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Zwitterionic Sulfonium Sulfonate Polymers: Impacts of Substituents and Inverted Dipole

Marcel U. Brown, Hong-Gyu Seong, Thomas P. Russell, and Todd Emrick*

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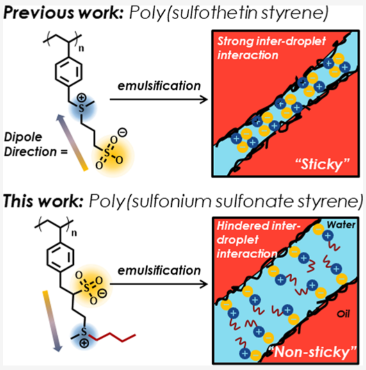
ABSTRACT: Research involving polymer zwitterions typically involves the preparation of ammonium-based structures and their study as coatings or gels that impart hydrophilicity and/or antifouling properties to substrates and materials. More recent synthetic advances have produced a significant expansion in polymer zwitterion chemistry, especially with respect to the composition of the cationic moieties that open new possibilities to examine polymer zwitterions as amphiphiles, functional surfactants, and components of complex emulsions. This article describes the synthesis of new zwitterionic sulfonium sulfonate monomers and their use as starting materials in controlled free radical polymerization to yield the corresponding polymers. These novel polymer zwitterions bear sulfonium sulfonate groups, that possess an inverted dipole directionality relative to prior examples that yields different and unexpected physical and chemical properties. For example, the polymer zwitterions described here are soluble in a wide range of nonaqueous solvents and possess significantly greater stability against nucleophiles relative to their dipole-inverted counterparts. Additionally, the amphiphilic character of these sulfonium sulfonate polymers makes them amenable to use as surfactants for stabilizing oil-in-water emulsions, a feature that is not possible using conventional ultrahydrophilic polymer zwitterions.



■ INTRODUCTION

Polymer zwitterions (PZs) comprise a unique class of macromolecular ampholytes that are characterized by their covalently linked cationic and anionic moieties that yield inner salt structures, and thus charge neutrality, throughout the entire polymer chain. The increasing interest in PZs is due in part to their ability to resist biofouling and, therefore, their relevance in applications involving implants and medical devices.[1−6] Current hypotheses attribute the antifouling properties of PZs to their extreme hydrophilicity and the hydrated environment associated with the zwitterionic dipoles that resist accumulation of biological matter.[7,8] However, greater expansion of PZs into new application areas that benefit from their unique properties will require diversifying the library of available structures with respect to both their chemistry and architecture. As such, recent work has focused on the design and synthesis of novel PZ structures.[9,10]

In general, the covalently bound ions of PZs may be arranged in a variety of ways, which allows for significant materials design flexibility. For example, the inner salt components may be contained within each monomer repeat unit as pendent groups on the polymer backbone[1−8] or may be embedded directly within the backbone.[11,12] When considering architectures in which zwitterionic moieties are positioned orthogonally to the backbone, the associated dipoles may be oriented toward the backbone (i.e., anions distal to the backbone, relative to the cations) or away from the backbone (i.e., anions proximal to the backbone).[9,13] In most PZ examples, the zwitterions are positioned pendent to the backbone with the molecular dipole pointing away from the main chain. In addition to dipole orientation, other key PZ design variables include the selection of backbone compositions, substituents on the ionic moieties, and the identities of the charge-carrying atoms.[14−18] For example, notably significant versatility in the cationic component has been achieved recently, such as for zwitterionic monomers and polymers containing phosphonium or sulfonium cations.[14,15] Focusing on this work, the illustration in Figure 1 compares polymeric sulfonium sulfonate (termed pSSS) and sulfothetin (termed pSTS) structures, noting the closely related chemical composition with inverted dipole orientation. As will be described, we specifically highlight a new route to PZs from the versatile 4-vinylbenzyl sultone monomer precursor that yields a novel zwitterionic sulfonium sulfonate monomer and the corresponding polymers. Key properties of these sulfonium sulfonates include their solubility, chemical stability, and interfacial activity, with enlightening comparisons to the known sulfothetin structures of similar chemical composition and inverted dipole directionality.

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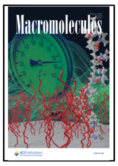

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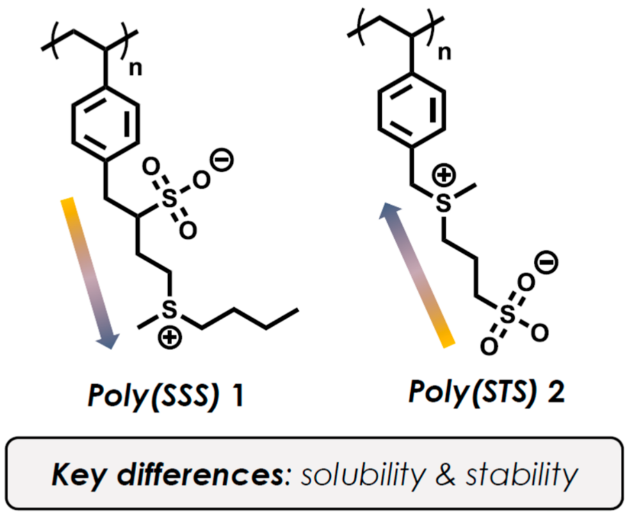

Figure 1. Chemical structures of the polymer zwitterions pSSS (**1**) and pSTS (**2**), noting their inverted dipole directionality and key distinguishing properties of solubility and chemical stability.

RESULTS AND DISCUSSION

Sulfonium Sulfonate-Substituted Styrenic Monomers.

4-Vinylbenzyl sultone has proven to be a valuable precursor to zwitterionic monomers and polymers, as described in our reports of phosphonium and ammonium sulfonate PZs.[15,16] Building further on this concept, here we describe the synthesis of styrenic sulfonium sulfonate PZs, denoted as pSSS. Our initial attempts to synthesize sulfonium sulfonates by ring-opening of sultone **3** with symmetric dialkyl sulfides as nucleophiles, such as diethyl and di-*n*-propyl sulfide, were unsuccessful and resulted in complex product mixtures that were difficult to separate and characterize. Fortunately, as illustrated in Figure 2, successful ring-opening of **3** was achieved by heating its acetonitrile solution in the presence of *n*-butyl methyl sulfide (with butylated hydroxytoluene (BHT) as inhibitor). The successful formation of monomer **4** in this latter case is attributed to the reduced steric influence of the methyl-containing disulfide and the resultant increase in its effectiveness as a nucleophile in sultone ring-opening.

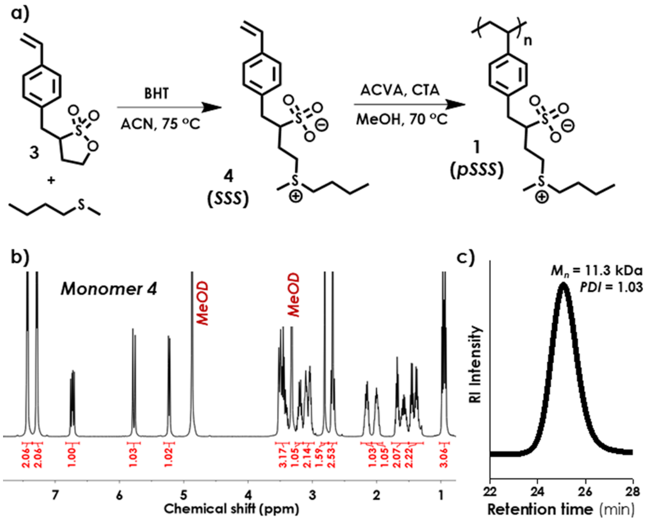

Figure 2. (a) Chemical reaction sequence for the conversion of 4-vinylbenzyl sultone **3** to the zwitterionic SSS monomer **4**, followed by RAFT polymerization to yield pSSS **1**. (b) ^{1}H NMR spectrum of SSS monomer **4**. (c) Representative GPC trace of polySSS **1** (eluting in trifluoroethanol (TFE) as the mobile phase).

The chemical structure of zwitterionic monomer **4** was confirmed by ^{1}H NMR spectroscopic characterization (shown in Figure 2b) and ESI mass spectrometry (m/z = 365.12). In the ^{1}H NMR spectrum, the protons of the aromatic ring appear as doublets (one at 7.29 ppm and another at 7.44 ppm), while the three vinyl proton signals resonate at 6.74, 5.78, and 5.24 ppm. The diasteromeric nature of **4**, arising from the presence of two chiral centers—the methine carbon adjacent to the sulfonate group and the sulfonium cation—results in complex splitting of the alkyl proton signals. For instance, the methyl protons adjacent to the sulfur cation resonate as two distinct singlets at 2.82 and 2.69 ppm, with equal intensities indicative of a lack of stereoselectivity associated with the ring-opening reaction. These results reinforce our prior studies using **3** in ring-opening reactions with amine and phosphine nucleophiles,[15,16] though the modest yields experienced when employing dialkyl sulfide nucleophiles, relative to tertiary amines and phosphines, may be attributed to their generally weaker nucleophilicity.[19,20]

Significant differences between the SSS and STS zwitterionic structures were observed with respect to their stability in the presence of nucleophiles. In experiments performed on the substituted styrenic monomers, while STS underwent slow dealkylation (over days) in the presence of weak nucleophiles, such as halide anions, the SSS monomer was significantly more stable, reacting very slowly even in the presence of strong nucleophiles, such as azide anions. Conducting the nucleophilic dealkylation and substitution experiments on the zwitterionic monomers, rather than the PZs, simplified analysis of the reaction mixtures and purification of the products.

To monitor the nucleophilic stability of these zwitterions, SSS and STS monomer solutions in deuterated DMSO (~23 mM) with 20 equiv of NaN_3 were prepared in NMR tubes, and ^{1}H NMR spectra were recorded at time intervals over the course of 7 days. The reaction shown in Figure 3a proceeds in high yield, in accord with that described by Santa Chalcara et al.[14] In contrast, inverting the zwitterionic structure to yield monomer **4** changes the electrophilicity of the benzyl position, whereas nucleophilic attack at carbon atoms adjacent to the sulfonium cation of **4** would yield products (i)−(iii) in Figure 3b. The relative stability of monomer **4** was demonstrated in ^{1}H NMR spectra recorded over time, which predominantly showed signals for the starting monomer, with smaller resonances suggestive of products (i)−(iii).

The formation of at least two dealkylation products was evident from the appearance of new aromatic proton signals (7.0−7.5 ppm) that increased in intensity over time (Figure 3c, left inset). The growth in intensity of a singlet at 2.89 ppm, immediately upfield of the methylene signals of **4** (Figure 3c, right inset), is attributed to methyl azide and suggestive of the formation of product pair (i). Integration of this singlet was used to approximate the degree of demethylation (i.e., relative to signals from **4**). For SSS **4**, only a trace of monomer was converted to products over a 2 h period, as noted by integration of the styrenic proton signals in the 7.05−7.16 ppm range. Because ^{1}H NMR spectroscopy cannot provide definitive evidence of whether all three types of substitution products formed, ESI mass spectrometry was conducted to confirm the identity of the products (Figure S9). After 7 days, the ^{1}H NMR spectra of the SSS reaction mixture indicated approximately 25% conversion to these products, most prominently the demethy-

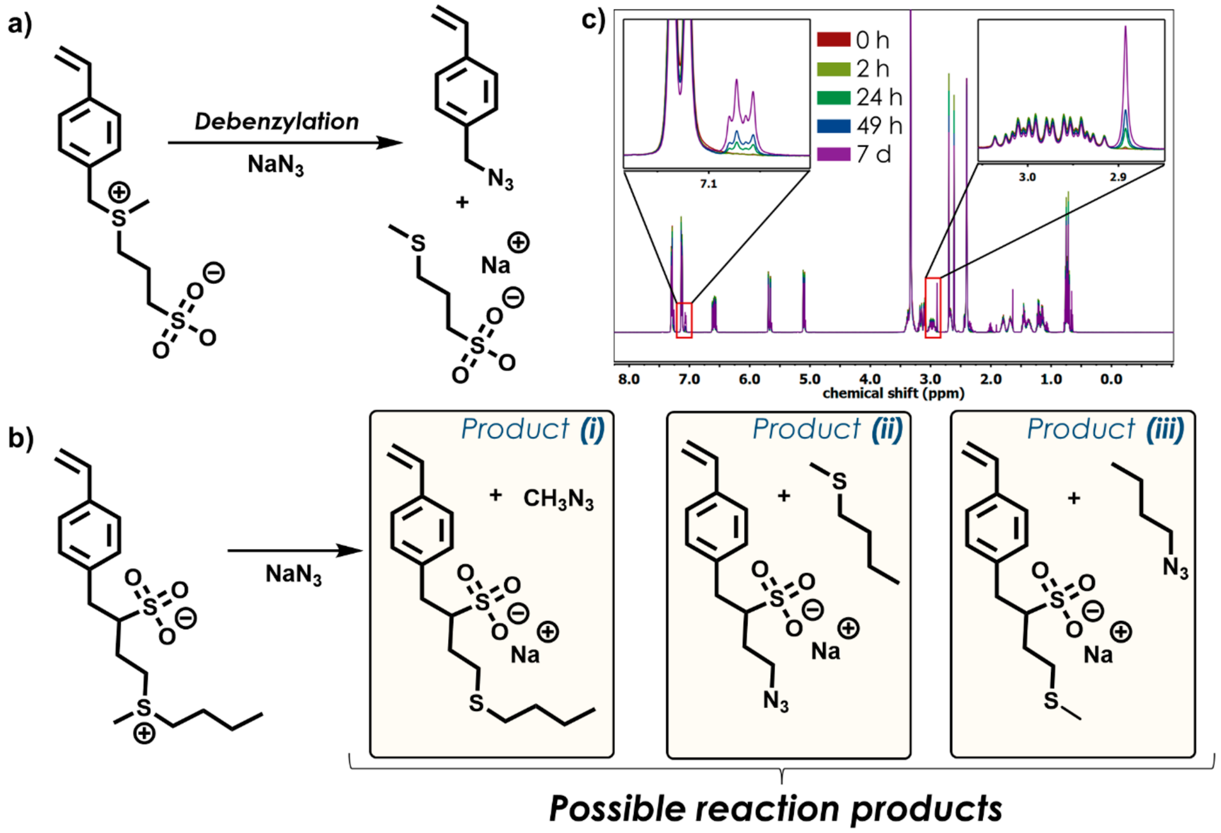

Figure 3. (a) Debenzylation products resulting from the reaction of STS with NaN_3. (b) Possible reaction products arising from reaction of SSS monomer **4** with NaN_3. (c) ^1H NMR spectrum of the reaction shown in (b), with insets of the aliphatic and aromatic regions for clarity.

lation product pair (i). In contrast, under similar conditions, the STS monomer underwent quantitative debenzylation in <2 h (Figure S8). The significantly better stability of monomer **4** against nucleophiles can be rationalized by considering the molecular structure surrounding the sulfonium cations; whereas the SSS sulfonium ion is entirely aliphatic, the benzylic arrangement of STS increases its susceptibility to nucleophilic attack. Overall, the greater stability of monomer **4**, combined with its solubility in a larger range of liquids, will be beneficial for utilizing sulfonium sulfonate PZs in situations where nucleophilic components are present in solution.

Synthesis of SSS Polymers. SSS monomer **4** was found to polymerize efficiently via reversible addition−fragmentation chain-transfer (RAFT) polymerization in MeOH at a monomer concentration of 1.3 M and a CTA-to-initiator ratio of 3:1, by placement of the reaction flask in a heating block set to 70 °C. This controlled free radical polymerization proved efficient and high yielding, affording the polymer product as a yellow solid in high monomer conversion (∼96%) and isolated yield (>90%) after purification by dialysis and lyophilization. Polymer characterization by ^1H NMR spectroscopy showed broadening of the characteristic resonances, with chemical shifts of the pendent zwitterions mirroring those of the monomer. As shown in the representative GPC trace of Figure 2c, RAFT conditions afforded a monomodal molecular weight distribution, with $Đ$ values (M_w/M_n) below 1.1, indicative of a well-controlled polymerization mechanism.

Interestingly, the pSSS-type PZs were found to be readily soluble in pure water at room temperature (>20 mg/mL), whereas the pSTS-type structures required the addition of salt to achieve aqueous dissolution. When analyzing aqueous solutions of pSSS **1** at 1 mg/mL concentration by dynamic light scattering (DLS), both very small (<10 nm) and much larger (∼180 nm) size distributions were observed (Figure S10). While the smaller distribution likely represents molecularly dissolved polymer chains, the latter should reflect the presence of multichain aggregates. Considering the chemical structures of these PZs, the greater aqueous solubility of pSSS **1** is counterintuitive because the pSSS-type structure has a greater extent of aliphatic content relative to pSTS. As illustrated in Figure 4, we speculate that the interplay between steric bulk and zwitterionic interactions determines their solubility profile, where the *n*-butyl substituent of the sulfonium cation hinders interzwitterion

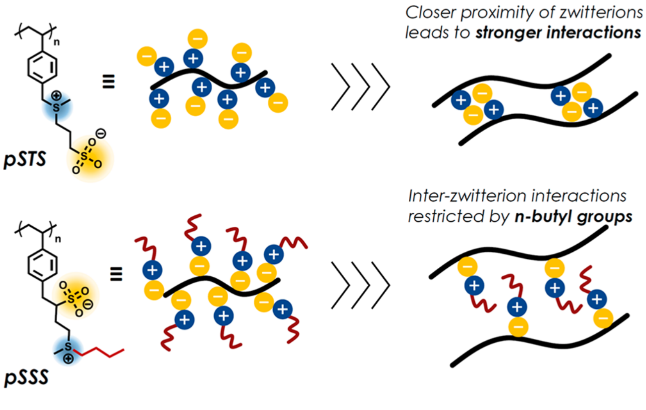

Figure 4. Illustration of anticipated interzwitterion interactions in pSTS and pSSS and the steric impact of the *n*-butyl groups in pSSS to restrict zwitterion−zwitterion pairing in solution.

interactions that would otherwise reduce their propensity to dissolve. For the STS-type monomers and polymers, which lack such a steric influence, screening of interzwitterion interactions by salt would facilitate their solubilization. Notably, the SSS-type monomer and polymers also dissolve at room temperature in organic solvents, such as MeOH and DMSO, at concentrations exceeding 100 mg/mL (monomer), while the STS monomer displays much lower solubility in MeOH (~5 mg/mL solubilization requires heating) and DMSO (7 mg/mL solubilization requires vortexing and heating). Moreover, although the pendent zwitterionic groups of the SSS-type structures are more stable toward nucleophiles, thermogravimetric analysis (TGA) showed these PZs to be more labile thermally than pSTS **2** (Figure S11), with degradation onset temperatures of ~120 °C observed for pSSS **1** and ~165 °C for pSTS **2**. Degradation of **1** appears to correspond to loss of the alkyl sulfide group, which accounts for ~30% of the overall mass, in accord with the weight loss observed by TGA. Nonetheless, stability up to ~120 °C will make polymer **1** useful well above temperatures experienced in many solution applications, with additional advantages of its enhanced stability toward nucleophiles.

Solution and Interface Properties. The fluid−fluid interfacial activity of these novel PZs was also examined, anticipating that the combination of hydrophobic (styrenic backbone) and hydrophilic (zwitterion) components in their chemical structures would impart appreciable surfactant properties. The results were compared to pSTS-based structures that are known to produce unusual "adhesive droplets" and which yield droplet-based objects by extrusion.[14,21] Using pendant drop tensiometry, the interfacial tension (IFT) of polymer solutions was examined at 0.5 mg/mL in 0.2 M $NaNO_{3(aq)}$ for pSTS **2** and pSSS **1** and in pure water for pSSS. As seen in Figure 5e, both polymers reduced the IFT of trichlorobenzene (TCB) in aqueous media in the very early time frames of the experiments.

As illustrated in Figure 5e,f, the difference in the quasi-equilibrium IFT values between the two PZs in aqueous $NaNO_3$ solution is relatively small, with measured experimental values of 10.1 mN/m for pSSS and 8.4 mN/m for pSTS, each reduced from ~42 mN/m for TCB in pure water. Similarly small differences between the recorded IFT values in pure water vs salt solution for the pSSS-type structures were observed. Therefore, while both sulfonium sulfonate PZs are appreciable surfactants, pSSS functions effectively in pure water, with no additional salt required for polymer dissolution; moreover, the resultant dispersed emulsion droplets lack any indication of the droplet-to-droplet adhesion observed for pSTS-stabilized droplets (Figure 5d), and as such the bulk solution properties of these PZs are reflected at the fluid−fluid interface. The pendent drop experiments were augmented by visual inspections of TCB-in-water emulsions prepared by combining 10 mg/mL aqueous polymer solutions with Nile Red (2 μg/mL) and vortexing in a glass vial. Pure water was used for pSSS **1** and 50 mM $NaNO_3$ for pSTS **2**. In both cases, stable oil-in-water droplets settled to the bottom of the vials. The droplets stabilized by pSSS **1** were examined by fluorescence confocal microscopy (Figure 5b), showing polydisperse droplets of diameter up to about 100 μm, with most in the 10−50 μm range. The aqueous supernatant was carefully removed with a graduated syringe, and the oil fraction of the emulsion phase was determined to be 0.78. Notably, more conventional polymer zwitterions like poly(2-methacryloyloxyethyl phosphorylcholine) (pMPC) do not possess these amphiphilic properties and in turn cannot stabilize emulsions by themselves. As shown in previous work, the TCB-in-water emulsions stabilized by pSTS **2** are notably adhesive, forming "sticky emulsions",[21] whereas droplets stabilized by pSSS **1** simply disperse without significant interdroplet interactions; this is shown in Figure 5c,d by inversion of the vials, in which the sticky droplets remaining at the top contrast the free-flowing behavior seen for pSSS **1**. Such observations reinforce our reasoning that the inter-zwitterion interactions of pSTS that impart adhesive properties are absent in the pSSS emulsions due to the influence of steric features associated with the *n*-butyl substituent on the sulfonium cation.

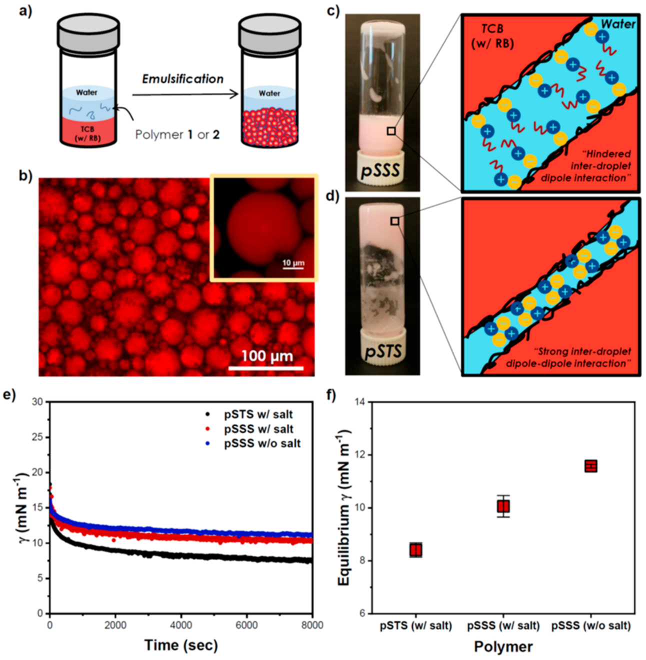

Figure 5. (a, b) Schematic of emulsification and fluorescence micrograph of oil-in-water droplets stabilized by pSSS. (c, d) Photographs and illustration of hypothesized interzwitterion interactions at the respective oil−water interfaces. (e) Plot of interfacial tension vs. time for pSSS **1** in pure water and $NaNO_{3(aq)}$ and pSTS **2** in $NaNO_{3(aq)}$ solution. (f) Plots of quasi-equilibrium interfacial tension for pSSS **1** and pSTS **2**.

In summary, we have described the synthesis of a novel sulfonium sulfonate monomer and polymer that reinforces the versatility of 4-vinylbenzyl sultone as a PZ precursor. Key differences were found in solution behavior, monomer and polymer stability, and interfacial activity between the new sulfonium sulfonate structures and STS polymers that are closely related structurally, but which possess inverted dipole directionality. Specifically, the significantly increased stability of the newly synthesized monomers and polymers toward nucleophiles, in addition to their extensive solubility over that of STS monomers and polymers, highlights their versatility for use as charge-neutral surfactants. Opportunities arising from these findings may extend to a range of zwitterionic structures wherein dipole inversion holds potential for altering and enhancing polymer properties in solution, at interfaces, and in the solid state as films or bulk structures.

■ EXPERIMENTAL SECTION

Materials. 4-Vinylbenzyl chloride (90%, with 500 ppm *tert*-butylcatechol), 1,3-propane sultone (98%), *n*-butyllithium (2.5 M in hexanes, *n*-BuLi), 4,4′-azobis(4-cyanovaleric acid) (98%, ACVA), 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (97%), sodium thiomethoxide (95%), *n*-butyl methyl sulfide, acetonitrile (anhydrous, 99.8%), 1,2,4-trichlorobenzene (anhydrous, 99%, TCB), and sodium azide (NaN_3) were purchased from Sigma-Aldrich. Sodium iodide (99+%, NaI), 2,2,2-trifluoroethanol (99+%, TFE), and butylated hydroxytoluene (99%, BHT) were purchased from Alfa Aesar. Acetone, diethyl ether (anhydrous), sodium sulfate ($Na_2SO_{4(s)}$), ethyl acetate, tetrahydrofuran, toluene, chloroform, methanol, hexanes, glass slides, and Spectra/Por7 dialysis membranes (3.5 kDa MWCO, pretreated regenerated cellulose tubing) were purchased from Fisher Scientific. Deuterated solvents (chloroform, dimethyl sulfoxide, and methanol) were purchased from Cambridge Isotope Laboratories, Inc. Silica gel (porosity: 60 Å; particle size: 40−75 μm (200 × 400 mesh)) and silica gel TLC plates (glass-backed; thickness: 250 μm, UV254 active) were purchased from Sorbent Technologies. Hermetic aluminum pans for differential scanning calorimetry (DSC) measurements were purchased from TA Instruments.

Tetrahydrofuran and toluene were dried over $Na_{(s)}$-benzophenone ketyl and freshly distilled before use. Prior to performing radical polymerizations, the reaction mixtures in methanol and TFE were degassed via three freeze−pump−thaw cycles. Milli-Q ultrapure water (18.2 MΩ·cm) was used for interfacial tension measurements. Blunt tip 21 gauge needles for pendant-drop tensiometry measurements were purchased from Brostown Technology.

Methods and Characterization. Conventional Schlenk techniques were employed for air- and moisture-sensitive reaction procedures. Gel permeation chromatography (GPC) for molecular weight analysis (M_n, M_w, and $Đ$ (M_w/M_n), using PMMA calibration standards) was conducted with an Agilent 1200 series system equipped with a degasser, RI detector, PFG guard column (8 × 50 mm^2), PFG analytical linear M columns (8 × 300 mm^2, particle size 7 μm, from Polymer Standards Service), and an isocratic pump and eluting with TFE containing 0.02 M sodium trifluoroacetate at a flow rate of 1 mL/min at 40 °C. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker 500 spectrometer, and the chemical shifts in the obtained spectra were referenced to the residual solvent signals where available. Mass spectra were obtained with a Bruker microTOFII mass spectrometer. Pendant-drop tensiometry measurements were conducted with a Data Physics OCA-15plus tensiometer operating in pendant drop mode. Dynamic light scattering (DLS) measurements were conducted on a Malvern Zetasizer Nano ZS at 25 °C. Thermogravimetric analysis (TGA) was performed using a Q50 Thermogravimetric Analyzer from TA Instruments. DSC experiments were conducted on a Q200 differential scanning calorimeter from TA Instruments.

Monomer Synthesis. The sulfothetin (ST)-substituted styrene (i.e., STS) was prepared according to procedures published previously by our group.[14]

Styrenic Sulfonium Sulfonate (SSS) Monomer 4. 4-Vinylbenzyl iodide and 4-vinylbenzyl sultone were prepared according to our previously published synthetic procedures.[13,14] *n*-Butyl methyl sulfide (1.0 g, 9.6 mmol), 4-vinylbenzyl sultone (1.2 g, 5.0 mmol), and BHT (0.22 g, 1.0 mmol) were dissolved in 5 mL of dry acetonitrile. The solution was heated under $N_{2(g)}$ at 75 °C for 4 days. After washing the crude precipitate three times each with acetonitrile and diethyl ether, and removing the solvents under reduced pressure, monomer **4** was isolated as colorless solid in 37% yield (640 mg). ^{1}H NMR (500 MHz, MeOD, δ): 7.44 (d, J = 7.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.74 (dd, J = 17.5, 11.0 Hz, 1H), 5.78 (d, J = 17.5 Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 3.46 ppm (m, 3H), 3.20 (m, 1H), 3.08 (m, 2H), 2.82 (s, 1.5H), 2.69 (m, 2.5H), 2.16 (m, 1H), 2.01 (m, 1H), 1.62 (m, 2H), 1.42 (m, 2H), 0.96 ppm (m, 3H). ^{13}C NMR (500 MHz, MeOD, δ): 139.4, 137.73, 137.68, 130.6, 127.7, 114.0, 61.0, 60.8, 42.4, 41.9, 41.4, 41.0, 37.2, 26.7, 24.9, 24.8, 23.0, 22.7, 22.3, 13.6 ppm. ESI (m/z): 365.12 ($C_{17}H_{26}O_3S_2Na$, calculated: 365.12).

Example Procedures for RAFT Polymerization of STS and SSS. The STS monomer (1.0 g, 3.5 mmol), CTA (70 mg, 0.17 mmol), and ACVA (4.9 mg, 0.02 mmol) were dissolved in TFE (2 mL). The solution was degassed via three freeze−pump−thaw cycles and then stirred at 70 °C for 18 h before terminating the reaction by exposure to air and submerging the reaction flask in $N_{2(l)}$. Dialysis of the crude product against 0.5 M aqueous $NaNO_3$, then water, followed by lyophilization yielded the polymer as a yellow solid (867 mg, 81% yield). Molecular weight data (GPC with TFE as eluent): M_n = 3.9 kDa, $Đ$ = 1.14. In similar fashion, a solution of SSS monomer **4** (200 mg, 0.58 mmol), CTA (11.8 mg, 0.03 mmol), and ACVA (2.7 mg, 0.01 mmol) in methanol was degassed via freeze−pump−thaw cycles and then stirred at 70 °C for 24 h. The reaction was terminated by exposure to air and cooling under $N_{2(l)}$, and the crude product was purified by dialysis against methanol and then water. Lyophilization yielded the polymer as a yellow solid (197 mg, 92% yield). Molecular weight data (GPC with TFE as eluent): M_n = 11.3 kDa, $Đ$ = 1.03.

General Procedure for Nucleophilic Dealkylation. Solutions of STS or SSS monomer at 23 mM were prepared in DMSO-d_6. Twenty equivalents of sodium azide was added, and the solutions were allowed to stand at room temperature (protected from light) for 7 days. ^{1}H NMR spectra were collected at different time intervals to assess the degree of nucleophilic dealkylation, calculated by integration of the styrenic signals in the range of 7.0−7.5 ppm.

Emulsification Experiments. For the SSS polymer, 2 mL of a Nile Red solution in TCB (2 μg/mL concentration) was added to 2 mL of an aqueous polymer solution (10 mg/mL) in four portions, and the resulting mixture was subjected to a vortex for ~1 min after each addition. For the STS polymer, aqueous polymer solutions (10 mg/mL) were prepared in 50 mM sodium nitrate at 70 °C, and 2 mL of the warm polymer solution was combined with 2 mL of TCB that was preheated to ~70 °C. The mixture was vortexed for 1 min and then allowed to cool for 30 min, during which time sedimentation was observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c02359.

Experimental details; Figures S1−S11 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Todd Emrick − *Polymer Science and Engineering Department, Conte Center for Polymer Research, University of Massachusetts, Amherst, Massachusetts 01003, United States;* orcid.org/0000-0003-0460-1797; Email: tsemrick@mail.pse.umass.edu

Authors

Marcel U. Brown − *Polymer Science and Engineering Department, Conte Center for Polymer Research, University of Massachusetts, Amherst, Massachusetts 01003, United States*

Hong-Gyu Seong − *Polymer Science and Engineering Department, Conte Center for Polymer Research, University of Massachusetts, Amherst, Massachusetts 01003, United States*

Thomas P. Russell − *Polymer Science and Engineering Department, Conte Center for Polymer Research, University of Massachusetts, Amherst, Massachusetts 01003, United States;* orcid.org/0000-0001-6384-5826

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.2c02359

Notes

The authors declare no competing financial interest.

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