Polymer 50 (2009) 6212–6217

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis of poly(trioctylammonium p-styrenesulfonate) homopolymers and block copolymers by RAFT polymerization

Yuqing Liu[a], Kevin L. Pollock[b], Kevin A. Cavicchi[a,*]

[a] Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301, USA
[b] Department of Chemistry, Carleton College, Northfield, MN 55057, USA

ARTICLE INFO

Article history:
Received 12 June 2009
Received in revised form
26 October 2009
Accepted 31 October 2009
Available online 5 November 2009

Keywords:
RAFT polymerization
Block copolymer
Polystyrene sulfonate

ABSTRACT

A method to prepare sulfonated polystyrene-containing block copolymers has been investigated by neutralizing styrene sulfonic acid with trioctylamine to produce the hydrophobic monomer trioctylammonium p-styrenesulfonate (SS–TOA). This monomer was polymerized by reversible addition fragmentation chain transfer (RAFT) polymerization to produce PSS–TOA homopolymers. A PSS–TOA homopolymer was then used as a macro-RAFT agent for the polymerization of styrene to prepare poly(trioctylammonium p-styrenesulfonate)-block-poly(styrene) (PSS-TOA-b-PS). These block copolymers could be ion-exchanged to produce either the hydrophilic sodium salt form of PSS or a hydrophobic quaternary ammonium salt. This approach will be useful for preparing PSS-containing block copolymers with a range of hydrophobic blocks for applications such as ion-exchange membranes.

1. Introduction

Poly(styrenesulfonic acid) (PSS) is a water soluble, strong acid polyelectrolyte. Recently, there has been interest in synthesizing amphiphilic block copolymers containing PSS blocks. The self-assembly of the neat block copolymers into ordered nanostructures is useful for producing ion-exchange membranes with tunable properties, such as water uptake, ionic conductivity and solvent selectivity for applications including fuel cells and reverse osmosis water desalination [1–6].

Sodium p-styrenesulfonate (SS–Na) is an inexpensive, commercially available monomer. However, the challenge in the preparation of amphiphilic PSS-containing block copolymers is the strong immiscibility of the hydrophilic SS–Na and PSS–Na with most hydrophobic monomers and organic solvents. While block copolymers of PSS–Na with polystyrene (PS) and poly(methyl methacrylate) (PMMA) have been prepared, the homogeneous copolymerization and subsequent characterization over a wide range of PSS–Na volume fractions is difficult [7,8].

Sulfonated polystyrene block copolymers have also been prepared by the post-polymerization sulfonation of polystyrene [1]. However, there are drawbacks to this approach. First, it is difficult to achieve 100% sulfonation of the PS block [9]. Second, side-reactions can occur during the post-polymerization sulfonation giving rise to intramolecular sulfone linkages [10]. Third, it is not always possible to selectively sulfonate the PS block. For example, polydienes are more reactive under polystyrene sulfonation conditions and can be selectively sulfonated in the presence of polystyrene using a sulfur trioxide/1,4 dioxane complex [11].

An alternative approach to the previous two methods is to modify the p-styrenesulfonate monomer to a more hydrophobic form, which is amenable to controlled free radical polymerization with hydrophobic monomers. Previously, this has been achieved by converting the sulfonic acid group to a sulfonate ester, which can be hydrolyzed back to the acid form after copolymerization. Neopentyl p-styrenesulfonate (SS-nP) was prepared by the esterification of p-styrene sulfonyl chloride with neopentyl alcohol and PS-b-PSS-nP block copolymers were prepared by nitroxide mediated free radical polymerization [12]. Ethyl p-styrenesulfonate (SS-E) was prepared by the metathesis reaction between silver p-styrenesulfonate and ethylbromide and PS-c-PSS-E comb polymers were synthesized by atom transfer radical polymerization [13–15].

A third monomer modification investigated was to neutralize p-styrene sulfonic acid with trioctylamine to produce a hydrophobic trioctylammonium p-styrenesulfonate monomer. This monomer was copolymerized with styrene by suspension polymerization to prepare sulfonated polystyrene ionomers, but has not been used in a controlled free radical polymerization [16]. Compared to the sulfonate esters, this method avoids the use of water sensitive sulfonyl chlorides or light sensitive silver sulfonate salts. In addition to using the tertiary amine to protect the p-styrene sulfonate groups, this acid–base neutralization approach has also

---

[*] Corresponding author. Tel.: +1 330 972 8368.
E-mail address: kac58@uakron.edu (K.A. Cavicchi).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.10.069

been used to prepare different ionic liquid polymers by varying the chemistry of the acidic monomer and tertiary amine and subsequent free radical polymerization [17–20].

This paper describes an investigation of the polymerization of trioctylammonium p-styrenesulfonate (SS–TOA) by reversible addition fragmentation chain transfer (RAFT) polymerization. These PSS–TOA polymers were subsequently used as macro-RAFT agents for the synthesis of PSS-TOA-b-PS block copolymers. The ion-exchange of the PSS with aqueous sodium hydroxide produces the amphiphilic PSS-Na-b-PS block copolymer. This can further be ion-exchanged to a hydrophobic quaternary ammonium salt.

2. Experimental

2.1. Materials

S-1-docecyl-S′-(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate (RAFT-COOH) was synthesized according to a previous reported procedure [21]. A PSS–Na homopolymer standard was purchased from Fluka (reported $M_w = 6530$, polydispersity < 1.2). All other reagents were used as-received.

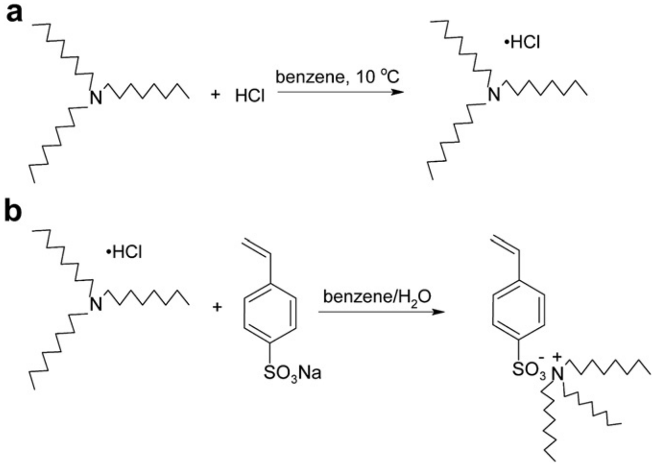
2.2. Trioctylammonium p-styrenesulfonate (SS–TOA) synthesis

Trioctylammonium hydrochloride was prepared based on a previously reported procedure [22]. 20 mL trioctylamine (TOA, 0.0457 mol) was dissolved in 40 mL hexane and placed in an ice bath followed by the dropwise addition of 5 mL of concentrated HCl (0.0605 mol). The solution was stored in the freezer for ~5 h and a white precipitate (trioctylammonium hydrochloride) formed. The precipitate was filtered and washed with cold hexane to remove excess HCl. The product (TOA–HCl) was dried in a vacuum oven overnight (16 h) at room temperature. White solid; yield 15.8 g (89%). ^{1}H NMR: δ 2.95(6H, s, N–CH_2–), 1.80 (6H, s, N–CH2–CH_2–), 1.27 (30H, s, –CH_2–), 0.89 (9H, s, CH_3).

10 g TOA–HCl (0.0256 mol) was dissolved in 50 mL benzene, and 5.8 g sodium p-styrenesulfonate (0.0282 mol) was dissolved in 40 mL deionized water. Both solutions were added to a separation funnel, mixed and allowed to settle. The top layer (benzene) was collected and washed three times with deionized water. The solution was concentrated on a rotary evaporator, frozen in a freezer and then dried in a vacuum oven overnight at room temperature to yield a white solid. White solid; yield 11.5 g (84%). ^{1}H NMR: δ 10.4 (1H, s, SO$_3H$) 7.84 (2H, d, aromatic), 7.42 (2H, d, aromatic), 6.70 (1H, d, CH_2═CH–), 5.81(H, d, CH_2═CH–), 5.31(H, d, CH_2═CH–), 3.02 (6H, s, N–CH_2–), 1.71 (6H, s, N–CH2–CH_2–), 1.27 (30H, s, –CH_2–), 0.89 (9H, s, CH_3).

2.3. RAFT polymerization of PSS–TOA

In a typical polymerization of SS–TOA 2 g SS–TOA monomer, RAFT-COOH, AIBN (1:5 molar ratio to RAFT-COOH) and 1.86 mL benzene were added to make a 2 M monomer solution. The solution and a stir bar were added to a round bottom flask sealed with a rubber septum. The solution was sparged with nitrogen for 15 min in an ice bath and heated to 80 °C. During the polymerization, aliquots were collected by a gas-tight syringe under nitrogen pressure. The aliquots were concentrated on a rotary evaporator and dried under vacuum at room temperature for 24 h. At the end of the polymerization the remaining viscous solution was added dropwise to cyclohexane to precipitate the polymer. Three polymerizations were run with RAFT agent concentrations of 0.0783 g/mL, 0.0391 g/mL, and 0.0196 g/mL (g RAFT-COOH/mL benzene) to target PSS–TOA molecular weights of 5 kDa, 10 kDa, and 20 kDa.



Scheme 1. Synthesis of (a) trioctylammonium hydrochloride and (b) trioctylammonium p-styrenesulfonate.

2.4. RAFT polymerization of PS-b-PSS-TOA block copolymers

PSS–TOA (5 kDa target) was used as macro RAFT agent to synthesize PSS-TOA-b-PS diblock copolymers. Two polymerizations were run with different PSS–TOA concentrations of 0.2 g/mL and 0.1 g/mL (g PSS–TOA/mL styrene). The solutions were sparged with nitrogen for 15 min and heated to 120 °C for 6 h. During the polymerizations, aliquots were removed by a gas-tight syringe under nitrogen pressure and precipitated in hexane. The samples were dried in a vacuum oven at 80 °C overnight.

2.5. Ion-exchange of PS-b-PSS-TOA block copolymers

To generate the sodium salt form of the PSS block, 0.05 g PSS-TOA-b-PS (75 wt% PS) was dissolved in 2 mL benzene and mixed with 2 mL 1 M aqueous NaOH for 24 h. The benzene layer was collected and the polymer was precipitated in hexane and dried under vacuum. The quaternary ammonium form of the PSS block was generated by dissolving 0.02 g of the polymer in the sodium salt form in 1 mL of a 0.1 M solution of Aliquat 336 (trialkylmethylammonium chloride with a mixture of octyl and decyl

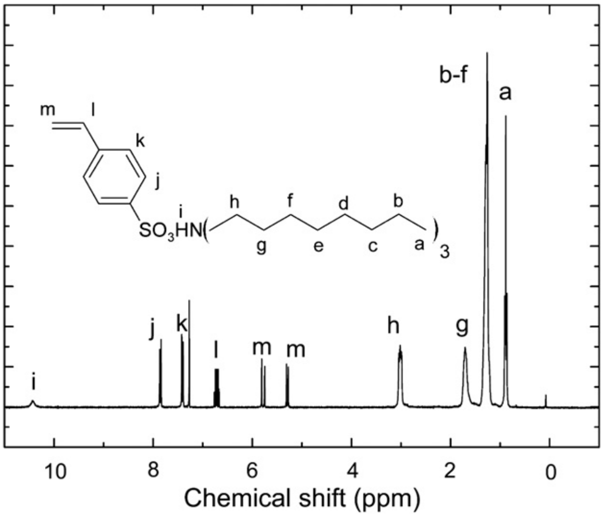
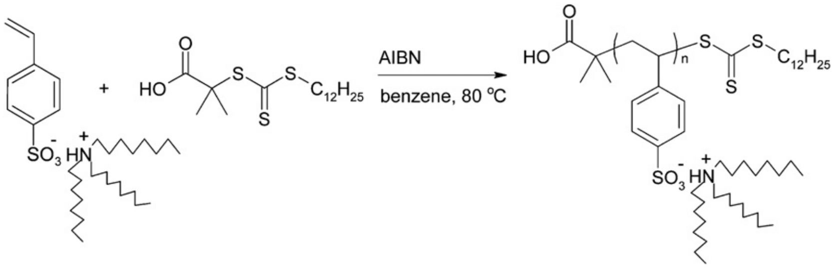


Fig. 1. ^{1}H NMR spectrum of SS–TOA monomer.



Scheme 2. RAFT polymerization of trioctylammonium p-styrenesulfonate.

chains) in benzene and stirred for 12 h. The polymer was precipitated in hexane and washed with hexane and dried under vacuum.

2.6. Characterization

^{1}H NMR spectra were measured on a Varian Mercury-300 MHz spectrometer. Samples were dissolved in deuterated chloroform or deuterated acetone at concentrations of 10 mg/mL and relaxation time of 5 s was used. The molecular weight and molecular weight distribution of the polymers was characterized by size exclusion chromatography (SEC) using a Waters Breeze system with three Styragel columns at 35 °C and a refractive index detector with either tetrahydrofuran (THF) or a mixture of THF and 2% trioctylamine (2 g/100 mL THF). The molecular weight vs. elution time was calibrated using low polydispersity polystyrene standards.

3. Results and discussion

3.1. Monomer preparation

The trioctylammonium p-styrenesulfonate (SS–TOA) monomer was prepared from sodium p-styrenesulfonate in two steps as shown in Scheme 1. This monomer was soluble in a wide range of organic solvents including cyclohexane, diethylether, tetrahydrofuran, toluene, benzene, chloroform and methanol at room temperature at a concentration of 10 mg/mL. The ^{1}H NMR spectrum of the monomer is shown in Fig. 1. Integration confirmed a stoichiometric ratio of styrene sulfonic acid and trioctylamine.

3.2. PSS–TOA homopolymers

SS–TOA was polymerized by RAFT polymerization in benzene at 2 M monomer concentration at 80 °C using RAFT-COOH as the RAFT agent and ABIN as the free radical source as shown in Scheme 2. 5 kDa, 10 kDa and 20 kDa molecular weights at 100% monomer conversion were targeted by varying the ratio of monomer to RAFT agent. Aliquots were removed during the polymerizations to monitor the conversion of the reaction. As SS–TOA is non-volatile the samples were dried under vacuum after evaporating the solvent, re-dissolved in deuterated chloroform and analyzed by ^{1}H NMR to determine the ratio of SS–TOA to PSS–TOA. The NMR spectra for the 5 kDa MW target are shown in Fig. 2. The conversion was determined by comparing the intensity of the peak at 0.9 ppm of the terminal methyl groups of trioctylamine, which is present in both the monomer and polymer, to the peaks at 5.3 and 5.8 ppm for the $CH_2{=}CH-$ peaks present in only the monomer. The pseudo first order kinetic plots are shown for each targeted molecular weight in Fig. 3. The solid lines are a linear fit to the data. The linearity of the data implies that the radical concentration is constant with time as expected for a controlled polymerization [23]. In the 20 kDa target polymerization it could be argued that there is some non-linearity in the data reflecting a reduction in the radical concentration with time due to a higher probability for irreversible termination reactions as the concentration of RAFT agent was decreased. A small induction time and retardation of the polymerization rate with increasing RAFT agent:monomer ratios was observed, which has been observed in other RAFT homopolymerizations [24]. High conversions are

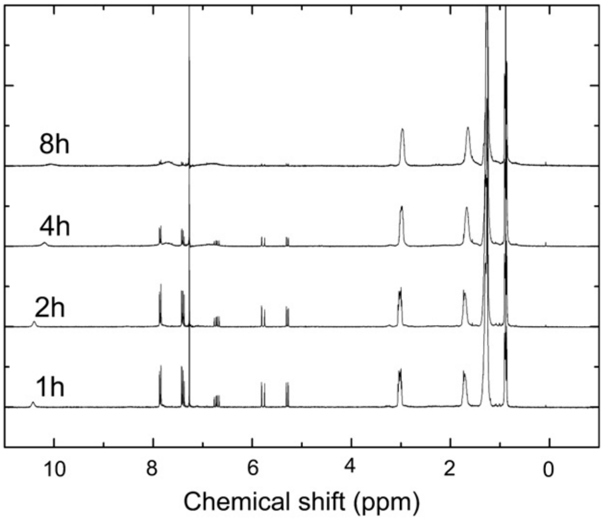


Fig. 2. ^{1}H NMR spectra of PSS–TOA 5 kDa target molecular weight at 1, 2, 4 and 8 h polymerization times.

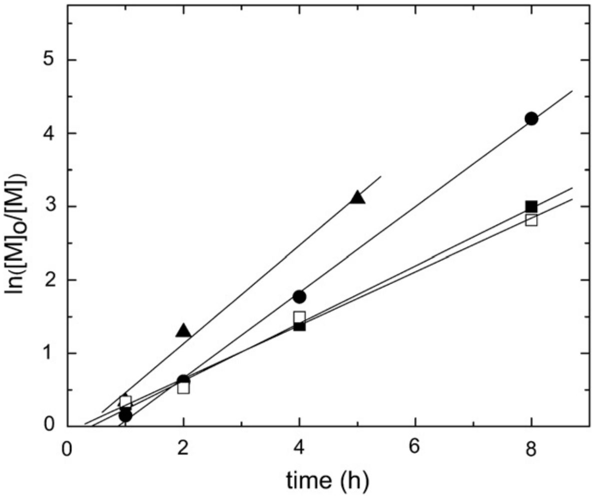


Fig. 3. Pseudo first order kinetic plots for the SS–TOA RAFT polymerizations. Target molecular weights: (■,□) 5 kDa (●) 10 kDa (▲) 20 kDa. The filled and open symbols indicate values determined from ^{1}H NMR experiments in deuterated chloroform and deuterated acetone, respectively.

observed after 8 h of polymerization with 95% conversion for the 5 kDa target polymer and 98% conversion for the 10 kDa polymer. The 20 kDa target polymerization was stopped after 5 h at 92% conversion due to cessation of stirring of the high viscosity solution.

Investigation of the ^{1}H NMR data of all three PSS–TOA polymerizations indicated that the intensity of the methylene peak (–N–CH_2–) at 3.0 ppm decreased with respect to the terminal trioctylamine methyl group peak at 0.9 ppm with increasing polymerization time. For example, while an integral ratio of 3:2 is expected for the methyl to methylene peaks, ratios of 3:1.8 to 3:1.6 were observed for the 5 kDa target polymer. One explanation for this data is that the solubility of the polymer decreases with increasing molecular weight and the mobility of the polymer near the sulfonic acid groups is reduced compared to the side-chains. For example, integral intensities different from the theoretical ratios have been observed in polyelectrolyte–surfactant complexes in water [25]. A second possibility is that an irreversible chain transfer reaction takes place with the monomer or polymer. Trialkylamines have been observed to act as chain transfer agents where hydrogen abstraction from the alpha carbon of the trialkylamine generates a new initiating radical [26]. For example, triethylamine was found to be a highly active chain transfer agent in the free radical polymerization of acrylonitrile and methyl acrylate, but only moderately active in the free radical polymerization of styrene and methyl methacrylate. The ^{1}H NMR characterization of the 5 kDa MW target polymers was re-run using deuterated acetone as the solvent. As shown in Fig. 3 similar kinetic data was obtained as when deuterated chloroform was used as the solvent. Integral ratios ranging from 3:2 to 3:1.7 were obtained that are closer to the expected ratio than observed in chloroform. This is consistent with the explanation that discrepancies in the integrated peak intensities are due to the solvation of the polymer although irreversible chain transfer reactions cannot be entirely ruled out.

The PSS–TOA homopolymers were soluble in tetrahydrofuran (THF), but no intensity was observed from the refractive index detector during size exclusion chromatography (SEC) measurements of these polymers using THF as the eluting solvent. This was likely due to the PSS–TOA polymer strongly interacting with the column. Similar effects have been observed with the SEC measurements of sulfonated polystyrene ionomers in THF [27]. One solution to mediate these interactions is to add a small molecule additive to the solution, such as an inorganic or quaternary ammonium salt [27–30]. 1 wt% solutions of lithium nitrate, tetrabutylammonium bromide, triethylamine in THF and 2% trioctylamine (TOA) in THF (2 g TOA/100 mL THF) were prepared. The PSS–TOA polymers were found to precipitate in all of these solutions except for the 2% TOA/THF. Fig. 4 shows the SEC traces of the 5, 10 and 20 kDa target PSS–TOA polymers, a PSS–Na standard that was converted to the PSS–TOA form, and a blank sample in 2% TOA/THF. In each sample a TOA peak is observed centered at an elution time of 21 min. The PSS–TOA standard was prepared by converting a commercial PSS–Na standard ($M_n = 5440$, polydispersity = 1.2) to the PSS–TOA form with a predicted M_n of 14,200. The M_n and polydispersity (PDI) values for each sample compared to polystyrene standards ($M_{n,\ SEC}$ and PDI$_{sec}$) and the M_n values determined by NMR ($M_{n,\ NMR}$ = (% conversion) × (target MW)) are listed in Table 1.

Table 1
PSS–TOA homopolymer data.

Polymer	$M_{n,SEC}$ (kDa)	PDI	$M_{n,NMR}$ (kDa)
PSS–TOA (standard)	8.3	1.14	N/A
PSS–TOA-5 kDa	2.9	1.09	4.8
PSS–TOA-10 kDa	4.4	1.20	9.8
PSS–TOA-20 kDa	8.3	1.51	18.4

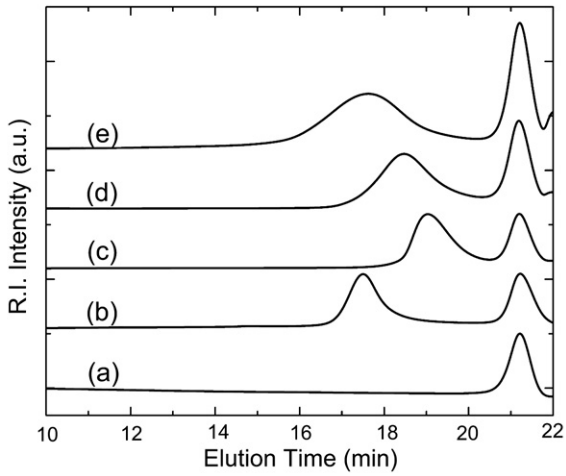


Fig. 4. GPC traces of: (a) THF + 2% TOA blank sample, (b) PSS–TOA standard (c) PSS–TOA-5 kDa target (d) PSS–TOA-10 kDa target and (e) PSS–TOA-20 kDa target.

The molecular weights obtained from the PS standards did not match the molecular weights obtained from the conversion data. This is not unexpected as the elution time is proportional to the hydrodynamic radius of the polymer, which is likely different for PS and PSS–TOA in THF. The polydispersity is narrow for the low target MW polymer and increases with increasing target MW indicating some loss of control with higher targeted molecular weights. To optimize the polymerization conditions and obtain lower polydispersity polymers 20 kDa target molecular weight polymerizations were run under different conditions varying the solvent, initial monomer concentration, AIBN:RAFT agent ratio, and polymerization temperature. The results of these polymerizations are listed in Table 2. In most cases it was found that changing the polymerization conditions were not beneficial as the polydispersity was found to either stay the same or increase compared to the initial polymerization conditions (Sample 1 in Table 2). However, it was found that a lower polydispersity could be achieved in the 20 kDa target polymerization if the initial monomer concentration was reduced to 1 M (Sample 2 in Table 2). A polymer with $M_{n,\ SEC} = 7900$ and PDI = 1.34 was obtained from a 5 h polymerization (88% conversion from ^{1}H NMR). Therefore, one factor for the loss of control in these polymerizations is the increase in solution viscosity with the increasing molecular weight of the polymer. Such a viscosity effect has been observed previously [31].

3.3. PSS-TOA-b-PS polymers

The 5k PSS–TOA polymer was used as a macro-RAFT agent for the synthesis of PSS-TOA-b-PS block copolymers. PSS–TOA was

Table 2
PSS-TOA-20 kDa Target polymerization data.

Sample	Solvent	T (°C)	$[M]_o$ [a]	AIBN:RAFT [b]	Time (h)	$M_{n,SEC}$ (kDa)	PDI
1	Benzene	80	2M	1:5	5	8.3	1.51
2	Benzene	80	1M	1:5	5	7.9	1.34
3	Benzene	80	1M	3:10	5	7.7	1.48
4	Benzene	80	2M	1:10	6.5 [c]	10.5	1.67
5	Benzene	80	1M	1:10	6	7.5	1.61
6	Benzene	65	2M	1:5	12	10.5	1.61
7	Chlorobenzene	80	2M	1:5	5	8.5	1.47
8	Chlorobenzene	100	2M	1:5	5	8.2	1.63
9	Chlorobenzene	100	1M	1:5	5	6.7	1.51

[a] Starting monomer concentration in solvent.
[b] Molar ratio of initiator to RAFT agent.
[c] Polymerization stopped stirring at this time.

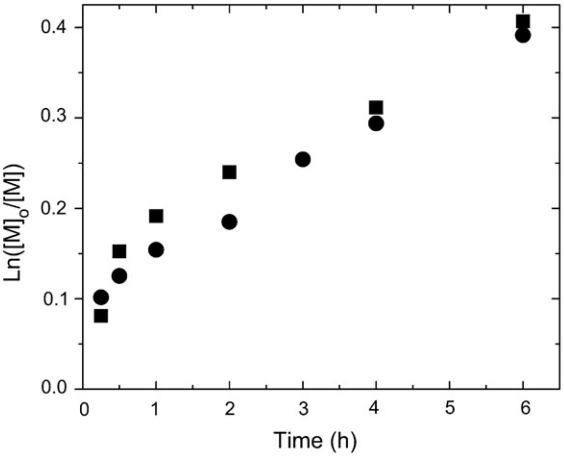


Fig. 5. Pseudo first order kinetic plots for the polymerization of styrene with a PSS–TOA RAFT agent: (■) 0.1 g PSS–TOA/1 mL styrene, (●) 0.2 g PSS–TOA/1 mL styrene.

Table 3
PSS-TOA-b-PS Block copolymer data.

PSS–TOA:styrene	Time (h)	$M_{n,SEC}$ (kDa)	$M_{n,NMR}$ (kDa)	PDI
0.1 g:1 mL	0.25	7.0	9.4	1.27
0.1 g:1 mL	0.5	8.5	10.4	1.30
0.1 g:1 mL	1	9.3	11.5	1.23
0.1 g:1 mL	2	13.4	12.7	1.25
0.1 g:1 mL	3	14.7	15.2	1.28
0.1 g:1 mL	4	17.6	16.6	1.29
0.1 g:1 mL	6	21.6	19.7	1.28
0.2 g:1 mL	0.25	4.5	6.8	1.15
0.2 g:1 mL	0.5	5.6	8.2	1.17
0.2 g:1 mL	1	7.0	9.0	1.18
0.2 g:1 mL	2	8.0	9.8	1.16
0.2 g:1 mL	4	9.9	11.0	1.19
0.2 g:1 mL	6	11.6	12.6	1.19

dissolved in styrene monomer to form a homogeneous solution. Polymerizations were run at 120 °C to generate radicals by the thermal initiation of styrene. Aliquots were removed periodically where the polymer was precipitated in hexane, dried under vacuum, dissolved in deuterated acetone and characterized by ^{1}H NMR to determine the mole and weight fraction of the PS block by comparing the integrated intensity of the methyl peaks from the trioctylamine units on the PSS block (0.9 ppm) to the benzyl protons on the PS (6–7.2 ppm) after subtracting the contribution from the benzyl protons of the PSS. For the low concentration of PSS-RAFT (0.1 g/mL styrene) PS weight fractions of 45–75% were obtained, while for the higher concentration of PSS-RAFT (0.2 g/mL styrene) PS weight fractions of 26–60% were obtained. The PS conversion was calculated by comparing the molecular weight of the PS block to the theoretical molecular weight of the PS block at 100% conversion assuming a 4.8 kDa PSS–TOA block. Fig. 5 shows the pseudo first order kinetic plots at both PSS–TOA:styrene ratios. The kinetics appear much faster at short time ($t \leq 0.5$). This is attributed to a change in the radical concentration with time during the polymerization. The radical concentration is dependent on the thermal initiation rate of the styrene monomer. As the radical concentration is increased relative to the RAFT agent concentration the probability of irreversible termination reactions will increase. As the styrene monomer is depleted the rate of radical formation and tendency towards irreversible termination reactions would decrease and therefore a steady-state concentration of radicals could be achieved. This would be consistent with an initial fast conversion leveling of to a slower, linear rate of conversion in the pseudo first order kinetic plots in Fig. 5.

The SEC traces of the PSS-TOA-b-PS block copolymers at different polymerization times are shown in Fig. 6a–b where 2% TOA/THF solution was used as the eluting solvent. Monomodal peaks are observed where their elution times increase with increasing polymerization time reflecting the increasing molecular

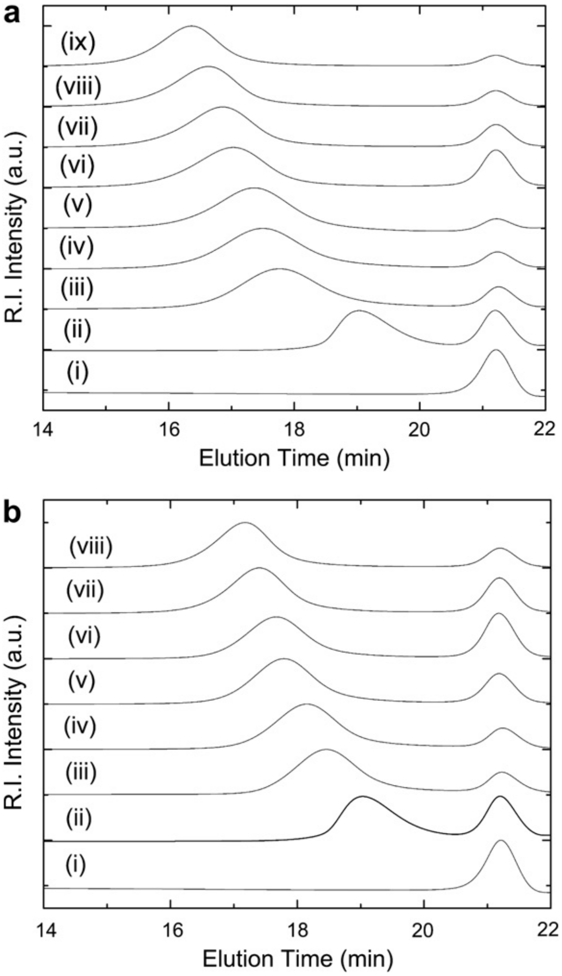


Fig. 6. SEC traces of PSS-TOA-b-PS (a) (0.1 g:1 mL PSS–TOA:styrene monomer) (i) THF + 2% TOA blank, (ii) 0 h, (iii) 0.25 h, (iv) 0.5 h, (v) 1 h, (vi) 2 h, (vii) 3 h, (viii) 4 h, (ix) 6 h polymerization time (b) (0.2 g:1 mL PSS–TOA:styrene monomer) (i) THF + 2% TOA blank, (ii) 0 h (iii) 0.25 h, (iv) 0.5 h, (v) 1 h, (vi) 2 h, (vii) 4 h, (viii) 6 h polymerization time.

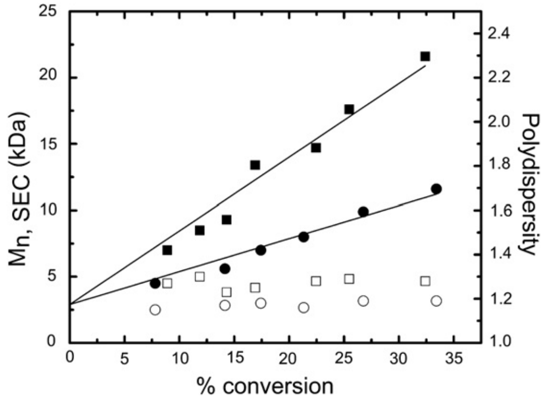


Fig. 7. $M_{n,SEC}$ (solid points) and polydispersity (hollow points) vs. conversion for the PSS-TOA-b-PS polymerizations: (■, □) 0.1 g PSS–TOA/1 mL styrene, (●, ○) 0.2 g PSS–TOA/1 mL styrene. The solid lines are linear fits to the $M_{n,SEC}$ vs. conversion data.

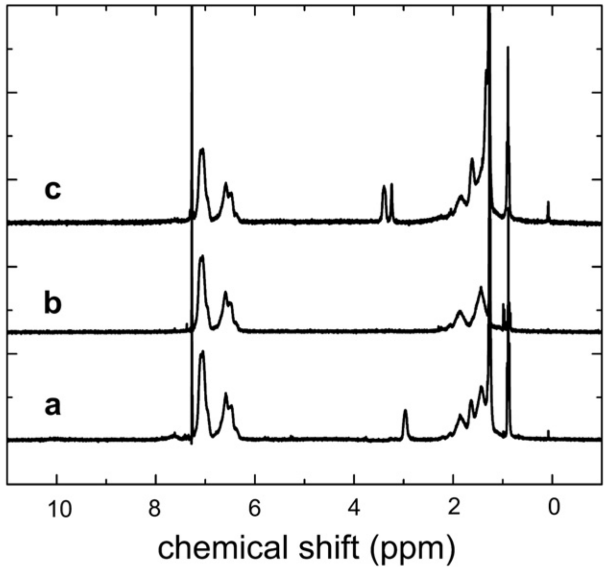


Fig. 8. ^{1}H NMR spectra of (a) PSS-TOA-b-PS, (b) PSS-Na-b-PS and (c) PSS-A336-b-PS.

weight of the PS block. The polydispersity of the polymers is 1.15–1.20 for the PSS–TOA:styrene ratio of 0.2 g:1 mL and 1.25–1.30 for the PSS–TOA:styrene ratio of 0.1 g:1 mL. The higher polydispersity at the lower PSS–TOA:styrene ratio is attributed to the increased tendency towards irreversible termination reactions broadening the molecular weight distribution. The molecular weight characteristics of the block copolymers are listed in Table 3. A plot of the $M_{n,\ SEC}$ and polydispersity vs. conversion is shown in Fig. 7. The $M_{n,\ SEC}$ values are not quantitative as they are determined from comparison to PS standards. However, good linear fits of the $M_{n,SEC}$ vs. conversion data are obtained for both PSS–TOA:styrene ratios using the SEC determined M_n of the starting PSS–TOA (2.9 kDa) as the as the y-intercept. This linear increase of the molecular weight with time demonstrates that the PSS–TOA macro-RAFT agent is able to control the polymerization of the styrene.

3.4. Ion-exchange to sodium poly(p-styrenesulfonate)

Ion-exchange reactions were carried out with aqueous sodium hydroxide to convert the PSS–TOA block to the sodium salt form (PSS–Na) and then with Aliquat 336 (mixture of trioctyl and tricaprylmethylammonium chloride) to convert the PSS–Na block back to the hydrophobic PSS-A336. Fig. 8 shows the ^{1}H NMR spectra of the PS-b-PSS in the trioctylammonium, sodium and Aliquat 336 salt forms. Both the ammonium salts formed clear solutions in deuterated chloroform while the sodium salt form was translucent. Since PSS–Na is insoluble in chloroform these blocks could aggregate in chloroform. After ion-exchange to the sodium salt form the peak from methylene protons on the alpha carbon of the trioctylamine at 3.0 ppm disappears. After ion-exchanging back to the A336 salt form the N–CH_2– peak reappears accompanied by the methylammonium peak (N–CH_3) at 3.5–3.7 ppm. Therefore, the ionic groups in these polymers can be exchanged to different forms from the starting TOA salt form.

4. Conclusions

PSS-TOA-b-PS block copolymers were successfully synthesized by the sequential RAFT polymerization of SS–TOA and styrene. These materials were successfully ion-exchanged to a hydrophilic sodium salt form and back to a hydrophobic quaternary ammonium salt form. Therefore, in addition to preparing amphiphilic PSS-containing block copolymers, this route will also be useful for making other types of PSS blocks, such as polyelectrolyte–surfactant complexes or polymeric ionic liquids. Future studies will concentrate on characterizing the thermodynamics and ordering of these block copolymers.

Acknowledgements

Acknowledgment is made to the National Science Foundation for support of K.L.P. through the University of Akron REU Site for Polymer Science and Engineering (DMR-0648318) and to the Donors of the American Chemical Society Petroleum Research Fund for support of Y.L.

References

[1] Elabd YA, Napadensky E, Walker CW, Winey KI. Macromolecules 2006;39:399–407.
[2] Rubatat L, Li C, Dietsch H, Nykanen A, Ruokolainen J, Mezzenga R. Macromolecules 2008;41:8130–7.
[3] Kim J, Kim B, Jung B. J Membr Sci 2002;207:129–37.
[4] Won J, Park HH, Kim YJ, Choi SW, Ha HY, Oh I-H, et al. Macromolecules 2003;36:3228–34.
[5] Rubatat L, Shi Z, Diat O, Holdcroft S, Frisken BJ. Macromolecules 2006;39:720–30.
[6] Park HB, Freeman BD, Zhang Z-B, Sankir M, McGrath JE. Angew Chem Int Ed 2008;47:6019–24.
[7] Bouix M, Gouzi J, Charleux B, Vairon J-P, Guinot P. Macromol Rapid Commun 1998;19:209–13.
[8] Oikonomou EK, Pefkianakis EK, Bokias G, Kallitsis JK. Eur Polym J 2008;44:1857–64.
[9] Mori S. J Liq Chromatogr Related Technol 1998;21:2935–45.
[10] Sen AK, Roy S, Juvekar VA. Polym Int 2007;56:167–74.
[11] Szczubialka K, Ishikawa K, Morishima Y. Langmuir 1999;15:454–62.
[12] Okamura H, Takatori Y, Tsunooka M, Shirai M. Polymer 2002;43:3155–62.
[13] Lienkamp K, Ruthard C, Lieser G, Berger R, Groehn F, Wegner G. Macromol Chem Phys 2006;207:2050–65.
[14] Lienkamp K, Schnell I, Groehn F, Wegner G. Macromol Chem Phys 2006;207:2066–73.
[15] Woeste G, Meyer WH, Wegner G. Makromol Chem 1993;1994:1237–48.
[16] Thaler WA, Turner SR, Lundberg RD. US Patent 4552939; 1985.
[17] Yoshizawa M, Ogihara W, Ohno H. Polym Adv Technol 2002;13:589–94.
[18] Ohno H, Yoshizawa M, Ogihara W. Electrochim Acta 2004;50:255–61.
[19] Ricks-Laskoski HL, Snow AW. J Am Chem Soc 2006;128:12402–3.
[20] Jimenez Z, Bounds C, Hoyle CE, Lowe AB, Zhou H, Pojman JA. J Polym Sci Part A Polym Chem 2007;45:3009–21.
[21] Lai JT, Filla D, Shea R. Macromolecules 2002;35:6754–6.
[22] Kertes AS. J Inorg Nucl Chem 1965;27:209–17.
[23] Favier A, Charreyre M-T. Macromol Rapid Commun 2006;27:653–92.
[24] Barner-Kowollik C, Buback M, Charleux B, Coote ML, Drache M, Fukuda T, et al. J Polym Sci Part A Polym Chem 2006;44:5809–31.
[25] Itaya T. Polymer 2002;43:2255–60.
[26] Bamford CH, White EFT. Trans Faraday Soc 1956;52:716–27.
[27] Siebourg W, Lundberg RD, Lenz RW. Macromolecules 1980;13:1013–6.
[28] Huckstadt H, Gopfert A, Abetz V. Polymer 2000;41:9089–94.
[29] Lindner SM, Kaufmann N, Thelakkat M. Org Electron 2007;8:69–75.
[30] Salamone JC, Tsai CC, Anwaruddin Q, Olson AP, Arnold M, Nagabhushanam T, et al. J Polym Sci Polym Chem Ed 1984;22:2005–16.
[31] Favier A, Charreyre M-T, Pichot C. Polymer 2004;45:8661–74.