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Title[a] Nitroxide Mediated Polymerization of an Organo-soluble Protected Styrenesulfonate: Development of Homo and Random Copolymers

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Abstract

A protected sulfonated monomer, trioctylammonium p-styrenesulfonate (SS-TOA), was polymerized at 90°C-105°C by nitroxide mediated polymerization (NMP) using BlocBuilder unimolecular initiator and additional *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] free nitroxide (SG1). Polymerizations were controlled for low theoretical molecular weight ($M_{n,theo} = 20$ kg·mol^{-1}), resulting in low polydispersities ($M_w/M_n < 1.1$) and a linear increase in number average molecular weight M_n up to ≈ 35% conversion. Product of the propagation rate constant k_p and equilibrium constant K (k_pK) for SS-TOA was 1.4-2 times greater than styrene at the same temperature, suggesting its suitability as a controlling co-monomer for BlocBuilder mediated NMP with methacrylates. SS-TOA was effective as a controlling co-monomer for gradient polymerization with glycidyl methacrylate (GMA), using *N*-hydroxy succinimidyl ester modified BlocBuilder (NHS-BlocBuilder). The resulting copolymer possessed a relatively narrow, monomodal molecular weight distribution ($M_w/M_n = 1.43$) and a linear increase in M_n with conversion, suggesting SS-TOA is an effective NMP co-monomer.

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[a] **Supporting Information** is available at Wiley Online Library or from the author. ((Other reference to the authors can also appear here, such as Author-One and Author-Two contributed equally to this work.))

Introduction

Controlled radical polymerization (CRP)[1] has enabled polymer chemists to approach the control of microstructure and molecular weight distribution, hallmarks of truly “living” polymerizations, with a relaxation of the conditions required of the latter (air-free transfers, functional group protection, rigorously pure reagent purification). CRP has achieved this control by various methods, such as those employing a reversible chain transfer (eg. RAFT)[2-4] or a reversible termination process (eg. nitroxide mediated polymerization (NMP)[5-9] or atom transfer radical polymerization (ATRP)[10,11]). The ability to make controlled structures, like those such as amphiphilic block copolymers, has been targeted and achieved by CRP.[12-21] In some cases, CRP has permitted the combination of two monomer types or incorporation of functional groups that were not possible with living polymerizations.[22]

One such functional group is the sulfonate group, which is of interest for nanoporous separations media, fuel cells, catalysis, reverse osmosis water desalination and biomineralization.[13,22,23] The direct sequential polymerization of block copolymers containing sulfonate groups in one segment is difficult for two reasons. First is the incompatibility of sulfonate monomers with controlled polymerization due to the highly charged and acidic species, which can degrade an initiator such as that used for NMP or poison a catalyst such as that used by ATRP. However, neutralization can be done and is easy to do in aqueous media.[24-27] Second is the strong immiscibility of the hydrophilic sodium p-styrenesulfonate (SS-Na) and poly(styrenesulfonic acid, sodium salt) (poly(SS-Na)) with hydrophobic monomers and organic solvents. This is the case even if the hydrophilic homopolymer block is synthesized in a controlled manner. To overcome these difficulties, post-modification of the precursor polymer or protection chemistry prior to synthesis is necessary, even when employing a CRP technique. Block copolymers containing poly(styrenesulfonate) segments have been made by selective post-polymerization sulfonation of poly(styrene), although there are several disadvantages to this technique. There is a possibility of side reactions that lead to intramolecular sulfone linkages, as it is not always possible to selectively sulfonate the poly(styrene) block and it is difficult to reach 100% sulfonation of the poly(styrene) block.[28,29] An alternative method involves modifying the p-styrenesulfonate monomer to a more hydrophobic form that is compatible with the desired polymerization chemistry. Using such an approach, Okamura and co-workers converted the sulfonic acid group to a sulfonate ester, which can be hydrolyzed back to the acid form after polymerization[30]. A third method is to neutralize the sulfonic acid site on the monomer with trioctylamine to produce a hydrophobic trioctylammonium p-styrenesulfonate monomer[22,31,32], as shown in **Figure 1a**. This avoids having to use light sensitive silver sulfonate salts or water sensitive sulfonyl chlorides as in the second method, where a sulfonate ester is prepared. The acid-base neutralization with trioctylamine has been used by Cavicchi and co-workers to prepare different ionic liquid polymers using RAFT by altering the tertiary amine and the chemistry of the acidic monomer.[22] It is a simpler and cheaper approach than the previous two methods and has been employed for the purpose of these works.

The controlled radical polymerization of trioctylammonium p-styrenesulfonate (SS-TOA) monomers has been demonstrated by using RAFT[22]. NMP[33] is desirable due to its simplicity, particularly when using unimolecular initiators such as *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder, commercially available from Arkema, Inc.)[34]. Thus, the following study focused on testing the amenability of NMP to polymerize SS-TOA and then to statistically copolymerize SS-TOA/styrene feeds using BlocBuilder. The latter is also here studied, as statistical copolymers are a step towards making gradient or tapered copolymers that could approximate the micro-phase separated microstructures associated with block copolymers. Gradient copolymers are attractive from an industrial perspective since an intermediate purification and re-initiation step is avoided.

A more attractive use of SS-TOA in copolymerization would be to use it as a controlling co-monomer for the BlocBuilder-controlled polymerization of methacrylates. Traditionally, NMP was limited to styrenic monomers using first-generation nitroxides such as 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) but second-generation nitroxides like BlocBuilder and 2,2,5-trimethyl-4-phenyl-3-azahexane nitroxide (TIPNO) have been able to control homopolymerizations of acrylates, acrylamides and nearly pure methacrylates, provided that a low concentration ~ 5 mol% controlling co-monomer like styrene was used for the latter.[35] More recent work has shown that methacrylate homopolymerizations could be controlled using the nitroxides such as those formed *in situ* from nitrites, 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide (DPAIO), and *N*-phenylalkoxyamines.[8,36-39]

The functionality of the SS-TOA monomer and its potential to control methacrylates by NMP coincides well for application to nanoporous membranes templated from block or gradient copolymers. For ABC triblock copolymers desired for nanoporous templates (A = sacrificial segment, B = functional segment, C = tough, matrix segment), the SS-TOA units could serve as the precursor for sulfonic acid sites on a membrane wall while the poly(methacrylate)[40] could serve as the matrix material. Even more desirable is to use a methacrylate that could be cross-linked, like the epoxy-functional glycidyl methacrylate (GMA)[41], which we have recently shown to be controllable with styrene co-monomer using *N*-hydroxy succinimidyl ester terminated BlocBuilder[42]. We thus attempt to also determine if an SS-TOA/GMA gradient[14] copolymerization could be controlled by NMP with NHS-BlocBuilder. The NHS group from the initiator fragment could later be transformed into an initiator for lactone or lactide polymerizations to provide the selectively degradable segment required of nanoporous membranes. The results of this study, for example, will be useful for developing NMP methods to produce block/gradient[43] copolymers suitable for nextgeneration nanoporous separations membranes with sulfonate groups on the membrane walls[44].

Experimental Section

Materials

Trioctylamine (TOA) (99%), 4-styrenesulfonic acid - sodium salt, basic alumina (Brockmann, Type 1, 150 mesh), calcium hydride (90-95%, reagent grade) were obtained from Sigma-Aldrich and used as received. Hexane (98.5%), cyclohexane (99.5%), tetrahydrofuran (99.9%), toluene (99.8%), benzene (99.8%), hydrochloric acid (37 wt% solution) were obtained from Fisher and used as received. Deuterated chloroform ($CDCl_3$) was obtained from Cambridge Isotope Laboratories. *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder®) (99%) was obtained from Arkema and *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) (85%) was kindly donated by Noah Macy of Arkema and used as received. *N*-hydroxysuccinimide (98%) and *N,N'*-Dicyclohexylcarbodimide (DCC, 99%) were received from Sigma-Aldrich and used in conjunction with BlocBuilder to synthesize the succinimidyl ester terminated alkoxyamine BlocBuilder (NHS-BlocBuilder) using the same procedure as Vinas et al.[42] Styrene (99%) and glycidyl methacrylate (GMA, 97%), purchased from Sigma-Aldrich, was purified by passing through a column of basic alumina mixed with 5% calcium hydride, then sealed with a head of nitrogen and stored in refrigeration until needed.

Synthesis of Trioctylammonium p-Styrenesulfonate Monomer

Trioctylammonium p-styrenesulfonate (SS-TOA) was synthesized from the two step procedure described by Liu et al[22,45]. In the first step, TOA was dissolved in hexane and HCl was added drop-wise (in an ice bath). The solution was placed in a freezer overnight to form trioctylammonium hydrochloride, that was then filtered, washed with cold hexane (to remove excess HCl) and dried under vacuum to form a white precipitate, trioctylammonium hydrochloride (TOA-HCl). In the second step, two solutions: TOA-HCl dissolved in benzene and sodium p-styrenesulfonate dissolved in deionized water, were combined, mixed and left to settle several hours in a separation funnel. The organic layer was collected and concentrated, frozen, filtered and then dried under vacuum overnight to yield the white SS-TOA product shown in Figure 1a; yield 21.3 g (90.7%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.4 (1H, $SO_3\mathit{H}$), 7.84 (2H, aromatic), 7.42 (2H, aromatic), 6.70 (1H, $CH_2{=}C\mathit{H}$–), 5.81 (H, $C\mathit{H}_2{=}CH$–), 5.31(H, $C\mathit{H}_2{=}CH$–), 3.02 (6H, N–$C\mathit{H}_2$–), 1.71 (6H, N–CH_2–$C\mathit{H}_2$–), 1.27 (30H, –$C\mathit{H}_2$–), 0.89 (9H, $C\mathit{H}_3$).

Synthesis of Trioctylammonium p-Styrenesulfonate Homopolymers (poly(SS-TOA))

Several nitroxide mediated homopolymerization experiments of SS-TOA (Figure 1b) in toluene were conducted at various temperatures: 90°C, 95°C, 100°C and 105°C. All homopolymerizations were performed in a 100 mL three-neck round bottom glass flask equipped with a magnetic stir bar, condenser and thermal well. The flask was set inside a heating mantle and placed on a magnetic stirrer. SS-TOA monomer and toluene (20 to 25 wt % solutions) were added to the flask with the stirrer according to the experimental conditions and formulations presented in **Table 1**. Two theoretical molecular weights at complete conversion were studied: 20 kg·mol^{-1} and 45 kg·mol^{-1}, calculated by the mass of monomer relative to the moles of BlocBuilder initiator. As an example, for experiment ID SS-

TOA-100, BlocBuilder (0.031 g, 0.081 mmol) and SG1 free nitroxide (0.0020 g, 0.0068 mmol, 8.5 mol% relative to BlocBuilder) were added to the flask, which was then sealed with a rubber septum. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the third neck of the flask. As stirring began and SS-TOA monomer was dissolved, the chilling unit (Neslab 740) using a glycol/water mixture that is connected to the condenser was set to 5°C. A nitrogen flow was introduced to purge the solution for 30 minutes. The reactor was heated to 100°C at a rate of about 5°C$\cdot$min^{-1} while maintaining the purge. Once the reaction reached the set-point temperature, the first sample was taken (t = 0, start of the reaction) with a 1 mL syringe followed by periodic sampling until the solution became too viscous to withdraw from. A portion of the sample was placed in a 5 mm Up tube for nuclear magnetic resonance (NMR) analysis. The remaining sample was precipitated in hexane, left to settle for several hours, then decanted and dried overnight in a vacuum oven at 60°C. In particular, for the synthesis of 1.60 g poly(SS-TOA) with target average molecular weight at complete conversion of 20 kg$\cdot$mol^{-1} at 100°C (SS-TOA-100), the final yield after 180 minutes was 0.85 g (52% conversion based on gravimetry) with number-average molecular weight M_n = 13.2 kg$\cdot$mol^{-1}, weight average molecular weight M_w = 16.9 kg$\cdot$mol^{-1} and polydispersity index of M_w/M_n = 1.28 determined by gel permeation chromatography calibrated with linear poly(styrene) standards in TOA/THF at 40ºC. The conversion was 51% based on ^{1}H NMR in $CDCl_3$.

Synthesis of Trioctylammonium p-Styrenesulfonate/Styrene Random Copolymers (poly(SS-TOA-*ran*-S))

The SS-TOA/S copolymerization (Figure 1c) experiments were performed in a 25 mL three neck-round bottom glass flask equipped with a magnetic stir bar, condenser and thermal well.

The flask was set inside a heating mantle and placed on a magnetic stirrer. Formulations for initial feed compositions, $f_{SS\text{-}TOA}$ = 0.10-0.80, were followed. Target molecular weights, calculated based on the mass of SS-TOA and styrene monomers relative to BlocBuilder initiator (0.031 g, 0.081 mmol), were nearly 30 kg·mol^{-1} for all experiments. 8.4 mol% SG1 free nitroxide relative to BlocBuilder was used to help control the polymerization. SS-TOA monomer and toluene (35-45 wt % solutions) were added to the flask with the magnetic stirrer. The experimental conditions and formulations for the set of SS-TOA/S copolymerizations are presented in **Table 2**. BlocBuilder and SG1 free nitroxide were added to the flask, which was then sealed with a rubber septum. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the third neck of the flask. As stirring began and the SS-TOA monomer was dissolved, the chilling unit (Neslab 740) using a glycol/water mixture that is connected to the condenser was set to 5°C to reflux any vapors produced during the experiments in order to prevent the loss of any styrene monomer due to evaporation (SS-TOA monomer is non-volatile). The previously purified styrene monomer was then injected into the flask using a disposable 5 mL syringe to accurately obtain the required feed compositions. A nitrogen flow was introduced to purge the solution for 15 minutes. The reactor was heated to 110°C at a rate of about 5°C·min^{-1} while maintaining the purge. The time when the reaction reached the set-point temperature was taken as the start of the reaction (t = 0). The first sample was taken after a 15 minute reaction time with a 1 mL syringe followed by periodic sampling over 2 to 3 hours. This was done to determine reactivity ratios, as low conversions are necessary to avoid any corrections for compositional drift. The samples were precipitated in hexane, left to settle for several hours, then decanted and dried overnight in a vacuum oven at 60°C. A portion of the dried sample was taken and inserted in 5 mm Up tubes for determining the compositions using NMR. In particular, for an initial SS-TOA feed composition, $f_{SS\text{-}TOA}$, of 0.43 (1.90 g

SS-TOA and 0.57 g styrene) with target average molecular weight of 30 kg·mol^{-1} at 110°C, the final yield after 120 minutes was 1.68 g with a SS-TOA composition, $F_{\text{SS-TOA}}$, of 0.45 in the copolymer using NMR spectroscopy. To establish the reactivity ratios of SS-TOA and styrene, the number average molecular weight M_n = 3.0 kg·mol^{-1}, weight average molecular weight M_w = 3.2 kg·mol^{-1} and polydispersity index of M_w/M_n = 1.06 were determined by gel permeation chromatography calibrated with linear poly(styrene) standards in TOA/THF at 40°C.

Synthesis of Trioctylammonium p-Styrenesulfonate/Glycidyl Methacrylate Gradient Copolymer (poly(SS-TOA-grad-GMA))

A gradient copolymerization experiment of SS-TOA with GMA in toluene was conducted at 90°C. A similar procedure used for the SS-TOA polymerizations and SS-TOA/styrene copolymerizations described in detail above was followed. 0.5 g of SS-TOA was used, with a *N*-hydroxy succinimidyl terminated BlocBuilder (NHS-BlocBuilder, 0.028 g, 0.063 mmol) in toluene (10 wt% of monomer in solvent). NHS-BlocBuilder is an attractive molecule as it is convenient for the functionalization of polymer chain ends. It has been an efficient initiator for styrene and *n*-butyl acrylate polymerizations.[42] We expect that the NHS can serve as a protecting group, but also it should sufficiently release enough SG1 from the start of the reaction to effectively control methacrylic polymerizations, such as for GMA. We seek to determine whether NHS-BlocBuilder would be an effective controller for SS-TOA/GMA gradient copolymerization without any added free nitroxide. After 220 min of reaction, 5.0 g of GMA was injected into the reactor and left to polymerize further for 3 hours. A portion of the sample was placed in 5 mm Up tube for nuclear magnetic resonance (NMR) analysis immediately before injecting GMA and during the following three hours of polymerization. During sampling, another portion was precipitated in hexane, left to settle and dried overnight in a vacuum oven at 60°C and then analyzed for molecular weight analysis in the GPC. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.4 (1H, SO_3H), 7.84 (2H, aromatic), 7.42 (2H, aromatic), 4.31 (1H, COO-CH_2-), 3.78 (1H, COO-CH_2), 3.22 (1H, COO-CH_2-CH-O-CH_2), 2.80 (1H, COO-CH_2-CH-O-CH_2), 2.59 (1H, COO-CH_2-CH-O-CH_2), 3.02 (6H, N–CH_2–), 1.71 (6H, N–CH_2–CH_2–), 1.27 (30H, –CH_2–), 1.0-2.0 (backbone), 0.90 (3H, CH_3 from GMA), 0.89 (9H, CH_3).

Characterization

^{1}H NMR spectra were measured using a 300 MHz and 400 MHz Varian Gemini 2000 spectrometer. Samples were dissolved in deuterated chloroform at a concentration of 10 mg/mL in 5 mm Up NMR tubes and were scanned 32 times. The molecular weight and molecular weight distribution of the homopolymers and copolymers were characterized by gel permeation chromatography (GPC) using a Waters Breeze system equipped with three Styragel columns (molecular weight ranges: HR1: 10^2 - 5×10^3 g·mol^{-1}, HR2: 5×10^2 - 2×10^4 g·mol^{-1}, HR3: 5×10^3 - 6×10^5 g·mol^{-1}) and a guard column heated to 40°C during analysis. Tetrahydrofuran (THF) was initially used as the mobile phase with an applied flow rate of 0.3 mL·min^{-1} during analysis. Non-polar polymers containing a low quantity of polar units can have unusual solution properties.[46-49] Polar polymers, like poly(SS-TOA), tend to have smaller hydrodynamic volumes in the THF solvent compared to poly(styrene) and tend to adsorb onto the column. Since a solvent's properties can be reproduced with a mixture of solvents, an appropriate solvent system should be possible to diminish the adsorption properties or solvation effects of polymers with polar and non-polar properties. For example, polar polymers with sulfonate groups as ionic substituents have a reduced solubility in non-polar solvents and a two-component solvent system of 2 wt% TOA in THF was required and used to fully dissolve the polymer.[50] All of the SS-TOA-containing homopolymers and copolymers were thus analyzed with 2 wt% TOA in THF solutions. The GPC was also equipped with ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The molecular weights were reported relative to calibration with linear, narrow molecular weight distribution poly(styrene) standards.

Results and Discussion

Trioctylammonium p-Styrenesulfonate Homopolymers (poly(SS-TOA))

The prepared SS-TOA monomer was soluble in several solvents including toluene, benzene, chloroform, tetrahydrofuran, methanol, and cyclohexane at room temperature. The ^{1}H NMR spectrum of the monomer confirmed a stoichiometric amount of trioctylamine to styrene sulfonic acid as reported by Liu et al.[22] SS-TOA was polymerized by NMP in 20 to 25 wt% solutions in toluene at 90°C, 95°C, 100°C, 105°C with 8.5 mol% SG1 free nitroxide relative to BlocBuilder initiator (Table 1). Samples were taken during the polymerizations to monitor the conversion throughout the reaction. The conversion was determined by comparing the ^{1}H NMR peak at 3.02 ppm of the methyl groups in trioctylamine, present in both the monomer and polymer, to the peaks at 5.3 and 5.8 ppm corresponding to the vinyl peaks present only in the monomer. **Figure 2** shows the first-order kinetic plot of $ln(1-X)^{-1}$ versus time for SS-TOA polymerizations at various temperatures. Conversion increased in a linear fashion for all four experiments, implying a constant radical concentration in the conversion ranges studied.

The first-order kinetic plot shown in Figure 2 was used to estimate the kinetic parameters for the SS-TOA polymerizations at various temperatures. The slopes are equal to $k_p[P^\cdot]$ where k_p is the propagation rate constant and $[P^\cdot]$ is the concentration of propagating macro-radicals. In each experiment, more kinetic information can be obtained given the expression for the equilibrium between dormant and active chains. Equation 1 gives the equilibrium constant, K, which is defined as:

$$K = \frac{[P\cdot][SG1]}{[P - SG1]} \tag{1}$$

where [P$^\bullet$] is the concentration of propagating macro-radicals, [SG1] is the concentration of free nitroxide, and [P-SG1] is the concentration of SG1-capped species. Multiplying Equation 1 by the propagation rate constant, k_p, gives the following expression.

$$k_p K = k_p \frac{[P\cdot][SG1]}{[P - SG1]} \tag{2}$$

Since the initial concentration of free nitroxide $[SG1]_0$ is high, [SG1] will not vary much and thus $[SG1] \approx [SG1]_0$. If the polymerization is assumed to be "pseudo-living", then [P-SG1] can be substituted by the initial concentration of BlocBuilder initiator ($[BlocBuilder]_0$) resulting in Equation 3.

$$k_p K \approx = \frac{k_p [P\cdot][SG1]_0}{[BlocBuilder]_0} \tag{3}$$

These assumptions should be satisfactory since M_n versus conversion is linear in the studied range as shown in Figure 2, thus Equation 3 can be rewritten as Equation 4 to estimate the kinetic parameters.

$$k_p K \approx = k_p [P\cdot] r \tag{4}$$

The parameter $r = [SG1]_0/[BlocBuilder]_0$ in Equation 4 is defined as the initial molar ratio of free nitroxide to that of BlocBuilder initiator. For this work, representative rate/equilibrium constant values, k_pK, were determined from experiments with an r-value of 0.085 and are presented in **Table 3** as a function of temperature. The k_pK values for SS-TOA polymerizations can be compared to styrene k_pK values that have been previously reported by various research groups.[6,37,51-54] The k_pK values for SS-TOA are greater than for styrene by a factor of ~1.4-2. However, as temperature increased, SS-TOA polymerizations approached the styrene polymerization kinetic parameters more closely.

Poly(SS-TOA) was soluble in THF, but very weak detector response was observed from the refractive index detector during GPC measurements using THF as the eluting solvent. The sulfonate groups (ionic substituents) in the homopolymer are not fully soluble in THF, resulting in column interactions and thus some tailing is apparent in the GPC traces. Due to this phenomenon, the resulting M_n values from the chromatogram are larger than expected. Adding trioctylamine (TOA) to THF (2 g TOA/100 mL THF) has been found to completely dissolve the SS-TOA homopolymers and to reduce the strong interactions to the column, thus improving the intensity from the refractive index detector.[22] The M_n versus conversion plots approached the theoretical values for poly(styrene) standards more closely when using the 2wt% TOA in THF solvent system as opposed to using only THF as solvent. This result is shown in **Figure 3** for SS-TOA-100 with target molecular weight of 20 $\mathrm{kg \cdot mol^{-1}}$ conducted at 100°C.

The conversions and molecular weight characteristics of the SS-TOA homopolymers are summarized and presented in **Table 4**. From **Figure 4**, a linear increase in M_n with conversion was seen for SS-TOA-90 and SS-TOA-100 (the experiments that used a lower theoretical molecular weight of 20 $\mathrm{kg \cdot mol^{-1}}$) until about 35 % conversion. For SS-TOA-95 and SS-TOA-105, (the experiments that used a higher theoretical molecular weight of 45 $\mathrm{kg \cdot mol^{-1}}$) the molecular weights initially overshoot the theoretical values and flatten as conversion increases. In all cases, the molecular weights obtained from the poly(styrene) standards deviated from the estimated theoretical linear behavior anticipated for a controlled polymerization. This is expected, as the elution time is proportional to the hydrodynamic radius of the polymer[55] which may be different for poly(SS-TOA) compared to poly(styrene), either in THF or in the other solvent system of 2 wt% TOA in THF. It is more difficult to control the high target molecular weight polymers, due in part to the increase in solution viscosity with increase in polymer M_n.[56] This can be seen in Figure 4 for SS-TOA-95 and SS-TOA-105, where M_n values do not increase linearly above 10% conversion but level off or even decrease at higher conversion. With the polymerizations targeting a higher theoretical molecular weight, there is more monomer present relative to initiator and polymer, thus it is likely that chain transfer and termination reactions will be more prevalent. Increasing the SG1 to BlocBuilder molar ratio may aid with the control of these polymerization experiments.[52] Still, polymerization experiments SS-TOA-90 and SS-TOA-100 with target molecular weights of 20 kg·mol^{-1} were more controlled as compared to SS-TOA-95 and SS-TOA-105 with target molecular weights of 45 kg·mol^{-1}, giving polymers with polydispersity indices, M_W/M_n, as low as 1.02 and a linear increase in number average molecular weight, M_n, with conversion up to about 35%. This range is satisfactory, as many applications may not require high degrees of polymerization of the SS-TOA.

At the lower target molecular weight experiments (20 kg·mol^{-1}), the polydispersities tend to increase relatively linearly, while at the higher target molecular weight experiments (45 kg·mol^{-1}), the polydispersities show a different trend (**Figure 5**). For SS-TOA-105, M_w/M_n values decrease from 1.35 to 1.18 until 15% conversion and then increase from 1.10 to 1.18 between 15% to 30% conversion. Similarly for SS-TOA-95, M_w/M_n values decrease from 1.18 to 1.11 until 15% conversion and then increase from 1.11 to 1.20 up to 30% conversion. The latter are typical in M_w/M_n trends, as at early conversions the polymerization was less controlled but leveled at later conversions showing better control, despite the downward deviation in M_n from $M_{n,\text{theoretical}}$ which indicates an increase in the rate of chain transfer is likely. The slight increase in M_w/M_n towards the end of the reaction may suggest irreversible chain transfer reactions to the solvent or consecutive side reactions onto intermediate radicals.[57] Trialkylamines have been observed to act as chain transfer agents where hydrogen abstraction from the α-carbon of the trialkylamine produces a new initiating radical.[58] Consequently, lowering the target molecular weight induces an improvement in the control of the polymerization.

Trioctylammonium p-Styrenesulfonate/Styrene Random Copolymer (poly(SS-TOA-ran-S))

The SS-TOA-*ran*-S copolymerizations done in toluene at 110°C, with target molecular weights of 30 kg·mol^{-1} and with feed compositions, $f_{\text{SS-TOA}}$, ranging from 0.10 to 0.80, are summarized in **Table 5**. Copolymerization is desirable as it may not be necessary to have the functional SS-TOA units as a homopolymer segment in all applications. Copolymer compositions were determined by NMR spectroscopy at less than 10 mol% conversion such that no significant compositional drift would be expected.[59] The GPC traces for several copolymerizations are displayed in **Figure 6a-d** using the solvent system of 2 wt% TOA to THF, again to prevent the strong interactions of the sulfonate groups to the GPC columns. The traces were monomodal in nature, with low polydispersities ($M_w/M_n < 1.3$) characteristic of a controlled polymerization.

Determination of Copolymerization Reactivity Ratios

Various styrene and neopentyl p-styrenesulfonate (SSPen) copolymers were prepared and are available in the literature by Okamura et al.[30]. They report random copolymerizations for poly(S-r*an*-SSPen), using NMP at 120°C but with azobis(isobutyronitrile)/2,2,5,5-Tetramethyl-1-4-diethylphosphono-3-azahexane-3 nitroxide (AIBN/DEPN) initiators for

SSPen molar feed composition, f_{SSPen}, of 0.33, 0.50 and 0.67. From the specified polymerization conditions and polymer properties for poly(S-r*an*-SSPen) with SSPen molar feed composition, f_{SSPen}, ranging from 0.33 to 0.67, reactivity ratios were evaluated using the Fineman-Ross and Kelen-Tüdös methods. The reactivity ratios were estimated as r_{Styrene} = 1.28, r_{SSPen} = 4.49 by Fineman-Ross and r_{Styrene}= 1.33, r_{SSPen} = 4.61 by Kelen-Tüdös. Although the values cannot be closely compared to our data due to the different experimental conditions, they can be used as a general reference for reactivity between the two monomers. The reactivity ratios of SSPen are significantly larger than for styrene indicating the distinct preference for SSPen to add to itself. For this particular system, the value of SSPen is roughly 3.5 times ($r_{\mathrm{SSPen}}/r_{\mathrm{Styrene}}$) more reactive than styrene, while for our system using NMP, the protected sulfonate monomer is roughly 6 (average of the three methods used) times more reactive than styrene. In both systems, styrene-sulfonated monomer reactivity ratios found by Fineman-Ross and Kelen-Tüdös are ≈ 4.5, whereas those of styrene are closer to unity (r_{Styrene} = 0.74-0.77 with our data and r_{Styrene} = 1.28-1.33 with Okamura et al.' data); therefore, a similar conclusion can be drawn regarding the reactivity between the styrene-sulfonated monomer and styrene.

Table 5 summarizes the compositions for the copolymers synthesized from various initial feed compositions. To predict the copolymer composition in terms of the initial monomer concentrations, a terminal copolymerization model as proposed by Mayo[60] was used.[22,50] This model assumes the active site reactivity depends on the nature of the reactive terminus. It is characterized by reactivity ratios[61-64] $r_{\mathrm{SS\text{-}TOA}}$ and r_{Styrene}, where $r_{\mathrm{SS\text{-}TOA}}$ is the relative preference for the SS-TOA monomer to add to a propagating chain with a terminal SS-TOA group, while r_{Styrene} is the relative preference of the styrene monomer to add to a propagating chain with a terminal styrene group. Monomer reactivity ratios for SS-TOA and styrene were determined from NMR data via the Fineman-Ross[61] and Kelen-Tüdös[63,65] methods and by a nonlinear least-squares minimization fit (using MatLab with 95%

confidence bound) to the Mayo-Lewis equation. The reactivity ratios are displayed in **Table 6**. The Mayo-Lewis plot is shown in **Figure 7** using the reactivity ratios obtained from all three methods with our experimental data. Each provides a good fit to the experimental data and the slight variance between models is barely noticeable.

The larger reactivity ratio of SS-TOA compared to that of styrene reveals that the propagating SS-TOA radicals preferentially add to SS-TOA monomer rather than to styrene monomer. $r_{Styrene}$ is less than unity with the Fineman-Ross and the Kelen-Tüdös methods and is 1.19 by regression, but in all cases $r_{Styrene}$ is significantly lower than $r_{SS\text{-}TOA}$. The product of the reactivity ratios is also often used to suggest microstructure of the copolymer. As the product is larger than unity, the microstructure is likely to be “blocky”.[66] This has important implications, particularly in the development of gradient copolymers that can approximate the microstructure of block copolymers. For this particular system, with $r_{SS\text{-}TOA} >> r_{Styrene}$, the transition will be sharper as the polymerization proceeds, from a SS-TOA-rich part of the chain and once the SS-TOA is depleted, the copolymer will become a predominantly styrene-rich segment.

Various styrene and neopentyl p-styrenesulfonate (SSPen) copolymers were prepared and are available in the literature by Okamura et al.[30]. They report random copolymerizations for poly(S-r*an*-SSPen), using NMP at 120°C but with azobis(isobutyronitrile)/2,2,5,5-Tetramethyl-1-4-diethylphosphono-3-azahexane-3 nitroxide (AIBN/DEPN) initiators for SSPen molar feed composition, f_{SSPen}, of 0.33, 0.50 and 0.67. From the specified polymerization conditions and polymer properties for poly(S-r*an*-SSPen) with SSPen molar feed composition, f_{SSPen}, ranging from 0.33 to 0.67, reactivity ratios were evaluated using the Fineman-Ross and Kelen-Tüdös methods. The reactivity ratios were estimated as $r_{Styrene} = 1.28$, $r_{SSPen} = 4.49$ by Fineman-Ross and $r_{Styrene}= 1.33$, $r_{SSPen} = 4.61$ by Kelen-Tüdös. Although the values cannot be closely compared to our data due to the different experimental conditions, they can be used as a general reference for reactivity between the two monomers.

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Gradient Polymerization of SS-TOA with GMA

A gradient polymerization of SS-TOA with GMA was performed to ensure a high concentration of sulfonate groups on one end of the chain. Based on its reactivity compared to styrene, SS-TOA was envisioned to be an effective controller for BlocBuilder mediated NMP of methacrylates using the co-monomer approach. [9,15] The GMA would then be added after a relatively low SS-TOA conversion was attained to gradually incorporate GMA into the polymer chain. Later processing, such as acid treatment, would remove the protecting group from the SS-TOA while also aid in cross-linking the epoxy group in GMA. From Figure 2, at a reaction temperature of 90 °C, SS-TOA conversion reached 25% after 220 min. Monomer conversion was determined using NMR from samples immediately before adding GMA and after 400 min, just before the polymerization was stopped. The results are summarized in **Table 7**. The molar ratio between unreacted SS-TOA and GMA at the injection time was reported as 0.01 (0.36 mmol SS-TOA/35 mmol GMA). Similarly, the samples were run in the GPC to characterize the molecular weight distribution just before and after GMA injection. The M_n increased from 2.1 to 15.7 kg·mol^{-1} while remaining monomodal and M_w/M_n increased from 1.28 to 1.43. From **Figure 8**, a clear shift was observed from the poly(SS-TOA) macroinitiator to the poly(SS-TOA-*grad*-GMA) copolymer after 400 min. These observations suggest that growth was occurring relatively steadily.

Conclusion

SS-TOA homopolymers and SS-TOA-*ran*-S copolymers of various SS-TOA/styrene mixtures were successfully synthesized by NMP. These materials were fully characterized with respect to kinetics, final polymer composition and molecular weight properties. Difficulties prevailed with the molecular weight characterization using GPC due to interactions of the sulfonate groups with the columns; although, the issue was reduced using a two-component solvent system of 2 wt% TOA in THF to completely dissolve the polymer samples. SS-TOA was polymerized in toluene at 90°C, 95°C, 100°C and 105°C by NMP using 8.5 mol% SG1 relative to BlocBuilder with target molecular weights of 20 $kg \cdot mol^{-1}$ and 45 $kg \cdot mol^{-1}$. Polymerizations were more controlled for theoretical molecular weight experiments of 20 $kg \cdot mol^{-1}$, giving polymers with M_w/M_n as low as 1.02 and a linear increase in M_n with conversion up to about 35%. This behavior was not observed for higher theoretical molecular weights that could be indicative of chain transfer and termination reactions since more monomer is present relative to initiator and polymer. [56-58] The k_pK values of SS-TOA were ~1.4-2 times greater compared to styrene homopolymerizations at the same temperature.

SS-TOA/styrene mixtures with SS-TOA molar feed composition, $f_{\text{SS-TOA}}$, ranging from 0.10 to 0.80 were copolymerized in toluene at 110°C with theoretical molecular weights at complete conversion near 30 $kg \cdot mol^{-1}$, which resulted in monomodal molecular weight distributions (M_n = 3.7-15.9 $kg \cdot mol^{-1}$) and low polydispersities (M_w/M_n = 1.21-1.26). Reactivity ratios for poly(SS-TOA-*ran*-S) were evaluated using Fineman-Ross, Kelen-Tüdös and nonlinear least-squares minimization methods. The copolymers were comparatively richer in SS-TOA for a given feed with reactivity ratios ranging from $r_{SS\text{-}TOA} = 4.43 \pm 0.16$ to

6.49 +/- 0.06 and $r_{Styrene}$ = 0.74 +/- 0.03 to 1.10 +/- 0.10.

The effectiveness of SS-TOA as a controlling co-monomer for NMP was tested using a gradient polymerization of SS-TOA with GMA using NHS-BlocBuilder initiator at 90ºC in toluene. Synthesis of poly(SS-TOA-*grad*-GMA) resulted in a monomodal molecular weight distribution with M_w/M_n = 1.43, suggesting SS-TOA behaves similarly to styrene as a controlling co-monomer for BlocBuilder-mediated NMP. The prepared sulfonated polymers and copolymers as amphiphilic precursors indicate NMP is a possible synthetic route towards achieving these materials for a number of applications such as templates for membranes.

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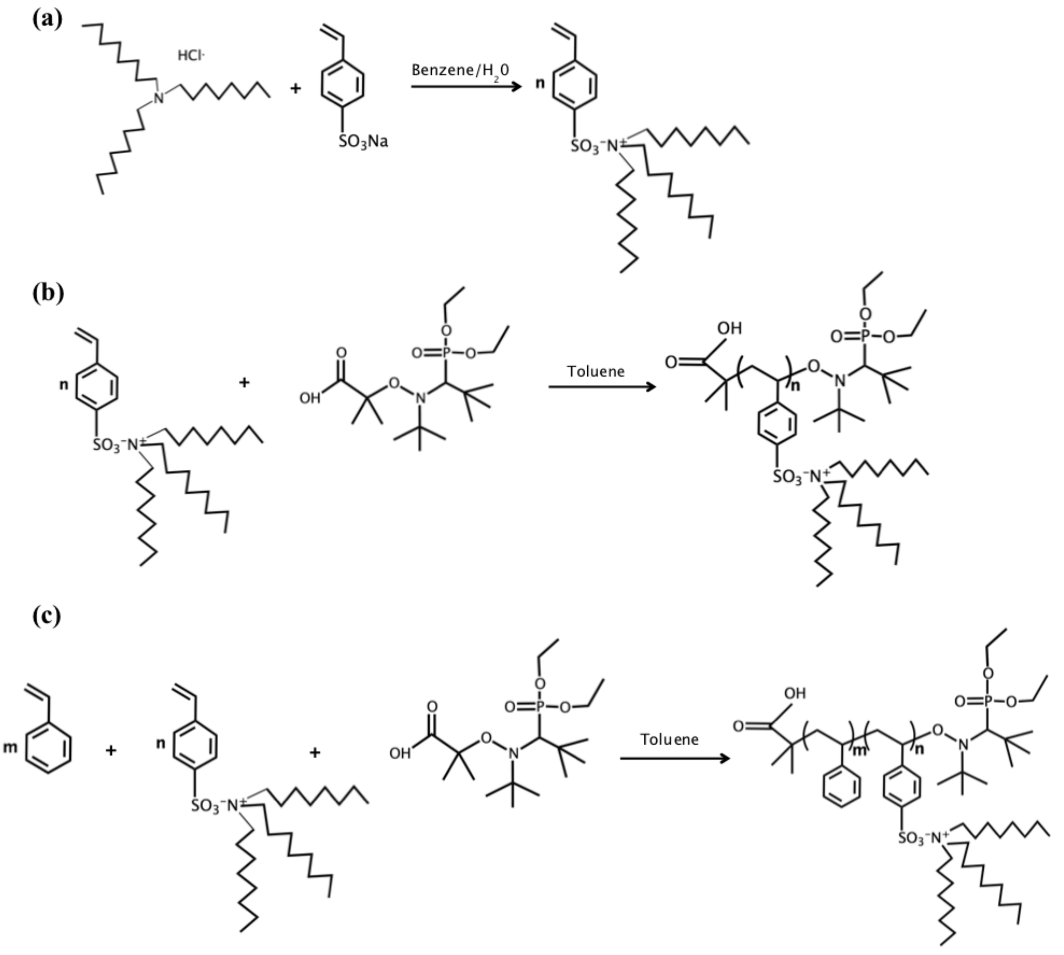

Figure 1. Synthesis of (a) trioctylammonium p-styrenesulfonate (SS-TOA) Monomer (b) trioctylammonium p-styrenesulfonate homopolymers (poly(SS-TOA)) and (c) trioctylammonium p-styrenesulfonate/styrene random copolymers (poly(SS-TOA-*ran*-S)).

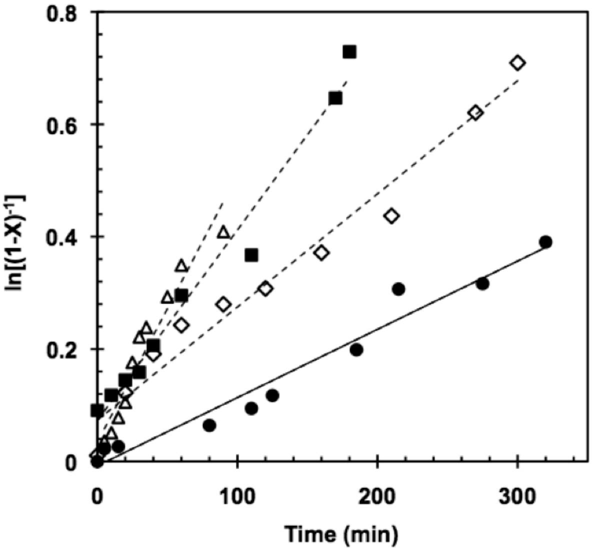

Figure 2. Semilogarithmic plot of $ln(1-X)^{-1}$ (where X = conversion) versus time for homopolymerizations of trioctylammonium p-styrenesulfonate (SS-TOA)) at various temperatures for two theoretical molecular weights at complete conversion using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (□) 90°C, (◇) 95°C, (□) 100°C and (△) 105°C. Filled symbols denote M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol^{-1} (——), while open symbols denote M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol^{-1} (- - - -). Note the plots do not always pass 0. The time for the start of the reaction was taken once the desired temperature was reached, but polymer may have started to form when temperatures sufficiently high for the BlocBuilder to dissociate (> 80°C) were approached.

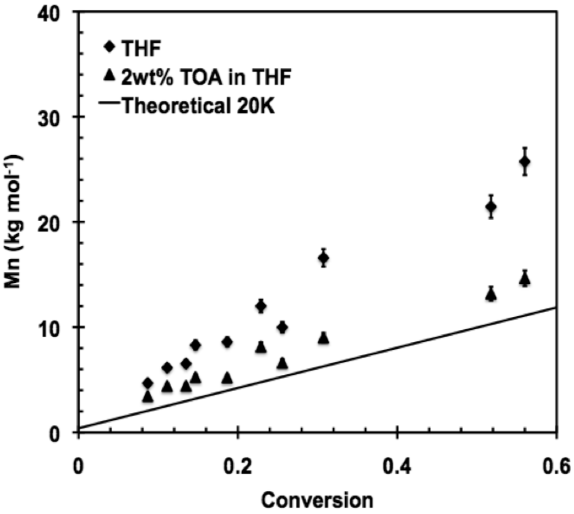

Figure 3. Number-average molecular weight (M_n) versus conversion (X) Trioctylammonium p-styrenesulfonate homopolymerization (SS-TOA-100) at 100°C with target molecular weight of 20 kg·mol^{-1} using 8.5 mol% SG1 free nitroxide relative to BlocBuilder.

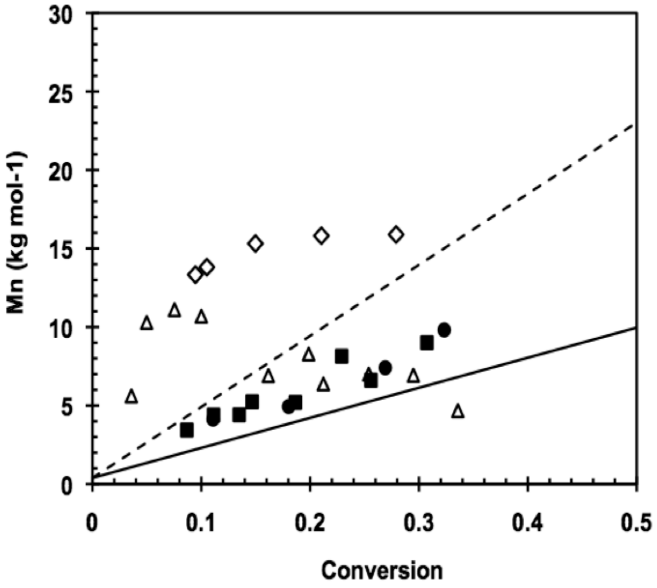

Figure 4. Number-average molecular weight (M_n) versus conversion (X) for trioctylammonium p-styrenesulfonate homopolymerizations at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (□) 90°C, (◇) 95°C, (□) 100°C, (△) 105°C. Filled symbols denote M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol^{-1} (——), while open symbols denote M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol^{-1} (- - - -).

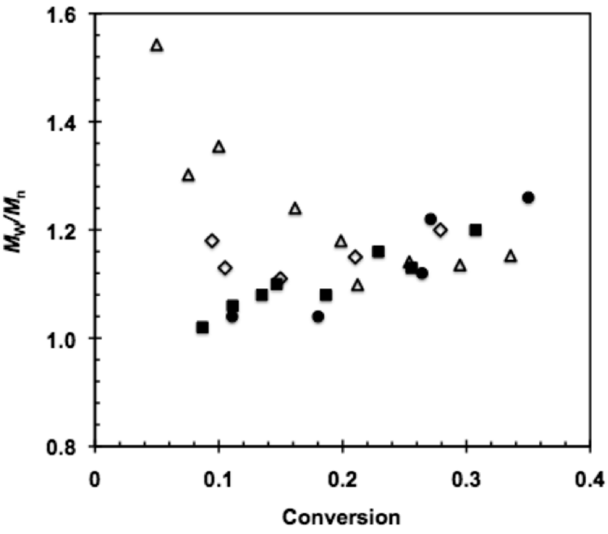

Figure 5. Polydispersity index (M_W/M_n) versus conversion (X) for trioctylammonium p-styrenesulfonate homopolymerizations at various temperatures for two target molecular weights using 8.5 mol% SG1 free nitroxide relative to BlocBuilder. The various temperatures are represented symbolically by: (□) 90°C, (◇) 95°C, (□) 100°C, (△) 105°C. Filled symbols denote M_W/M_n versus X for homopolymerizations with a target molecular weight of 20 kg·mol^{-1} (——), while open symbols denote M_W/M_n versus X for homopolymerizations with a target molecular weight of 45 kg·mol^{-1} (- - - -).

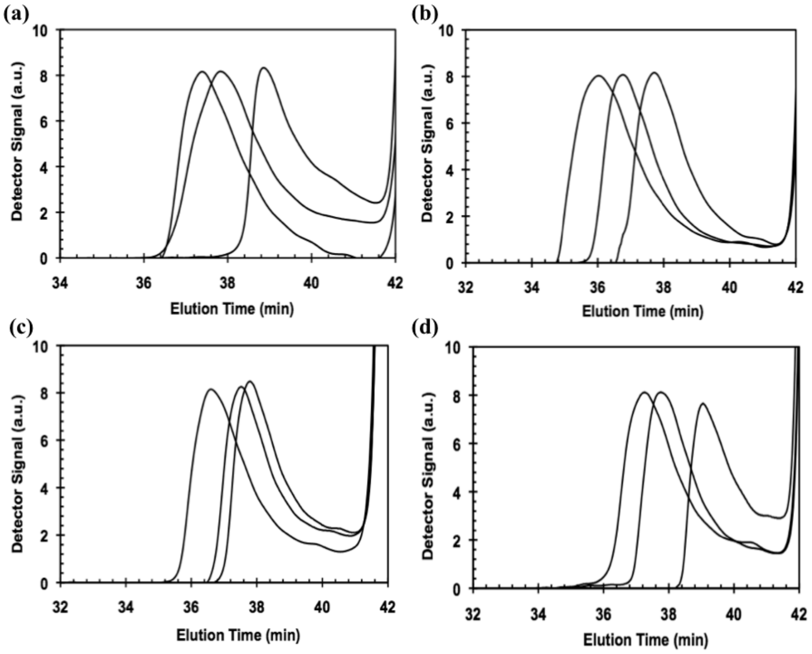

Figure 6. Gel permeation chromatograms of samples taken at various times for SS-TOA/S copolymerizations (denoted by SS-TOA-*ran*-S) performed at 110°C in toluene with theoretical molecular weights at complete conversion of 30 kg·mol^{-1} and with different monomer feed concentrations (initial molar feed concentration of SS-TOA is given by $f_{\text{SS-TOA},0}$) using SG1/BlocBuilder initiator: (a) SS-TOA/S-20/80: $f_{\text{SS-TOA},0} = 0.23$; (b) SS-TOA/S-40/60: $f_{\text{SS-TOA},0} = 0.43$; (C) SS-TOA/S-50/50: $f_{\text{SS-TOA},0} = 0.50$; (d) SS-TOA/S-60/40: $f_{\text{SS-TOA},0} = 0.63$. Please refer to Table 5 for complete characterization information. All GPC samples were prepared by dissolving in a 2 wt% TOA/THF mixed solvent.

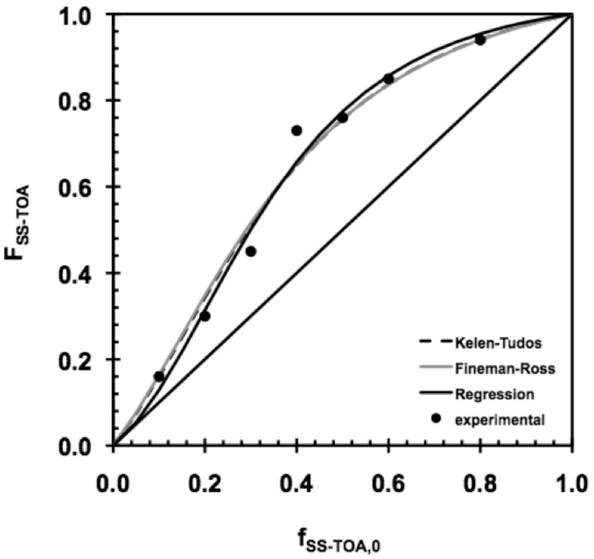

Figure 7. Mayo-Lewis plot of copolymer composition with respect to *SS-TOA*, F_{SS-TOA}, versus monomer feed composition, $f_{SS-TOA,O}$, using *SS-TOA* and styrene reactivity ratios determined from Fineman-Ross and Kelen-Tüdös methods and from nonlinear least-squares fitting of the Mayo-Lewis equation to the experimental data (r_{SS-TOA} = 4.43 to 6.49 and $r_{Styrene}$ = 0.74 to 1.10). The fits are indicated by the dashed lines while the experimental data for copolymerizations done in toluene at 110 °C using BlocBuilder as the unimolecular initiator and 8.5 mol % free nitroxide SG1 relative to BlocBuilder is indicated by the solid circles. The straight line indicates the azeotropic composition ($f_{SS-TOA} = F_{SS-TOA}$).

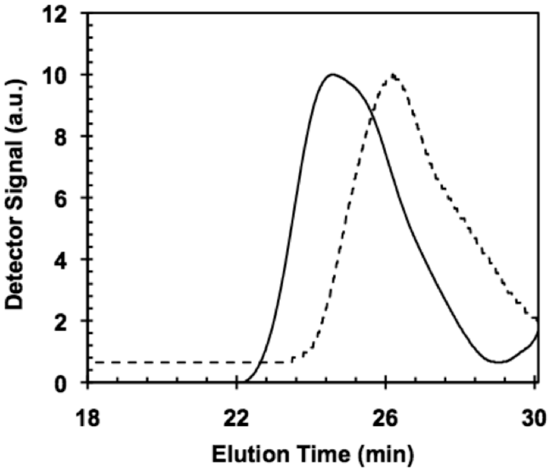

Figure 8. Gel permeation chromatogram of samples taken just before addition of glycidyl methacrylate (GMA) to SS-TOA (at 220 min) denoted by (------) and at a later time (at 400 min) denoted by (——) for gradient polymerization at 90°C using poly(SS-TOA) as macroinitiator ($X_{SS\text{-}TOA}$ = 25%) to polymerize GMA.

Table 1. Experimental Conditions for Synthesis of Trioctylammonium p-Styrenesulfonate Homopolymers (poly(SS-TOA)) in Toluene.

Experiment ID	**T [°C]**	$\phi_{Solution}$[a]	$M_{n,\mathrm{theoretical}}$ **[kg mol^{-1}]**	**[BB]$_0$ [M]**	**[SG1]$_0$ [M]**	r[b]	**[SS-TOA]$_0$ [M]**	**[Toluene]$_0$ [M]**
SS-TOA-90	90	0.20	20	0.011	0.001	0.085	0.40	9.44
SS-TOA-95	95	0.25	45	0.012	0.001	0.085	0.51	9.44
SS-TOA-100	100	0.21	20	0.012	0.001	0.084	0.44	9.44
SS-TOA-105	105	0.25	45	0.011	0.001	0.084	0.55	9.44

a) $\phi_{Solution}$ = weight fraction of SS-TOA monomer in SS-TOA/toluene solution mixture = mass SS-TOA/ (mass SS-TOA + mass toluene); b) r = ratio of initial moles of SG1 to initial moles of BlocBuilder = [SG1]$_0$/ [BlocBuilder]$_0$.

Table 2. Experimental Conditions for Synthesis of Trioctylammonium p-Styrenesulfonate/Styrene Random Copolymers (poly(SS-TOA-*ran*-S)) at 110 °C with Target Molecular Weight of 30 kg·mol^{-1} in Toluene.

Experiment ID	$\phi_{Solution}$[a]	$f_{\mathrm{SS\text{-}TOA},0}$[b]	**[BB]$_0$ [M]**	**[SG1]$_0$ [M]**	r[b]	**[SS-TOA]$_0$ [M]**	**[S]$_0$ [M]**	**[Toluene]$_0$ [M]**
SS-TOA/S-10/90	0.45	0.11	0.015	0.001	0.084	0.33	3.01	6.19
SS-TOA/S-20/80	0.45	0.23	0.018	0.001	0.084	0.57	2.19	7.10
SS-TOA/S-30/70	0.35	0.32	0.013	0.001	0.084	0.51	1.24	8.10
SS-TOA/S-40/60	0.45	0.43	0.019	0.002	0.083	0.87	1.34	8.00
SS-TOA/S-50/50	0.35	0.50	0.014	0.001	0.084	0.67	0.78	8.60
SS-TOA/S-60/40	0.35	0.63	0.015	0.001	0.083	0.73	0.51	8.90
SS-TOA/S-80/20	0.35	0.80	0.015	0.001	0.083	0.85	0.24	9.18

a) $\phi_{Solution}$ = weight fraction of SS-TOA monomer in SS-TOA/toluene solution mixture = mass SS-TOA/ (mass SS-TOA + mass toluene); b) $f_{\mathrm{SS\text{-}TOA}}$ is the initial molar feed composition of SS-TOA; c) r = ratio of initial moles of SG1 to initial moles of BlocBuilder = [SG1]$_0$/ [BlocBuilder]$_0$.

Table 3: Kinetic Parameters for BlocBuilder/SG1 Nitroxide-Mediated Polymerization of Trioctylammonium p-Styrenesulfonate and Styrene at Various Temperatures with Target Molecular Weight of 20 kg·mol^{-1} and 45 kg·mol^{-1} in Toluene[a].

	Trioctylammonium p-styrenesulfonate		***styrene***[7]
T **[°C]**	$\langle k_p\rangle[P]$ **[10^5 s^{-1}]**	$\langle k_p\rangle[K]$ **[10^6 s^{-1}]**	$\langle k_p\rangle[K]$ **[10^6 s^{-1}]**
90	2.0 ± 0.3	1.7 ± 0.3	0.9 ±- 0.1
95	2.6 ± 0.5	2.2 ± 0.4	1.4 ± 0.2
100	5.7 ± 0.9	4.8 ± 0.2	3.2 ± 0.2
105	7.9 ± 0.9	6.7 ± 0.9	5.1 ± 0.3

a)Kinetic parameters determined from initial slopes k_p[P•] of semilogarithmic plots of $ln(1 - X)^{-1}$ versus time where X = conversion of monomer, k_p = propagation rate constant, and [P•] = concentration of growing chains. K is the equilibrium constant defined in Equation 3. Error bars are derived from the standard error of the slopes (k_p[P•]) from the linear fits of $ln(1 - X)^{-1}$ versus time.

Table 4. Summary of Conversions and Molecular Weight Characteristics for Trioctylammonium p-Styrenesulfonate (SS-TOA) Homopolymers Synthesized at Various Temperatures with SG1/BlocBuilder Initiator in Toluene.

Experiment ID[a]	**Conversion *X***	M_n **[kg mol^{-1}]**	M_w/M_n
SS-TOA-90	0.35	9.8	1.26
SS-TOA-95	0.28	15.9	1.20
SS-TOA-100	0.32	9.0	1.21
SS-TOA-105	0.34	15.2	1.18

a)Experiment ID refers to experiments listed in Table 1.

Table 5. Summary of Compositions and Molecular Weight Characteristics for SS-TOA/Styrene Copolymers Synthesized in Toluene at 110 °C with SG1/BlocBuilder Initiator to Determine Reactivity Ratios of SS-TOA and Styrene.

Experiment ID	$f_{\mathrm{SS\text{-}TOA},0}$[a]	$F_{\mathrm{SS\text{-}TOA}}$[b]	**Conversion** X	M_n **[kg mol^{-1}]**	M_w/M_n
SS-TOA/S-10/90	0.11	0.16	0.092	3.6	1.23
SS-TOA/S-20/80	0.23	0.30	0.101	2.9	1.21
SS-TOA/S-30/70	0.32	0.45	0.097	3.0	1.22
SS-TOA/S-40/60	0.43	0.73	0.098	3.0	1.26
SS-TOA/S-50/50	0.53	0.76	0.097	2.9	1.25
SS-TOA/S-60/40	0.63	0.85	0.095	2.9	1.25
SS-TOA/S-80/20	0.80	0.94	0.096	3.7	1.26

a) $f_{\mathrm{SS\text{-}TOA}}$ is the initial molar feed composition of SS-TOA; b) $F_{\mathrm{SS\text{-}TOA}}$ is the final molar composition of SS-TOA determined using ^{1}H NMR.

Table 6. Summary of Monomer Reactivity Ratios by Three Methods for Trioctylamine p-Styrenesulfonate (SS-TOA)/Styrene Copolymerizations at 110 °C with SG1/BlocBuilder in Toluene.

Method	$r_{\mathrm{SS\text{-}TOA}}$	r_{Styrene}	$r_{\mathrm{SS\text{-}TOA}}/r_{\mathrm{Styrene}}$
Fineman-Ross	4.43 ± 0.16	0.74 ± 0.03	5.99
Kelen-Tüdös	4.52 ± 0.68	0.77 ± 0.12	5.87
Regression	6.49 ± 0.06	1.10 ± 0.10	5.90

Table 7. Summary of Trioctylamine p-Styrenesulfonate/Glycidyl Methacrylate Gradient Copolymerization (SS-TOA/GMA) Conversions and Molecular Weight Characteristics at 90 °C with NHS-BlocBuilder in Toluene.

Sample	**Time (min)**	**Conversion $X_{\text{SS-TOA}}$**	**Conversion X_{GMA}**	**Copolymer Composition $F_{\text{SS-TOA}}$**	**M_n [kg mol^{-1}]**	**M_w/M_n**
Poly(SS-TOA) macroinitiator	220	0.25	0	-	2.1	1.28
Poly(SS-TOA-*grad*-GMA)	400	0.85	0.75	0.17	15.7	1.43

Text for Table of Contents

Trioctylammonium p-styrenesulfonate (SS-TOA) nitroxide mediated polymerization kinetics were similar to styrene, revealing homopolymers and styrene copolymers with $M_w/M_n < 1.1$. SS-TOA was tested as a controlling monomer for BlocBuilder-mediated methacrylate copolymerizations. Gradient copolymerization of SS-TOA with glycidyl methacrylate (GMA) resulted in a monomodal copolymer (M_n = 15.7 kg·mol^{-1}) with low M_w/M_n = 1.43 and GMA content = 85 mol%.

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Nitroxide Mediated Polymerization of an Organo-soluble Protected Styrenesulfonate: Development of Homo and Random Copolymers