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Synthesis of Midblock-Sulfonated Triblock Copolymers

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Polymers with ionic groups serve the critical functions of water and ion transport in applications such as fuel cells[1,2] and water treatment membranes[3] and can be engineered to tune the permselectivity of chemical protection barriers.[4] Sulfonation of polymers introduces strongly ionizing groups to generally hydrophobic polymer chains which have significant influence on intermolecular interactions and can create new phases through ion clustering or can affect the self-assembly behavior of multiphase block copolymers. Block copolymers with sulfonate groups confined in one block have shown promise in terms of their good ion conduction properties and are recognized as the next generation of materials in this field. However, there have only been a few topologies studied in terms of the location of the sulfonate groups, and limited studies are available that address how the composition and properties of the unsulfonated blocks influence membrane transport properties.[5−9] Midblock-sulfonated copolymers have been reported using anionic methods.[10−12] To foster increased understanding of these types of materials, a modular, facile synthetic method is desired where the chemical composition of both hydrophobic and hydrophilic blocks can be varied systematically to create a wide range of materials for study.

Researchers have conventionally reported sulfonated triblock copolymers, ABA, where the outer blocks are sulfonated, due to the commercial availability of the precursor thermoplastic elastomers having styrene end blocks or AB diblocks with one end of the diblock sulfonated. Designing midblock-sulfonated triblock architectures has received less attention than other approaches to ion-containing polymers. The design of placing sulfonated blocks in the center of the ABA triblock, where the outer blocks are hydrophobic, is expected to provide more mechanical integrity to the membrane and control of the water swelling of the center sulfonated block as opposed to placing sulfonated blocks at the end of the chains (Figure 1). Additionally, the modular controlled radical polymerization scheme employed in the reported synthesis is amenable to systematically varying the properties of the hydrophobic block while keeping the molecular weight of the hydrophilic block constant for a series of different materials.

Poly(hexyl methacrylate)-*b*-poly(styrene)-*b*-poly(hexyl methacrylate) (PHMA-*b*-PS-*b*-PHMA) and poly(perfluorooctyl methacrylate)-*b*-poly(styrene)-*b*-poly(perfluorooctyl methacrylate) (PFMA-*b*-PS-*b*-PFMA) were first synthesized using atom-transfer radical polymerization (ATRP). The experimental procedure is reported in the Supporting Information in detail. In the first step, difunctional poly(styrene) macroinitiators were prepared via bulk ATRP of styrene in the presence of copper(I) bromide (CuBr), 2,2′-bipyridyl (bpy), and α,α′-dibromo-*p*-xylene at 110 °C for 7 h (Scheme 1 (1)). The resulting isolated poly(styrene) macroinitiator, Br−PS−Br, was dissolved in toluene solution with hexyl methacrylate or dissolved in toluene:trifluorotoluene = 1:1 solution with 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (Scheme 1 (2)) in the presence of CuBr and bpy, and the reactions proceeded at 105 °C for 24 h. ^{1}H NMR (Figure S1 in Supporting Information) and SEC (Figure S3 in Supporting Information) were used to determine the molecular weight of the polystyrene macroinitiator (Br−PS−Br). The number-average molecular weight (M_n) was calculated using the integration of the ^{1}H NMR resonance for the methyne adjacent to the bromide ($-CH_2C\mathit{H}Br$) at 4.3−4.6 ppm to the integration of the ^{1}H NMR resonance for the aromatic protons at 6.0−7.4 ppm. M_n from ^{1}H NMR was in good agreement with M_n from SEC (Table 1), implying that the quantitative end-capping with bromides was achieved. The SEC curve resulted in a monomodel shape (Figure S3 in Supporting Information), and M_w/M_n was in a typical range for ATRP, which confirmed minimized side reactions. The molecular weights of PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA were determined using ^{1}H NMR (Figure S2 in Supporting Information) and SEC. M_n from ^{1}H NMR for PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA were calculated from the integration of the ^{1}H NMR resonance for the ester methylene in hexyl methacrylate ($-C\mathit{H}_2OCO-$) at 3.8−4.1 ppm or in perfluorooctyl methacrylate ($-C\mathit{H}_2OCO-$) at 4.2−4.5 ppm to the integration of the ^{1}H NMR resonance for aromatic protons at 6.0−7.4 ppm with previously determined Br−PS−Br M_n. M_n from ^{1}H NMR for both PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA agreed well with M_n from SEC (Table 1). The monomodel SEC curve and narrow M_w/M_n indicate quantitative difunctionality of Br−PS−Br macroinitiator and formation of triblock copolymers.

PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA were subsequently sulfonated using acetyl sulfate in 1,2-dichloroethane (Scheme 1 (3)). The amount of acetyl sulfate as well as reaction time was varied to achieve different degrees of sulfonation (DS) (Figure S4 in Supporting Information). ^{1}H NMR spectra were used to determine the DS and corresponding IEC of sulfonated PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA. The degree of sulfonation was readily calculated using the shift of the aromatic protons next to the sulfonic acid resonance from 6.8−7.2 to 7.2−7.6 ppm. Increased acetyl sulfate reactant and reaction time resulted in an increase of the degree of sulfonation (Tables S1 and S2 in Supporting Information). PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA with different degrees of sulfonation (0−100%) were successfully prepared. ^{1}H NMR spectra and the good solubility of the polymers after reaction also indicated no evidence of ester hydrolysis of the methacrylates or cross-linking due to the mild sulfonating procedure.[13]

Differential scanning calorimetry (DSC) showed two glass transition temperatures (T_g) for both the PHMA and PFMA series, indicating that phase separation occurred in both cases. The T_g of the sulfonated PS phase increased from 104 to 166 °C as the DS increased from 0% to 29%. At higher DS, the T_g of the sulfonated PS phase was not measurable due to the temperature range (−80 to 210 °C) of the DSC experiment and degradation of sulfonate groups at temperatures greater than 220 °C. This observation of increased T_gs of the sulfonated PS block is consistent with other reports.[14−16] The T_g for PHMA, −6 to 0 °C, or PFMA, 28 to 36 °C, blocks did not change with sulfonation, indicating that the interaction between the blocks was minimal.

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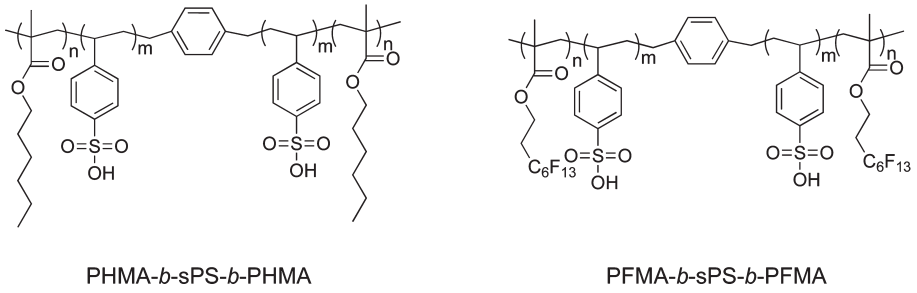

Figure 1. Chemical structures of midblock-sulfonated triblock copolymers with reinforcing hydrophobic end blocks.

Scheme 1. Synthetic Scheme of PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA via ATRP with Subsequent Sulfonation of the Center PS Blocks

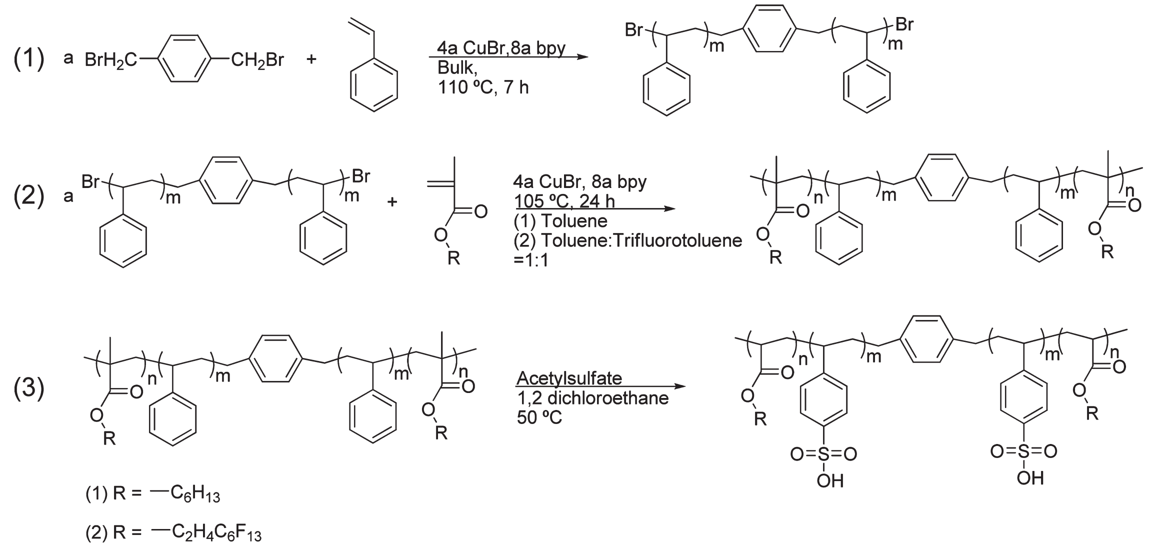

Table 1. Molecular Weights of Br—PS—Br, PHMA-*b*-PS-*b*-PHMA, and PFMA-*b*-PS-*b*-PFMA[a]

	M_n^{NMR}	M_n^{NMR}	M_n^{SEC}	M_w/M_n^{SEC}
Br—PS—Br		69.1	57.3	1.27
PHMA-*b*-PS-*b*-PHMA	58.6-*b*-69.1-*b*-58.6	186.0	171.0	1.17
PFMA-*b*-PS-*b*-PFMA	33.1-*b*-69.1-*b*-33.1	135.0	130.0	1.25

[a] All values given in kg/mol.

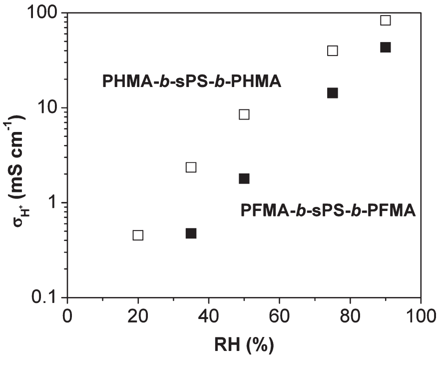

Figure 2. Proton conductivity of fully sulfonated PHMA-*b*-sPS-*b*-PHMA and PFMA-*b*-sPS-*b*-PFMA cast films.

As the relative humidity of the sample environment was raised, the proton conductivity of PHMA- and PFMA-based cast films increased (Figure 2), as is consistent with the trend observed for other proton exchange membranes. Interestingly, the conductivity of the non-fluorinated samples was higher than that of the fluorinated materials. Other studies of sulfonated polymers have shown that the addition of fluorine increases the proton conductivity of the membrane. The presence of fluorine is thought to drive the phase separation of the hydrophilic and hydrophobic components of the polymer, resulting in formation of self-assembled hydrophilic phases containing high concentrations of ions. This evolution of the hydrophilic/hydrophobic nanophase structure tends to increase the ion conductivity of the membrane. Small angle X-ray scattering revealed the formation of more ordered morphologies in PHMA-*b*-sPS-*b*-PHMA than PFMA-*b*-sPS-*b*-PFMA (Figure 3) as evidenced by two reflections in the scattered intensity for the PHMA-*b*-sPS-*b*-PHMA. The higher T_g of the PFMA and the poor solubility of the perfluorooctyl methacrylate blocks during solvent casting lead to a morphology that was more disordered than with the more soluble, flexible PHMA system. Thus, the PHMA outer blocks promoted self-assembly of the sulfonated PS domains and induced high conductivity. The fully sulfonated PS block was identical in both cases, so these data show the clear effect that the hydrophobic blocks can have on the transport properties of the material.

In conclusion, well-defined midblock-sulfonated PHMA-*b*-PS-*b*-PHMA and PFMA-*b*-PS-*b*-PFMA were successfully synthesized using ATRP methodology to prepare the triblock copolymers in two steps using a difunctional initiator with subsequent sulfonation. The modular ATRP scheme used in this work enables a new series of sulfonated polymers to be explored by systematically varying both the sulfonation level of the center block as well as the reinforcing properties of the outer hydrophobic blocks. The proton conductivity of these samples was comparable to other examples of sulfonated polymers. The addition of fluorine to the outer blocks did not enhance the phase development or proton conductivity of these materials due to the poor self-assembly of the fluorinated end blocks compared to more flexible alkyl-containing methacrylate blocks. This study demonstrates that the hydrophobic potions of the

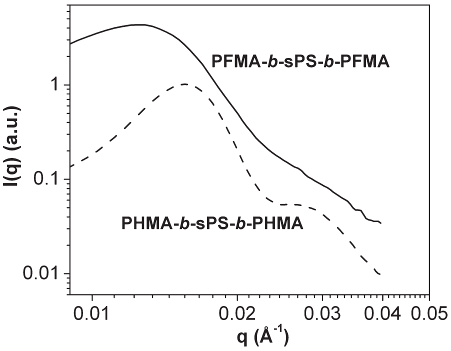

Figure 3. SAXS profiles of fully sulfonated PHMA-*b*-sPS-*b*-PHMA and PFMA-*b*-sPS-*b*-PFMA.

polymer can have a distinct effect on the conductivity properties of the sample. Further investigation of the structure−property relationship of these well-defined midblock-sulfonated triblock copolymers will be reported in subsequent work.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hamrock, S. J.; Yandrasits, M. A. *Polym. Rev.* **2006**, *46*, 219–244.
(2) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587–4611.
(3) Matsuura, T. *Desalination* **2001**, *134*, 47–54.
(4) Chen, H.; Palmese, G. R.; Elabd, Y. A. *Macromolecules* **2007**, *40*, 781–782.
(5) Saito, T.; Mather, B. D.; Costanzo, P. J.; Beyer, F. L.; Long, T. E. *Macromolecules* **2008**, *41*, 3503–3512.
(6) Tsang, E. M. W.; Zhang, Z.; Shi, Z.; Soboleva, T.; Holdcroft, S. *J. Am. Chem. Soc.* **2007**, *129*, 15106–15107.
(7) Lee, H. S.; Badami, A. S.; Roy, A.; McGrath, J. E. *J. Polym. Sci., Part A* **2007**, *45*, 4879–4890.
(8) Park, M. J.; Downing, K. H.; Jackson, A.; Gomez, E. D.; Minor, A. M.; Cookson, D.; Weber, A. Z.; Balsara, N. P. *Nano Lett.* **2007**, *7*, 3547–3552.
(9) Xu, K.; Li, K.; Khanchaitit, P.; Wang, Q. *Chem. Mater.* **2007**, *19*, 5937–5945.
(10) Yang, J. C.; Mays, J. W. *Macromolecules* **2002**, *35*, 3433–3438.
(11) Flood, J.; Willis, C. L.; Bening, R. C.; Dubois, D. Abstracts of Papers, 238th ACS National Meeting **2009**, POLY-222.
(12) Willis, C. L.; Handlin, Jr., D. L.; Trenor, S. R.; Mather, B. D. US patent application 20070021569.
(13) Baigl, D.; Seery, T. A. P.; Williams, C. E. *Macromolecules* **2002**, *35*, 2318–2326.
(14) Mauritz, K. A.; Blackwell, R. I.; Beyer, F. L. *Polymer* **2004**, *45*, 3001–3016.
(15) Shi, Z. Q.; Holdcroft, S. *Macromolecules* **2005**, *38*, 4193–4201.
(16) Yang, S.; Sun, K.; Risen, W. M. *J. Polym. Sci., Part B* **1990**, *28*, 1685–1697.