

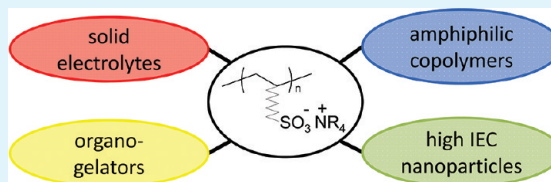
Synthesis and Polymerization of Substituted Ammonium Sulfonate Monomers for Advanced Materials Applications

Kevin A. Cavicchi*

Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301, United States

ABSTRACT: Sulfonated polymers have found use as ion-exchange membranes for use in fuel cells, water purification, electroactive devices, and inorganic materials templating and synthesis. Improving the materials for these applications and opening up new applications requires the ability to synthesis targeted or more complex sulfonated polymers, which includes tailoring the chemistry (copolymerization across a wider range of solubility) and/or polymer architecture (block, graft, nanoparticle). This article will summarize the recent work using sulfonated monomers with substituted ammonium counterions as a versatile route for enabling this goal. Two main benefits of these monomers are as follows. First, they are useful for preparing amphiphilic copolymers, which is a challenge using traditional acidic or alkali salt forms of sulfonated monomers. Second, sulfonated polymers with substituted ammonium counterions are useful polymers for obtaining unique material properties, such as organo-gelation of low polarity solvents or obtaining ionic liquid polymers for the fabrication of solid polymer electrolytes.

KEYWORDS: polyelectrolyte, ionomer, free radical polymerization



INTRODUCTION

The incorporation of ionic groups into polymers provides advanced materials for a range of applications. For example, sulfonate groups have been incorporated into various polystyrene-containing polymers through postpolymerization sulfonation.¹ These have been used to fabricate membranes for water purification, proton exchange membrane fuel cells, and electroactive actuators;^{2–4} as templating agents for metal nanoparticle and inorganic/organic hybrid materials;^{5,6} and as additives for improving the toughness of thermoplastics.⁷ Many of these applications are useful in the aerospace industry for energy generation or advanced structural materials.^{8,9}

A key advance in materials fabrication would be the ability to incorporate sulfonate groups into polymers of any arbitrary chemistry and/or architecture. This would lead to extraordinary ability to fine-tune material properties. For example, block copolymers containing sulfonated and neutral, hydrophobic blocks are very attractive for membrane applications.¹⁰ Their self-assembly into neutral and ionic domains allows for greater control over both the transport and mechanical properties of the membrane. Utilizing a cross-linkable, hydrophobic block has been found to be beneficial for confining the ionic domains and tuning the water uptake and selectivity of the membrane.¹¹ However, postpolymerization sulfonation is not compatible with all chemistries, limiting the range of different polymers that can be copolymerized. For example, polydienes are cross-linked under most sulfonation conditions.¹² An example of an architecture incompatibility is the postpolymerization sulfonation of polystyrene nanoparticles, where coarsening of the particles is observed.¹³ An alternative approach to prepare sulfonated polymers would be the direct copolymerization of sulfonated monomers. A number of free-radically polymerizable

sulfonated monomers are commercially available in the acid or alkali salt neutralized form. They can be copolymerized with other polar monomers, but solubility issues limit their copolymerization with a wider range of hydrophobic monomers.^{14–16}

In light of the difficulty of copolymerizing sulfonated monomers with more hydrophobic monomers, protection chemistries have been investigated that convert the sulfonated monomer to a more lipophilic form. A widely used approach is the synthesis of sulfonate ester monomers, which have been polymerized by atom transfer radical polymerization (ATRP), nitroxide mediated free radical polymerization (NMP) and reversible addition–fragmentation chain transfer (RAFT) polymerization.^{17–21,11,22} After polymerization the sulfonate ester is converted back to the sulfonic acid group by thermolysis or hydrolysis. However, the preparation of this monomer requires the use of water sensitive sulfonyl chlorides or light sensitive silver salts.^{23,17}

An alternative protection chemistry is to use the ionic character of a sulfonated monomer to add a hydrophobic counterion and shift the solubility of the monomer to enable copolymerization with a wider range of monomers. This was first reported by Thaler et al. for the suspension polymerization of polystyrene ionomers.²⁴ Various sulfonated monomers, including vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and *p*-styrene sulfonic acid, were neutralized with tri-*n*-octylamine to form a hydrophobic monomer, which was copolymerized with styrene in water by

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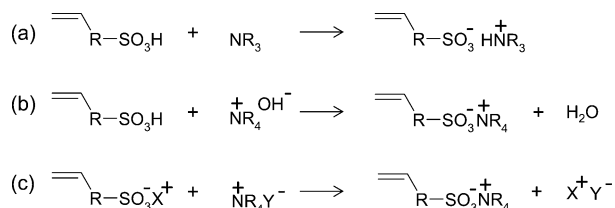
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suspension polymerization to form polymer beads of 10–5000 μm . Experiments with other tertiary amine neutralizing agents with AMPS, such as tri-*n*-butylamine or N,N-dimethyl-*n*-dodecylamine showed that the ammonium counterion must contain greater than 16 carbons for the sulfonated monomer to be strongly hydrophobic and contain less than 10 carbons in the longest segment to prevent emulsion rather than suspension polymerization. These limiting numbers are likely to depend on the specific sulfonated monomer investigated. The sodium salt form of the polymer was recovered by treating the dissolved polymer in toluene with sodium methoxide. This neutralization approach is potentially a very useful technique for synthesizing sulfonated copolymers. The protecting and deprotecting steps are both facile and performed at room temperature under air.

The growing interest in ionic polymers for advanced materials has seen a renewed interest in the preparation and polymerization of sulfonated monomers with substituted ammonium counterions and has been used for bulk, solution, emulsion and controlled free radical polymerization.^{25–32,13} This work includes using substituted ammonium counterions as protecting groups for preparing amphiphilic copolymers, but also to add new functionality through the substituted ammonium counterion. This spotlight article will focus on these recent advances in the preparation of sulfonated polymers and their applications by the author and others in the field. This work is divided into four sections: (1) synthesis of substituted ammonium sulfonate monomers; (2) conventional bulk and solution free radical polymerization of substituted ammonium sulfonate monomers; (3) emulsion polymerization of quaternary ammonium *p*-styrene sulfonates; (4) controlled free radical polymerization of trialkyl ammonium sulfonate homopolymers, random copolymers, and block copolymers. The examples given in each section will demonstrate that this general approach of polymerizing substituted ammonium sulfonate monomers is useful for preparing a variety of different sulfonated polymers. In each section, an effort is made to discuss any physical property characterizations of the polymers and highlight their potential applications.

1. Substituted Ammonium Sulfonate Monomer Synthesis. The synthesis of substituted ammonium sulfonate monomers is accomplished by one of two routes, acid–base neutralization or metathesis ion-exchange, as shown in Scheme

Scheme 1. Routes to Prepare Substituted Ammonium Sulfonate Monomers: (a, b) Acid-Base Neutralization and (c) Metathesis Ion-Exchange

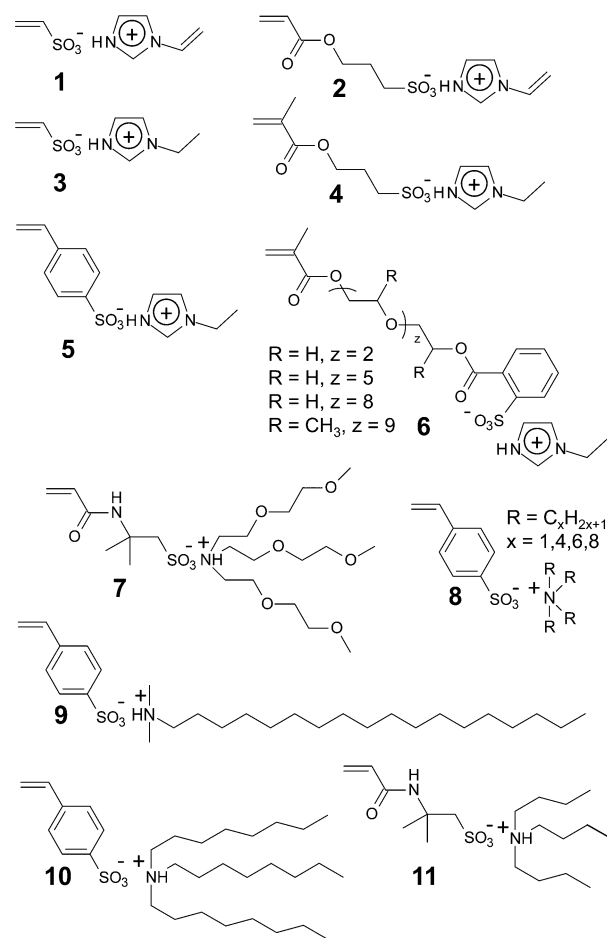


1. The acid–base neutralization has been carried out with tertiary amines and substituted imidazoles (Scheme 1a).^{25–27} At stoichiometric ratios, the acid–base neutralization produces no byproducts. But, many sulfonated monomers are sold in salt forms, such as sodium *p*-styrene sulfonate and potassium 3-sulfopropyl acrylate. These sulfonate salts can be converted to their acid form, such as by passage through a cation exchange

resin for acid–base neutralization.^{24,25} Otherwise, a tertiary amine may be converted to a halogen salt by treatment with the appropriate acid and mixed with the sulfonated monomer salt to prepare the substituted ammonium sulfonate monomer through metathesis ion-exchange (Scheme 1c).^{33,29} For the substitution of a quaternary ammonium ion the alkali salt of a sulfonated monomer can be exchanged (Scheme 1c) or the quaternary ammonium can be converted to the hydroxide ion form and used to neutralize the acid form of the sulfonated monomer (Scheme 1b).¹³

Scheme 2 shows the range of different substituted ammonium sulfonate monomers that have been reported in

Scheme 2. Substituted Ammonium Sulfonate Monomers



the literature. Monomers 1–6 were polymerized by conventional free radical polymerization to combine the properties of ionic liquids and polymers for electronics applications.^{25–28} In these systems, the acid form of the sulfonate monomer was mixed with the substituted imidazole or tertiary amine (Scheme 1a). Compared to ionic liquid synthesis by metathesis ionic exchange, this method has the advantage of no reaction byproducts, such as halogen salts. These byproduct have been found to complicate structure–property investigations because of the ability of impurities to affect the physical properties of ionic liquids, such as the viscosity.³⁴ Monomer 8 was prepared by Scheme 1b.¹³ It was used for the emulsion polymerization of high ion-exchange capacity ion-exchange nanoparticles for dispersion into polymer matrices for the fabrication of proton exchange membrane fuel cells. Monomers 9–11 were

polymerized by controlled free radical polymerization.^{29–32} Monomer **11** was prepared by Scheme 1a, whereas monomers **9** and **10** were prepared by Scheme 1c. It was shown that these monomers undergo controlled polymerization and can be copolymerized with other hydrophobic monomers including styrene, glycidyl methacrylate and alkyl acrylates as random, block, or gradient copolymers. These methods are useful to combine the chemical properties of sulfonate groups with the broader chemical and architectural control of controlled polymerization techniques for advanced materials development.^{35–37}

2. Bulk and Solution Free Radical Polymerization of Substituted Ammonium Sulfonate Monomers. Ohno and co-workers first reported the homopolymerization of substituted ammonium sulfonate monomers to prepare polymer electrolytes.^{25,26} Here ionic liquid monomers were used with the aim of combining the useful electrochemical properties of ionic liquids (high dielectric constant and ionic conductivity) with the film forming properties of polymers for electronics applications.³⁸ These polymers can be classified as polymerized ionic liquids, which have been proposed for a number of applications including electrolytes in batteries, dispersants, sorbents, porous materials, carbon templates, and electroactive polymers, the details of which are found in a number of recent reviews.^{39–43} The examples in this section will discuss different polymerized ionic liquids that can be prepared from substituted ammonium sulfonate monomers. These polymers are a subset of the wider range of polymerized ionic liquids that are possible. However, the ease of synthesis of the substituted ammonium sulfonate monomers makes them especially useful for synthesizing a range of polymers to study fundamental structure property relationships for material development. In addition, it should be noted that ionic liquid monomers have been prepared using the approaches in Scheme 1 with other acidic monomers, such as acrylic acid or vinyl phosphonic acid for use in electrolytes and coatings.^{26,44,45} In this section four investigations are discussed where substituted ammonium sulfonate monomers are polymerized by conventional bulk and solution free radical polymerization. These approaches are useful when the molecular weight dependence of the properties show little variation or are of secondary importance.

Yoshizawa et al. prepared ionic liquid monomers from the neutralization of vinyl sulfonate or potassium 3-sulfopropyl acrylate (monomers **1** and **2**, Scheme 2).²⁵ This route was based on their previous synthesis of ionic liquids by neutralization of tetrafluoroboric acid with different tertiary amines.⁴⁶ These monomers were polymerized by free radical polymerization in ethanol. Since both the sulfonate and imidazole in these monomers contain vinyl groups a densely cross-linked polymer network is formed during polymerization. This material does not have mobile ions, but does provide a high dielectric constant for the dissociation of added lithium salts. Therefore, these materials could be useful as solid polymer electrolytes for lithium ion batteries where only the transport of lithium ions is desired. The polymer prepared from monomer **1** was a solid like material with no measurable glass transition temperature (T_g). It showed a conductivity of less than 1×10^{-9} S/cm. When doped with equimolar amounts LiBF_4 or LiCF_3SO_3 little increase in the ionic conductivity was observed. However, when doped with lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) an ionic conductivity of 7.2×10^{-7} S/cm at 50°C was measured. Here the LiTFSI was thought to act as a plasticizer lowering the T_g of the

polymer network and increasing the ion mobility. The polymer prepared from monomer **2** was found to have a T_g of -30°C . This was attributed to the flexible alkyl spacer in the acrylate monomer, which increased the free volume of the polymer. After doping with an equimolar amount of LiTFSI an ionic conductivity of 1.2×10^{-5} S/cm was measured at 50°C , nearly 20 times that of the polymer without a spacer chain in the side-group. It was further proposed that more conductive networks could be obtained if spacer chains were included between both ions in the polymer network.

In a second investigation from the same research group Ohno et al. reported the synthesis and conductivity measurements of sulfonated polymers neutralized with 1-ethyl imidazole (EIm) prepared from monomers **3–6** (Scheme 2).²⁶ Attaching the anion of the ionic liquid to the polymer backbone was investigated to increase the mobility of the imidazolium cation and therefore increase the ionic conductivity of the polymerized ionic liquid. First the polymers prepared from monomers **3–4** with poly(vinyl sulfonate) (PEImVS), poly(styrene sulfonate) (PEImSS) and poly(3-sulfopropyl acrylate) (PEImSA) backbones, respectively, were compared. The ionic conductivities of the PEImVS and PEImSA were both ca. 1×10^{-4} S/cm at 30°C . The authors commented that the effect of the alkyl spacer plasticizing the polymer on the ionic conductivity may be offset by the lower ion concentration in PEImSA compared to PEImVS. The ionic conductivity of the PEImSS was much lower (1×10^{-8} at 30°C) and was attributed to the stiffness of the backbone, although no T_g could be measured for this polymer by DSC. The ionic conductivity of the benzene sulfonate-containing polymers was increased by incorporating flexible poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO) spacer chains (monomer **6**, Scheme 2). At a spacer length of 2 repeat units the T_g of the polymer was greatly reduced and ionic conductivities of 1×10^{-6} to 1×10^{-5} were observed. The PPO was found to have a higher ionic conductivity due to less interaction with the EIm cations. As shown in Figure 1 the ionic

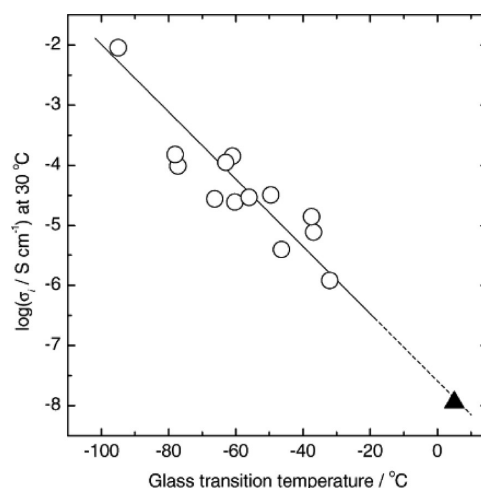


Figure 1. Relation between T_g and ionic conductivity (30°C) for polyanion type ionic liquids. (○) Experimental data, (▲) expected T_g from the ionic conductivity for P(EImSS). Reprinted with permission from ref 26. Copyright 2004 Elsevier.

conductivity, σ_i , was found to have a strong relationship with the T_g of the polymer. The open symbols in the plot represent the experimentally measured data for all of the polyanion type

ionic liquids where each point represents a different polymerized monomer. This relationship between σ_i and T_g was also used to predict the T_g of the PEImSS by extrapolation, which is shown as the solid triangle in Figure 1.

Monomer 6 (Scheme 2, $R = H$, $z = 5$) was also investigated by Vidal et al. for the formation of an interpenetrating polymer network (IPN) by the simultaneous free radical polymerization and cross-linking of the ionic liquid monomer and the step growth polymerization of a dihydroxyl terminated polybutadiene with an isocyanate cross-linker.²⁸ An IPN was prepared with 72% polymerized ionic liquid as determined by dynamic mechanical analysis. Further characterization of this material was not reported, but characterization of IPNs prepared with other ionic liquid monomers have been reported.⁴⁷ The authors comment that these materials are useful for polymer electrolytes in electronic applications where the nonionic network can improve the mechanical properties, such as the strength or swelling resistance in solvent.

The polymer obtained from the free radical polymerization of monomer 7 (Scheme 2) was investigated as an electro-wetting agent by Ricks-Laskoski and Snow, where the wetting of a liquid on a substrate varies as a function of the applied voltage.²⁷ This phenomena has applications in optics, electronic displays and microfluidics.^{48–50} The electro-wetting was characterized by measuring the contact angle of the ionic liquid monomer or polymer as a function of applied voltage (Figure 2). Both compounds were electro-wetting. The polymer

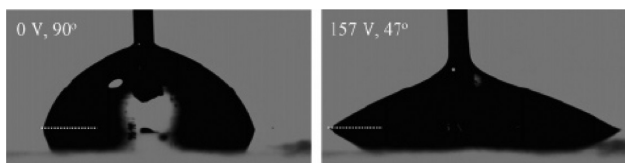


Figure 2. Electro-wetting AMPS oxyethylene ammonium salt polymer as voltage increases from 0 V (left) to 157 V (right), wherein a large decrease in contact angle is clearly visible. Reprinted with permission from ref 27. Copyright 2006 American Chemical Society.

showed an additional dependence on the polarity of the voltage due to the disparate sizes of the polyelectrolyte backbone compared to the small molecule counterion.

3. Emulsion Polymerization of Substituted Quaternary Ammonium Styrene Sulfonate. Pitia et al. reported the emulsion polymerization of different tetra-*n*-alkyl ammonium styrene sulfonate monomers (monomer 4, Scheme 2) with styrene and divinyl benzene (DVB) with the aim of preparing high ion exchange capacity (IEC), cross-linked nanoparticles.¹³ Emulsion polymerization is a natural choice for the polymerization of polymer particles, where a mixture of hydrophobic monomer, surfactant and water are used to generate stable droplets of the monomer in water (oil-in-water emulsion). The other main advantage of emulsion polymerization is the presence of the water phase, which results in low viscosity and good heat transfer.⁵² The main focus of these materials was for composite proton exchange membranes for fuel cells. It has previously been shown that incorporating high IEC capacity sulfonated, cross-linked microparticles into a second polymer matrix can produce membranes with high ionic conductivity.^{53–58} In these membranes the two phase structure allows the transport and mechanical properties to be decoupled, which is difficult to optimize in simple homopolymer membranes where the mechanical properties and ionic

conductivity are typically inversely dependent on the IEC of the membrane.⁵⁹ Both the encapsulation of the particles in a second polymer matrix and the cross-linking of the particles should shift the equilibrium water uptake of the high IEC particles, which would have excessive swelling problems as simple homopolymers. However, a weak point of blending microparticles is that their size is on the same order as the membrane thickness, which can adversely affect membrane transport and mechanical properties.⁵⁸ While nanoparticles would be more desirable they are difficult to obtain by the conventional methods of preparing cross-linked sulfonated polystyrene particles. While emulsion polymerization produces cross-linked polystyrene particles on the order of 50–500 nm the postpolymerization sulfonation can result in a coarsening of the particle size.¹³ The direct emulsion polymerization of cross-linked sodium poly(styrene sulfonate-co-styrene) has been used to produce ca. 50 nm nanoparticles, but an upper limit of the IEC of 2.2 meq/g was observed.⁶⁰ This is attributed to the water solubility of the sulfonated monomer and the formation of water-soluble polymer.^{61,62} To overcome this solubility issue Pitia et al. synthesized a series of tetra-*n*-alkyl ammonium styrene sulfonate monomers with either tetramethyl (TMA-SS), tetra-*n*-butyl (TBA-SS), tetra-*n*-hexyl (THA-SS) or tetra-*n*-octyl (TOA-SS) groups on the ammonium counterion (monomer 8, Scheme 2). These were copolymerized with styrene by emulsion polymerization. For comparison the lithium (Li-SS) and sodium salts (Na-SS) of styrene sulfonate were also investigated. The Li-SS, Na-SS, TMA-SS, and TBA-SS were copolymerized without any cross-linker, the THA-SS and Na-SS was copolymerized with DVB to produced cross-linked nanoparticles (XLPSS-THA and XLPSS-Na). For the SS-TMA and SS-TBA polymerizations an upper IEC limit for the particles of ca. 2 meq/g was observed. At loadings of higher than 50 mol % sulfonated monomer a significant amount of water-soluble sulfonated homopolymer was prepared. High IEC sulfonated nanoparticles (4.5–5.4 meq/g) were obtained when tetra-*n*-hexylammonium was used as the quaternary ammonium counterion at higher loading. As shown in Figure 3 near

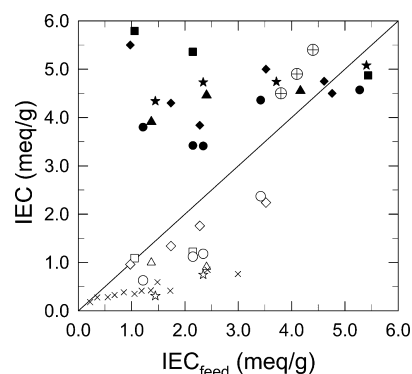


Figure 3. IEC of the water-soluble and nanoparticle fractions of the emulsion polymerization product versus the concentration of M-SS in the feed. The filled symbols are for the water-soluble polymer and the open symbols are for the insoluble nanoparticles: (Δ , \blacktriangle) Li-SS, (\star , \blackstar) Na-SS (\square , \blacksquare) TMA-SS, (\circ , \bullet) TBA-SS, (\times) from ref 51, (\diamond , \blacklozenge) XLPSS-Na, and (\oplus) XLPSS-THA. Reprinted with permission from ref 13. Copyright 2011 Elsevier.

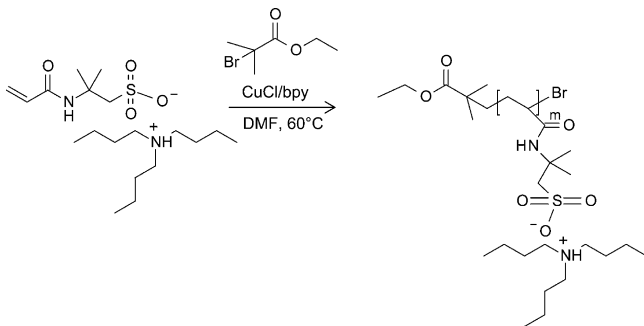
stoichiometric incorporation of the sulfonated monomer into the XLPSS-THA nanoparticles was achieved compared to the feed ratio of the polymerization. The higher than expected IEC

compared to the feed ratio was attributed to the loss of some unsulfonated monomer due to evaporation or incomplete conversion during the synthesis. Particle sizes were measured by TEM for the PSS-THA at 3.8 and 4.4 meq/g feed concentration to be 83 ± 22 and 156 ± 156 nm, respectively. Therefore, these nanoparticles should be useful for the fabrication of thin, composite ion-exchange membranes.

4. Controlled Free Radical Polymerization of Tri-*n*-alkylammonium sulfonates. Controlled free radical polymerizations are useful to produce polymers with targeted molecular weights and more complex chemistries and architectures, such as linear block copolymers or star polymers, respectively. In this section it is shown that tri-*n*-alkylammonium sulfonates can be polymerized by three different controlled free radical polymerization techniques, atom transfer radical polymerization, reversible addition–fragmentation chain transfer polymerization, and nitroxide-mediated free radical polymerization.

McCullough et al. reported the polymerization of tri-*n*-butylammonium 2-acrylamido-2-methyl propanesulfonate (AMPSA-TBA, monomer **11**, Scheme 2) by atom transfer radical polymerization (ATRP) and activators generated by electron transfer (AGET) ATRP (Scheme 3).³⁰ The monomer

Scheme 3. Preparation of Poly(AMPSA) by ATRP (EBiB/AMPSA/CuCl/bpy = 1:300:1:2). Redrawn with permission from ref 30. Copyright 2009 Wiley.



was formed by the neutralization of AMPSA with tri-*n*-butyl amine in the polymerization reactor prior to the addition of the copper/ligand complex. Low molecular weight dispersity (\mathcal{D}) polymers ($\mathcal{D} = 1.1 - 1.2$) were obtained using a CuCl/4,4'-dinonyl-2,2'-bipyridine (dN bpy) copper/ligand system and ethyl 2-bromoisobutyrate (EBiB) as the initiator. No reaction occurred if 95 or 120 mol % TBA to AMPSA was used, although polymerizations were successful at 100 and 105 mol % TBA to AMPSA. The conversions were low (10–20%) after

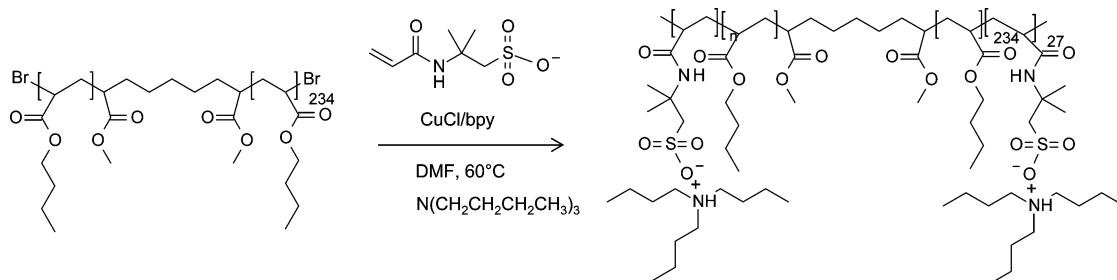
18–24 h of reaction. This authors attributed this low conversion to five possible factors, “(1) complexation of the copper by the polyacrylamide groups,^{63,64} (2) destruction of the copper by replacement of the bpy ligand with TBA, (3) creation of an unfavorable equilibrium between the activating and deactivating copper species, (4) degradative transfer with amines,⁶⁵ or (5) quaternization of terminal alkyl halides.”^{66,67} To address this third factor, AGET ATRP was also investigated by adding a reducing agent, ascorbic acid, to the polymerization to shift the equilibrium toward the activating copper species. This was found to significantly reduce the polymerization time and conversions of 20–50% were observed after 30 min of reaction, although some loss of control and higher molecular weight dispersities were observed ($\mathcal{D} = 1.2-1.35$).

Linear di- and triblock copolymers were also prepared by McCullough et al. using poly(methyl acrylate) (PMA) (diblock), poly(ethyl acrylate) (PEA) (diblock), and poly(*n*-butyl acrylate) (PBA) (diblock and triblock) as macroinitiators for the ATRP of AMPSA-TBA in anisole (Scheme 4). Clean block addition was observed by the decrease in the elution time of a monomodal peak ($\mathcal{D} = 1.1-1.2$) by gel permeation chromatography and appearance of PAMPSA-TBA peaks in ¹H NMR. This was an improvement over previous PAMPS-b-PBA synthesis using the sodium salt of AMPSA and BA or MA copolymerized in *N*-methylpyrrolidone (BA) or methanol (MA), respectively, using RAFT polymerization.^{68,69} The PAMPSA-b-PBA-b-PAMPSA were found to form micelles in water in both the amine protected and acid form as measured by dynamic light scattering. Bottlebrush polymers were also prepared by polymerization of poly(hydroxyl ethyl methacrylate), addition of a bromine groups by esterification of the hydroxyl group on each repeat unit, and ATRP of BA followed by AMPSA-TBA.

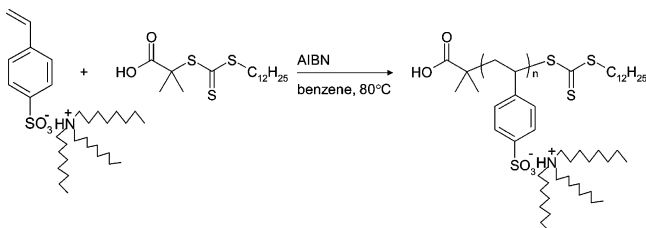
The authors suggested two possible applications for these polymers. First, the stable micellization in water makes them useful as possible surfactants.⁷⁰ The second application is dopants for conducting polymers, such as polyaniline. Here, the presence of the nonsulfonated block can produce film-forming materials with better processability and mechanical properties compared to neat polyaniline without sacrificing electrical properties.⁶⁹

Liu et al. reported the polymerization of tri-*n*-octylammonium *p*-styrene sulfonate (SS-TOA) (monomer **10**, Scheme 2) by reversible addition–fragmentation chain transfer (RAFT) polymerization to prepare homopolymers and block copolymers by the sequential addition of styrene.²⁹ The homopolymerization scheme is shown in Scheme 5. Monitoring of the polymerization kinetics of the homopolymerization by NMR demonstrated pseudofirst order kinetic behavior

Scheme 4. Extension of Difunctional Acrylate Macroinitiators with AMPSA via ATRP (dimethyl 2,6-dibromoheptanedioate/AMPSA/CuCl/bpy = 1:600:1:2). Redrawn with permission from ref 30. Copyright 2009 Wiley.



Scheme 5. RAFT Polymerization of Tri-*n*-octylammonium *p*-Styrenesulfonate. Reproduced with permission from ref 29. Copyright 2009 Elsevier.



consistent with controlled free radical polymerization for target molecular weights between 5 to 20 kDa. Conversions of greater than 90% were achieved after 8 h of polymerization. Gel permeation chromatography measurements showed that an increase in the molecular weight dispersity from 1.09 to 1.51 with increasing target molecular weight from 5 to 20 kDa. By optimization of the polymerization conditions it was found that a \bar{D} of 1.34 could be obtained for a 20 kDa target molecular weight by reducing the monomer concentration from 2 to 1 M in benzene.

Liu et al. obtained block copolymers by polymerizing styrene in the presence of a PSS-TOA macro-RAFT agent. A 4.8 kDa PSS-TOA homopolymer (0.1 g) was dissolved in either 1 or 2 mL of styrene and stirred at 120 °C to thermally initiate the styrene polymerization. The molecular weight determined by GPC showed a linear dependence on the conversion determined by NMR and \bar{D} of 1.2–1.3 was observed up to 35% conversion (Figure 4). A PS-*b*-PSS-TOA block copolymer

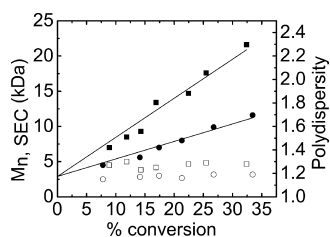


Figure 4. $M_{n, SEC}$ (solid points) and polydispersity (hollow points) vs conversion for the PSS-TOA-*b*-PS polymerizations: (■, □) 0.1 g PSS-TOA/1 mL styrene, (●, ○) 0.2 g PSS-TOA/1 mL styrene. The solid lines are linear fits to the $M_{n, SEC}$ vs conversion data with a y-intercept of 2.9 kDa. Reproduced with permission from reference 29. Copyright 2009 Elsevier.

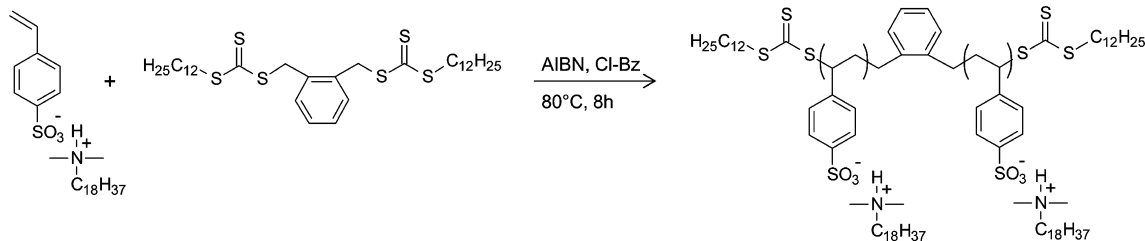
(75 wt % PS) was converted to the sodium salt form (PS-*b*-PSS-Na) by mixing an organic solution of the polymer with 1 M aqueous NaOH. After exchange, this polymer formed a opalescent solution in chloroform, characteristic of micelle

formation, because of the insolubility of the PSS-Na block and the tri-*n*-octylamine peaks were no longer present in the NMR. This polymer was converted to a third salt form by stirring with Aliquat 336, a hydrophobic quaternary ammonium salt.

In addition to the applications suggested by McCullough et al. for sulfonated block copolymers these polymers should also be useful for the fabrication of new ion-exchange membranes. The thermodynamic incompatibility between the blocks will drive the formation of periodic ordered structures composed of domains of the sulfonated and unsulfonated blocks.⁷¹ The combination of the nanostructure and chain connectivity can give rise to unique combinations of properties that are difficult to obtain in analogous random copolymers or ionomers, such as higher selectivity and lower water uptake making them useful for applications, such as fuel cells and water purification.^{10,3} The amphiphilic nanostructure is also useful for materials templating including hybrid organic/inorganic materials and porous carbons.^{5,72} The main advantage of the polymers reviewed here is their straightforward synthesis where the direct polymerization of the sulfonated monomer and its compatibility with hydrophobic materials allows for flexibility in designing new polymers.

In an attempt to prepare lower molecular polydispersity polymers Liu et al. investigated the RAFT polymerization of *N,N*-dimethyl-*n*-octadecylammonium *p*-styrene sulfonate (SS-DMODA) (monomer 9, Scheme 2) as shown in Scheme 6.³² Much better polymerization control was obtained with \bar{D} = 1.18–1.26 for target molecular weights between 10 and 50 kDa. Although these polymers were soluble in tetrahydrofuran and chloroform for GPC and NMR measurements they showed different behavior in low polarity aromatic solvents. A polymer with a degree of polymerization (N) of 38 (PSS-DMODA-38, M = 18.3 kDa) was insoluble in benzene, *o*-xylene, toluene and chlorobenzene at room temperature, but formed homogeneous solutions when heated. However, upon cooling self-supporting gels were formed (Figure 5). Freeze-dried PSS-DMODA xerogels from benzene were investigated by SEM and showed the formation of sheet-like networks reminiscent of the bilayer ordered structures observed in bulk polyelectrolyte–surfactant complexes (Figure 6).⁷³ Longer-term annealing of the gels at room temperature showed syneresis and solvent expulsion at low PSS-DMODA concentration and clouding at high PSS-DMODA concentration. This implies that the gels are not in thermodynamic equilibrium and rather are a kinetically trapped state. From this evidence it was hypothesized that the gelation was due to the clustering of the ionic groups as predicted for weakly associating polymers in solution.⁷⁴ As the strength of the ionic interactions should depend on the choice of cation, its effect on the gelation behavior would be an interesting topic for future study.

Scheme 6. RAFT Polymerization of SS-DMODA Monomer to Produce PSS-DMODA. Redrawn with permission from ref 32. Copyright 2011 American Chemical Society.



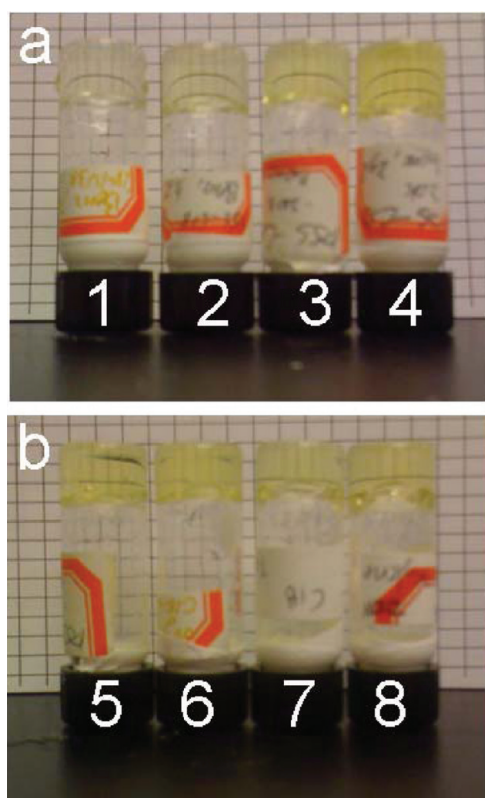


Figure 5. PSS-DMODA-38/aromatic solvent organogels. (a) Benzene organogels at (1) 2.5, (2) 5, (3) 10, (4) 20 w/v% PSS-DMODA-38. (b) 10 w/v% PSS-DMODA-38 in (5) benzene, (6) styrene, (7) toluene, and (8) *o*-xylene. Reprinted with permission from ref 32. Copyright 2011 American Chemical Society.

Organogelators are used as viscosity modifiers in a range of applications including foodstuffs, organic electronics, oil recovery and pharmaceuticals.^{75–77} These polymers are a potentially versatile organogelator platform through the variation of the counterion, backbone chemistry and degree of polymerization. These type of amphiphilic polymers are also useful for the formation of hierarchical nanostructures when used in a block copolymer architecture that can serve as templates for mesoporous materials.^{78–80} Again, the versatility of substituted ammonium sulfonate polymers would offer opportunities to tune the properties in these types of systems.

The nitroxide-mediated free radical polymerization (NMP) of SS-TOA was recently investigated by Consolante and Maric.³¹ They used *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxyprop-2-yl)hydroxylamine (BlocBuilder, commercially available from Arkema, Inc.) as the NMP initiator (Scheme 7).⁸¹ The first experiment was the homopolymerization of SS-TOA. A 20 kDa target polymer had a $\bar{D} = 1.28$ and a conversion of 52% after 3 h of polymerization at 100 °C. Investigation of the polymerization kinetics by NMR during polymerizations at different temperatures showed pseudofirst order kinetics expected for a controlled radical polymerization. A second experiment was the copolymerization of SS-TOA with styrene to prepare random copolymers. Polymerizations stopped at low conversion were used to determine the radical reactivity ratios of SS-TOA ($r_{\text{SS-TOA}}$) and styrene (r_{S}). A $r_{\text{SS-TOA}}/r_{\text{S}}$ of ca. 6, an $r_{\text{SS-TOA}}$ of 4.4–6.5 was found for SS-TOA, and a r_{S} of 0.74–1.1 was found for styrene using different fitting methods. The authors comment that this should give a blocky copolymer microstructure, which would be useful for the synthesis of gradient copolymers. This is due to both the higher reactivity of SS-TOA compared to styrene ($r_{\text{SS-TOA}} > r_{\text{S}}$) and the preference of the SS-TOA radical to react with SS-TOA ($r_{\text{SS-TOA}} > 1$).⁵² In a final experiment gradient copolymers of SS-TOA and glycidyl methacrylate (GMA) were investigated using the *N*-hydroxysuccinimidyloxy terminated form of Blocbuilder, by first starting a polymerization of SS-TOA and then adding GMA monomer at low PSS-TOA conversion (ca. 25%). A monomodal peak was observed in the GPC before adding GMA that shifted to lower elution volume after additional polymerization indicating a steady polymerization. This experiment demonstrates that these polymers are useful for gradient polymerization, which is attractive industrially as it produces block copolymer like materials from a one-pot polymerization. Also, the GMA monomer has a reactive functionality, which can be subsequently used for further chemical transformations or cross-linking.⁸² The direct polymerization approach of GMA and SS-TOA provides a way to incorporate both the epoxy and sulfonate functionalities that would be difficult by a postpolymerization modification route. The authors comment that these polymers would be useful for the templating of functional mesoporous materials. Using an ABC block copolymer a mesoporous material would be generated by chemically degrading block C, leaving a matrix of the A block coated with a functional B block. In this case, the poly(GMA)

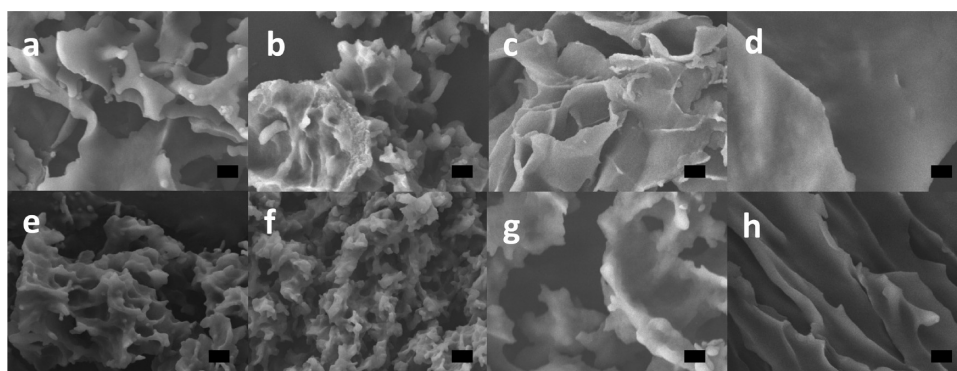
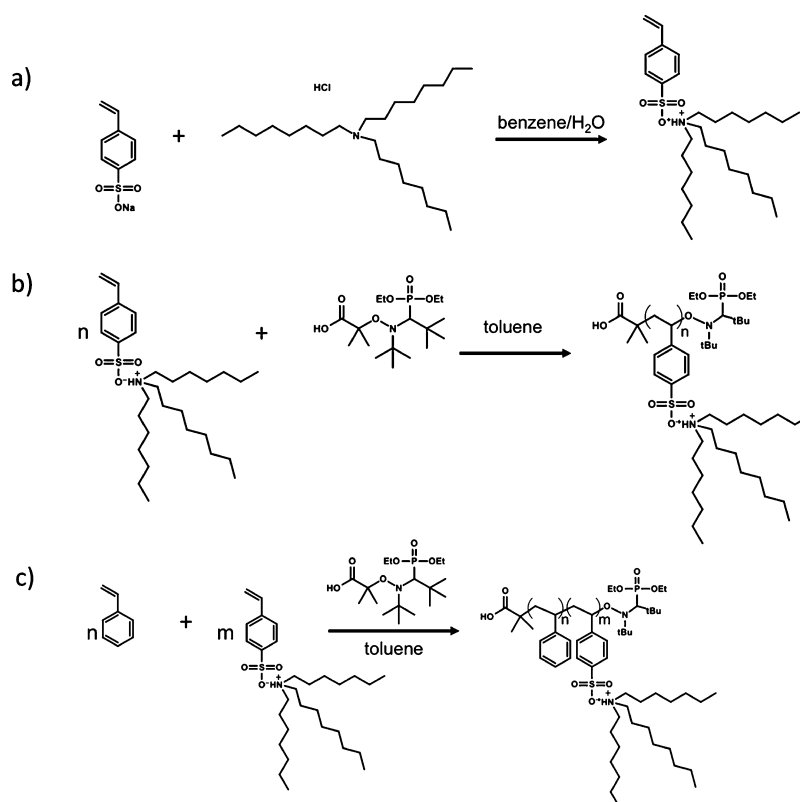


Figure 6. SEM micrographs of PSS-DMODA/benzene gels: (a) $N = 90$, $c = 2.5\%$, (b) $N = 90$, $c = 5\%$, (c) $N = 90$, $c = 10\%$, (d) $N = 90$, $c = 20\%$, (e) $N = 38$, $c = 10\%$, (f) $N = 38$, $c = 20\%$, (g) $N = 20$, $c = 10\%$, (h) $N = 20$, $c = 20\%$. The scale bars are 2 μm . Reprinted with permission from ref 32. Copyright 2011 American Chemical Society.

Scheme 7. Synthesis of (a) SS-TOA Monomer (b) SS-TOA Homopolymers [poly(SS-TOA)], and (c) SS-TOA/Styrene Random Copolymers [poly(SS-TOA-*ran*-S)]. Reprinted with permission from ref 31. Copyright 2011 Wiley.



could be used as a cross-linkable, matrix forming block, whereas the sulfonated polystyrene would serve as the functional polymer lining the pores. A degradable block could be introduced by using the NHS group on the initiator to polymerize polylactide, a polymer commonly used in the block copolymer templating of porous materials.⁸³

CONCLUSION

This article has highlighted the use of sulfonated monomers with substituted ammonium counterions for the synthesis of amphiphilic copolymers, high ion exchange capacity cross-linked nanoparticles, thermo-reversible organo-gelators, and polymeric ionic liquids. Many of these materials should be useful for improvements in different energy applications, such as fuel cells and batteries. The straightforward synthesis of these monomers should open up new possibilities for the targeted synthesis of complex sulfonated polymers for advanced applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kac58@uakron.edu. Phone: 330-972-8368.

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