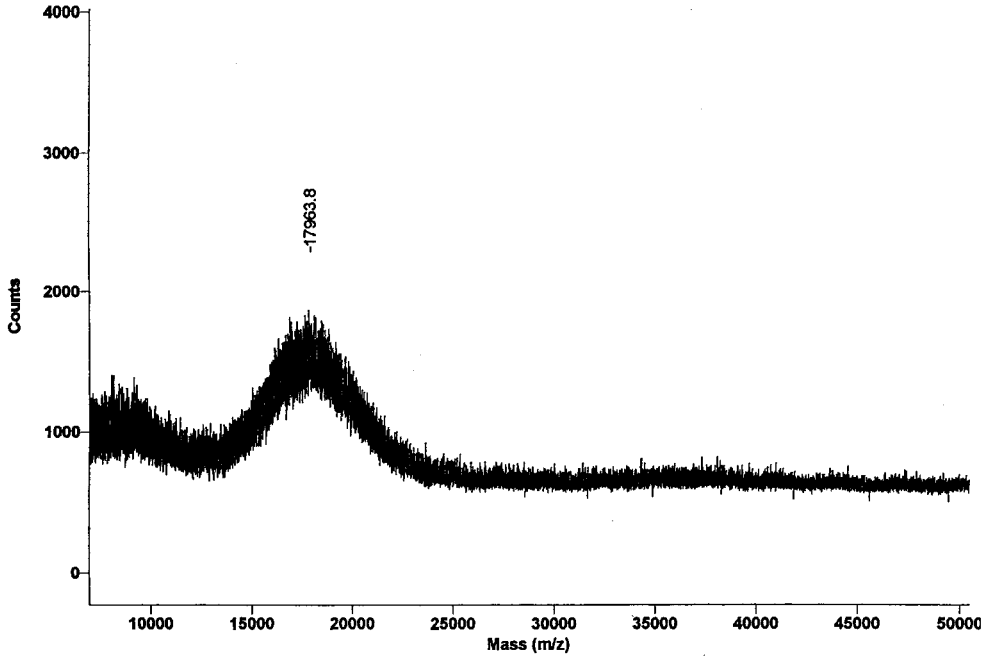


Figure 6. MALDI−TOF-MS of NaPSS-*b*-P*t*BS block copolymer (M_n = 17 900 g/mol, M_w/M_n = 1.02) (negative ion mode).

trapped inside formed during dialysis of these materials. This gelation is clearly due to hydrophobic association of their end blocks. When this gel was further diluted with water, two layers were formed. The upper layer was a clear colorless solution while the lower level was clear colorless gel. After sonication the solution for at least 2 min one can see small gel particles suspended in the solution. These small gel particles precipitated to the bottom of the vial after a while. They then remained as small gel particles and did not consolidate to re-form one piece of gel.

To gain further insight into the structure of the sulfonated products and any potential side reactions or degradation during sulfonation, we analyzed some of the NaPSS-*b*-P*t*BS specimens by FT-IR, NMR, and MALDI−TOF-MS.

The FT-IR spectra of SB10/307b, TB427/23/204, and DB678/38 are shown in Figure 3. The SO_3^- groups characteristic of antisymmetric and symmetric stretching vibrational bands[31] are found at about 1200 and 1040 cm^{-1}, respectively. These spectra, especially in the fingerprint region, are essentially the same as observed for model sodium poly(4-styrenesulfonate) (NaP4SS) made via radical polymerization of pure 4-styrenesulfonate,[30] which indicates that the sulfonated PS segments have structures very similar to that of pure NaP4SS polymer. The content of the P*t*BS block is so small that it does not cause much change in the block copolymer FT-IR spectrum. The small band at about 700 cm^{-1} for DB678/38 is due to its relatively high P*t*BS content (5.4 mol % P*t*BS) or lower PS sulfonation level.[30]

Figure 4 shows a typical NMR spectrum for the sample DB678/38. The peak at about 7.5 ppm is the resonance of aromatic protons next to the aromatic carbons connected to SO_3^- groups. The peaks at about 6.5 and 7.1 ppm are the resonances of other aromatic

protons on both the sulfonated and unsulfonated benzene rings. After comparison with the NaP4SS model polymer,[30] it was confirmed that the SO_3^- group was connected at the para position of the benzene rings. The sulfonation level of the PS block can be calculated from the integral peak areas of these three aromatic protons and the P*t*BS content. The sulfonation degree of the PS block calculated from the ^{1}H NMR spectrum for DB678/38 is 83%, which is very close to the elemental analysis result (86%).

MALDI−TOF-MS was utilized in our lab to characterize such neutral/ionic block copolymers.[25] It has been shown to be a very effective method in analysis of this kind of micelle-forming copolymer. However, because of the high molecular weights of these samples, MALDI−TOF-MS measurements on most of the materials of this work were not successful. Figures 3 and 4 show the MS spectra of a similar sample with lower molecular weight prior to (Figure 5) and after the sulfonation reaction (Figure 6). Figure 5 shows that, before sulfonation, PS-*b*-P*t*BS has a symmetric narrow molecular weight distribution (MWD). The number-average molecular weight obtained from MS is 12 000 g/mol, which agrees with the value of 12 500 g/mol obtained from SEC. The oligomer peaks are also shown in the inset in Figure 5. The sulfonated sample, NaPSS-*b*-P*t*BS, has the same symmetric narrow MWD, which indicates that the sulfonation reaction was conducted uniformly for all molecules (see Figure 6). The increase of the molecular weight is due to the addition of SO_3H group onto the repeat unit.[25] From the increment in molecular weight, a sulfonation degree of 86.3% (the percentage of PS repeat unit been sulfonated in whole PS block) was calculated, which is close to the result obtained from the elemental analysis.

Conclusions

Diblock, triblock, and star-block copolymers of PS and P*t*BS were synthesized by anionic polymerization techniques. By reversing the monomer addition sequence, triblock copolymers with both P*t*BS in the middle PS block at the ends, and PS in the middle P*t*BS at the ends can be prepared. Also, by using the same method, star-block copolymers with either P*t*BS or PS on the inside of the star can be prepared. After selective sulfonation of the PS block(s), corresponding neutral/ionic diblock, triblock, and star-block copolymers with very narrow MWDs were synthesized. For star-block copolymers with the hydrophilic NaPSS blocks on the inside of the star and hydrophobic P*t*BS blocks on the outside, a gel was formed in aqueous solution. FT-IR, NMR, and MALDI/TOF/MS were employed to characterize these materials. It was found that the sulfonated PS block has a very similar structure to the model polymer NaP4SS. The sulfonation degree could be derived from NMR and MS spectra, in addition to elemental analysis.

Acknowledgment. This work was supported by the National Science Foundation (DMR and CTS Divisions).

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MA011992B