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Synthesis and Characterization of Sulfonated Poly(arylene ether) Polyimide Multiblock Copolymers for Proton Exchange Membranes

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Abstract: Novel multiblock copolymers, based on segmented sulfonated hydrophilic-hydrophobic blocks, were synthesized and investigated for their application as proton exchange membranes. A series of segmented sulfonated poly(arylene ether sulfone)-*b*-polyimide multiblock copolymers, with various block lengths, were synthesized via the coupling reaction between the terminal amine moieties on the hydrophilic blocks and naphthalene anhydride functionalized hydrophobic blocks. Successful imidization reactions required a mixed solvent system, comprised of NMP and m-cresol, in the presence of catalysts. Proton conductivity measurements revealed that the proton conductivity improved with increasing hydrophilic and hydrophobic block lengths. The morphological structure of the multiblock copolymers was investigated using tapping mode atomic force microscopy (TM-AFM). The AFM images of the copolymers demonstrated well-defined nanophase separated morphologies, with the changes in the block length having a pronounced effect on the phase separated morphologies of the system. The self diffusion coefficient of water, as measured by ^{1}H NMR, provided a better understanding of the transport process. Thus, the block copolymers showed higher values than Nafion, and comparable proton conductivities in liquid water, as well as under partially hydrated conditions at 80 °C. The new materials are strong candidates for use in PEM systems.

Keywords: multiblock copolymer, sulfonated poly(arylene ether), polyimide, proton exchange membrane.

Introduction

The fuel cell is one of the most efficient energy converting devices which transforms chemical energy directly into electrical energy. Its environmentally friendly nature has attracted much attention for making the fuel cell a promising alternative to conventional energy sources. There are several types of fuel cells, but polymer electrolyte fuel cells (PEFCs) are attractive systems. The core component polymer membrane of a PEFC, its proton exchange membrane (PEM), must have several critical characteristics such as high proton conductivity, chemical and mechanical stability, and low fuel permeability.[1] The current state-of-the-art PEMs are perfluorosulfonic acid membranes such as Nafion® manufactured by DuPont. Our research group has been engaged in the past few years in the synthesis and characterization of wholly aromatic biphenol-based partially-disulfonated poly(arylene ether sulfone) (BPSH) random copolymers as potential PEMs.[2] Both Nafion and BPSH show high proton conductivity at fully-hydrated conditions. However proton transport is limited at low hydration levels for the BPSH and other random copolymers. At low hydration levels most of the water is tightly associated with sulfonic groups and has a low diffusion coefficient, leading to the formation of an isolated domain morphology. Thus, although there may be significant concentrations of protons, the transport is limited by the discontinuous morphological structure.

Block copolymers consist of two or more chemically dissimilar backbone segments (i.e. blocks) that are chemically bonded through covalent bonds in the same chain.[3] A block copolymer ionomer can be obtained when one of the blocks is fully or partially modified with ion-containing groups. These ionic groups act as proton conducting sites within the block ionomer while the nonionic component provides dimensional strength and, in the case of DMFCs, may serve as a barrier for methanol transport. Significant attention has been given to polyimide membrane materials for PEFC applications because of their well-known high performance properties such as excellent thermal stability, high mechanical strength, good film forming ability, low permeability, and superior chemical resistance.[4-6] However, five-membered ring polyimides are easily degraded under acidic conditions due to the ease of hydrolysis of imido rings and are not suitable for fuel cell membrane use. Several scientists have

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shown that this problem can be partially addressed by using six-membered ring polyimides which are found to be more stable under acidic conditions.[7-9] However, slow hydrolysis can still be problematic.

Recently, we successfully synthesized multiblock copolymers based on sulfonated poly(arylene ether sulfone) hydrophilic blocks and six-membered ring polyimide hydrophobic blocks. These materials had good mechanical properties and low methanol permeability because of the polyimide segments and also showed good proton conductivity due to the sulfonated poly(arylene ether sulfone) segments. One very significant observation from these block copolymers was morphologies. The multiblock copolymers could exhibit well-defined nanophase morphologies[10] which permitted high proton conductivity even under low relative humidity (RH) conditions.[11,12] They also displayed much better hydrolytic stability than the random copolymers.[5] This paper describes the synthesis and characterization of segmented sulfonated poly(arylene ether sulfone)-*b*-polyimide multiblock copolymers in details.

Experimental

Materials. 4,4-Dichlorodiphenylsulfone (DCDPS; Solvay Advanced Polymers), 4,4-biphenol (BP; Eastman Chemical), and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA; Aldrich) were all obtained in monomer-grade purity and were dried prior to use. Bis[4-(3-aminophenoxy)phenyl]sulfone (*m*-BAPS) was purchased from TCI and recrystallized from ethanol. Fuming sulfuric acid (SO_3 content ~30%) was obtained from Alfa Aesar and used as received. m-Aminophenol (*m*-AP) was received from Aldrich and purified by sublimation. Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (MNP), *m*-cresol and toluene (all from Aldrich) were distilled at reduced pressure before use. Potassium carbonate (Aldrich) was dried in a vacuum oven at 130 °C for 12 h. Benzoic acid and isoquinoline were purchased from TCI and used without further purification.

Sulfonated Monomer Synthesis. 3,3'-Disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS) was prepared by the reaction of 4,4'-dichlorodiphenylsulfone (DCDPS) and fuming sulfuric acid as reported earlier.[13] It was neutralized with a base and purified by recrystallization.

Synthesis of Sulfonated Poly(arylene ethers) of Controlled Molecular Weights. For various molecular weights of sulfonated poly(arylene ether sulfone), different amounts of BP, SDCDPS, and *m*-AP were used. A sample polymerization is as follows: 40.5 mmol BP, 44.0 mmol SDCDPS, 7.1 mmol *m*-AP, and 51 mmol potassium carbonate (15 mol% excess) were dissolved in 70 mL of distilled DMAc and 35 mL of toluene in a three-necked 250 mL flask equipped with a condenser, a Dean Stark trap, a nitrogen outlet, and a mechanical stirrer. The reaction mixture was heated at 150 °C for 4 h with refluxing toluene as the azeotropic agent. The reaction temperature was slowly increased to 180 °C by distillation and removal of toluene and allowed to react for 96 h. The resulting viscous reaction mixture was diluted with DMAc and precipitated in isopropyl alcohol. The coagulated polymer was filtered and dried in a vacuum oven at temperatures up to 100 °C.

Synthesis of Naphthalene Dianhydride-Terminated Polyimides of Controlled Molecular Weights. For various molecular weights of naphthalene dianhydride-based polyimide, different amounts of monomers were also used. A sample polymerization is as follows: 18.5 mmol NDA, 16.3 mmol *m*-BAPS, and 18.5 mmol benzoic acid were dissolved in 108 mL of *m*-cresol in a three-necked 250 mL flask equipped with a condenser, a Dean Stark trap, a nitrogen inlet and a mechanical stirrer. The reaction mixture was heated at 80 °C for 4 h and then at 180 °C for 12 h. Then 18.5 mmol of isoquinoline was added and the reaction was conducted at 180 °C for another 12 h. The obtained dark reddish polymer solution was precipitated in isopropyl alcohol. The coagulated polymer was filtered and purified in a Soxhlet extractor with methanol overnight. The resulting polymer was dried in a vacuum oven at temperatures up to 100 °C.

Synthesis of Sulfonated Segmented Hydrophilic-Hydrophobic Multiblock Copolymers. The multiblock copolymers having various block lengths of hydrophilic and hydrophobic blocks were synthesized utilizing a 1:1 stoichiometry. A sample coupling reaction is as follows: A 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap was charged with 0.6 mmol of hydrophilic oligomer ($\overline{M_n}$=5,000 g/mol), 0.6 mmol hydrophobic oligomer ($\overline{M_n}$=5,000 g/mol), 6 mmol of benzoic acid, and 30 mL of NMP. The reaction mixture was heated at 80 °C for 4 h to obtain a homogeneous solution. Approximately 15 mL of *m*-cresol was slowly added until the mixture just became inhomogeneous. Homogeneous solutions required that extra amounts of NMP be added to the mixture. The final concentration of the reaction solution was 10% (w/v) solid. A coupling reaction was conducted at 180 °C for 12 h and then isoquinoline was added. The reaction was allowed to proceed for another 12 h at 180 °C. The resulting dark reddish polymer solution was precipitated in isopropyl alcohol. The coagulated polymer was filtered and purified in a Soxhlet extractor with methanol overnight. The resulting polymer was dried in a vacuum oven at temperatures up to 100 °C.

Characterization of Chemical Structure and Intrinsic Viscosity. ^{1}H NMR spectroscopy was conducted using a Varian UNITY 400 MHz spectrometer using DMSO-d_6 as a solvent. This permitted both composition analysis and $\overline{M_n}$ via end group analysis. Intrinsic viscosity (IV) measurements were determined in NMP containing 0.05 M LiBr at 25 °C using an Ubbelohde viscometer.

Film Casting and Membrane Acidification. Copolymers in their potassium sulfonate salt form were dissolved in

NMP (10% (w/v)). The solutions were syringe filtered through 0.45 μm Teflon® filters and cast onto clean glass substrates. The transparent solutions were dried under a 120 V, 250 W infrared lamp for 48 h and the resultant films were dried under vacuum at 120 °C for 24 h. Films were lifted from their substrates by immersion in deionized water. All films were converted to their acid form by boiling in 0.5 M sulfuric acid for 2 h, rinsing in deionized (DI) water, and then boiling in DI water for 2 h. Samples were dried under vacuum at 60 °C for 12 h.

Determination of Proton Conductivity and Water Uptake. Proton conductivity was determined using a Solartron (1252A + 1287) Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz - 1 MHz. The cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. The resistance of the film was taken at the frequency that produced the minimum imaginary response. For determining proton conductivity under partially hydrated conditions, membranes were equilibrated in a relative humidity (RH) chamber (ESPEC SH-240) at specified RH and at 80 °C before each measurement. To obtain water uptake values, membranes were dried for 24 h at 100 °C, weighed, and immersed in deionized water at room temperature for 24 h. The wet membranes were blotted dry and immediately weighed again. Water uptake was calculated as the ratio of the difference between wet and dry membrane weight divided by dry membrane weight and expressed as a weight percent.

Determination of Self-Diffusion Coefficient of Water Using Pulse Gradient Stimulated Echo NMR Technique.[12,14] Water self-diffusion coefficients were measured in a Varian Inova 400 MHz (for protons) nuclear magnetic resonance spectrometer with a 60 G/cm gradient diffusion probe.

Atomic Force Microscopy (AFM) Characterization. AFM images were obtained using a Digital Instruments MultiMode scanning probe microscope with a NanoScope IVa controller (Veeco Instruments, Santa Barbara, CA) in tapping mode. A silicon probe (Veeco) with an end radius of <10 nm and a force constant of 5 N/m was used to image samples. Samples were equilibrated at 30% RH for at least 12 h before being imaged immediately at room temperature and approximately 15-20% RH.

Results and Discussion

Synthesis of Controlled Molecular Weight Hydrophilic and Hydrophobic Blocks. The series of controlled molecular weight hydrophilic blocks and hydrophobic blocks were synthesized by stoichiometric imbalance of monomers. Sulfonated poly(arylene ether sulfone) hydrophilic blocks were synthesized via step-condensation process of SDCDPS and BP (Figure 1). *m*-AP was used as an endcapping material. Naphthalene dianhydride based polyimide hydrophobic blocks were also synthesized by a step-condensation reaction (Figure 2). However, to overcome low reactivity of the six-membered ring anhydride toward amines, special reaction conditions were needed. For our research, we conducted the reaction at high temperatures (180-190 °C) in *m*-cresol with benzoic acid and isoquinoline catalysts. This is the only known good reaction scheme to successfully synthesize six-membered ring polyimides. The targeted number average molecular weights for both hydrophilic and hydrophobic blocks were 5,000, 10,000, 15,000, and 20,000 g/mol. NMR end group analysis allowed for a good estimation of $\overline{M_n}$. Integration of selected peaks of ^{1}H NMR spectra and the estimation of intrinsic viscosity values confirmed the control of molecular weights was successful. A summary of the molecular weight characterization is shown in Table I.

Synthesis of Hydrophilic - Hydrophobic Segmented Multiblock Copolymers in Mixed Solvents System. A series of multiblock copolymers having various hydrophilic and hydrophobic block lengths were synthesized (Figure 3). Coupling was achieved by the reaction between primary amine moieties on hydrophilic blocks and anhydride moieties

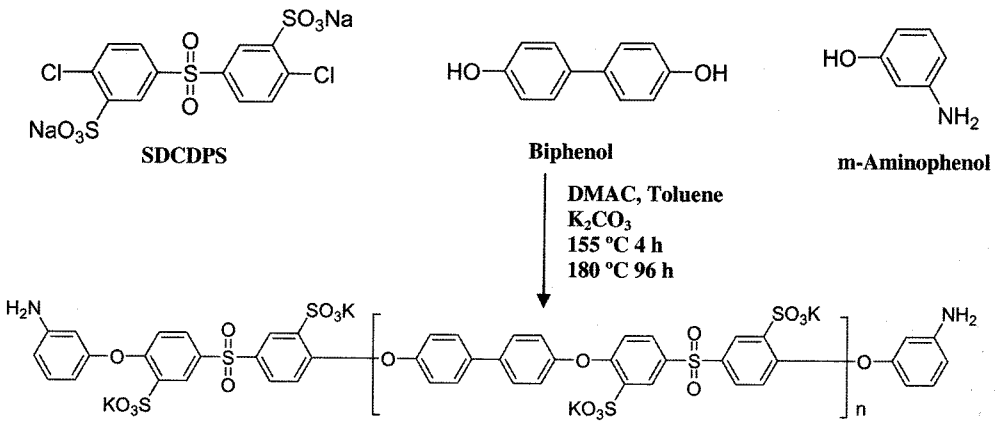

Figure 1. Synthesis of amine-terminated sulfonated poly(arylene ether sulfone) hydrophilic oligomer.

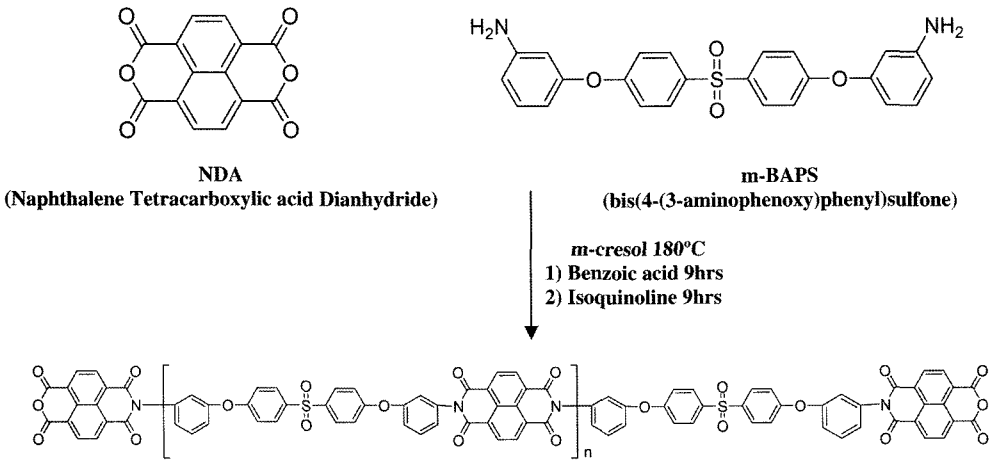

Figure 2. Synthesis of anhydride-terminated naphthalene dianhydride based polyimide hydrophobic oligomer.

Table I. A Summary of the Molecular Weight Characterization

Target $\overline{M_n}$ (g/mol)	Hydrophilic Blocks		Hydrophobic Blocks	
	$\overline{M_n}$ by NMR (g/mol)	IV (dL/g)	$\overline{M_n}$ by NMR (g/mol)	IV (dL/g)
5,000	5,500	0.18	5,600	0.16
10,000	9,800	0.28	10,500	0.22
15,000	14,500	0.30	17,200	0.34
20,000	20,100	0.47	23,800	0.41

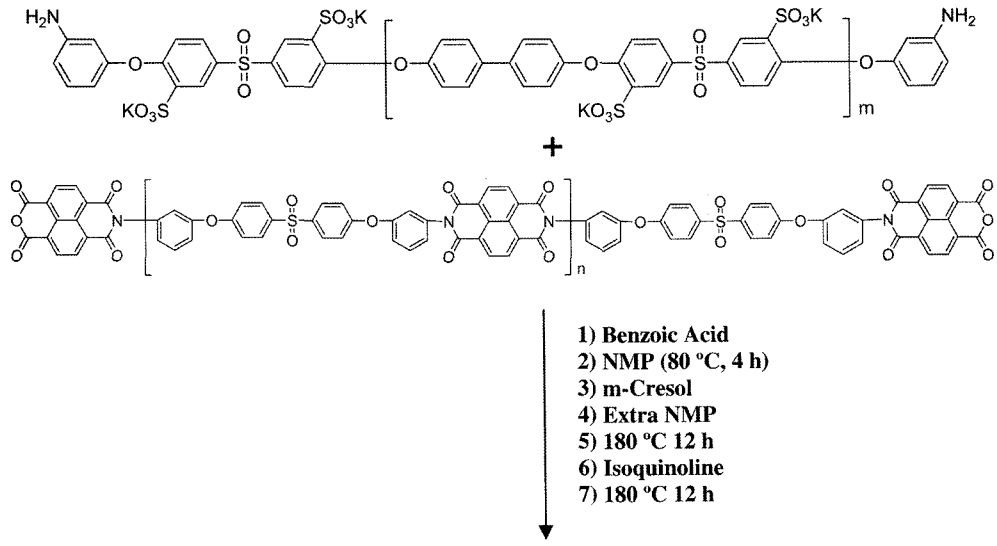

Figure 3. Synthesis of sulfonated segmented poly(arylene ether sulfone)-*b*-polyimide multiblock copolymer.

on hydrophobic blocks. Poor solubility of hydrophilic blocks in *m*-cresol required use of a mixed solvent system which consists of NMP and *m*-cresol. For this particular mixed solvent system, NMP acts as the common solvent for both hydrophilic and hydrophobic oligomers and provides a homogeneous reaction condition while *m*-cresol promotes a successful imidization reaction.

Characterization of the Multiblock Copolymers as PEM Materials. Several properties of the multiblock copolymers were examined to determine their potential for fuel cell

Table II. Characterization Summary of Multiblock Copolymers

	IEC[a] (meq/g)	IV (dL/g)	Water Uptake (%)	Proton Conductivity[b] (S/cm)	Diffusion Coefficient of Water[c] (10^{-6} cm^2/s)
Nafion 112	0.91	-	24	0.090	4.2
BPSH-5-PI-5	1.65	0.50	59	0.080	4.7
BPSH-10-PI-10	1.57	0.63	67	0.085	7.5
BPSH-15-PI-15	1.55	0.68	85	0.100	11.0
BPSH-20-PI-20	1.22	1.20	57	0.100	-

[a]Theoretical values for the multiblock copolymers are 1.65 meq/g. [b]Measured in water at 30 °C. [c]Measured at 25 °C.

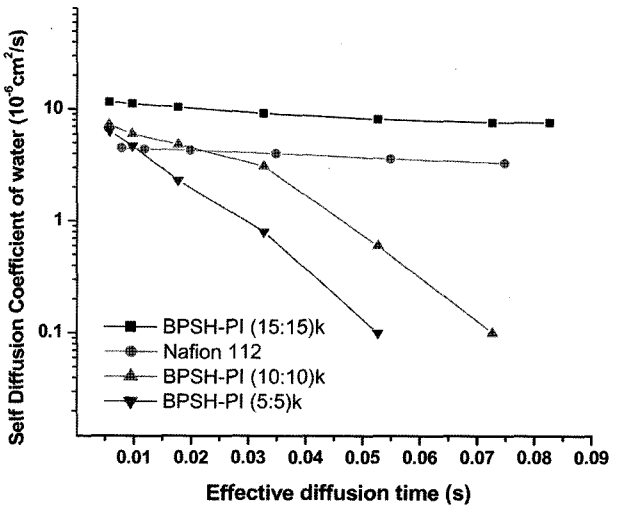

Figure 4. Self-diffusion coefficient of water scales with morphology.

applications. Table II shows the summary of ion exchange capacity (IEC), water uptake, proton conductivity, and self-diffusion coefficients of water for the multiblock copolymers. Though all copolymers have similar IEC values, the water uptake and proton conductivity values strongly depended on both hydrophilic and hydrophobic block lengths. The water uptake and proton conductivity were found to increase with increasing block lengths for the multiblocks having similar IEC.

The self-diffusion coefficient of water increased with increasing block lengths for the samples with similar IECs. The self-diffusion coefficient of water can be related to the extent of morphological barrier of water and proton transport.[12] This can be well understood if one can measure the diffusion coefficient of water as a function of diffusion time (Figure 4). For the BPSH-5-PI-5 sample, the diffusion coefficient value decreased with diffusion time. This indicates the presence of a morphological barrier to the translational motion of water. However with increasing block lengths, particularly for BPSH-15-PI-15, the self-diffusion coefficient of water is independent of diffusion time. The morphological barrier for the transport is expected to be very low. Similar dependency was also seen for Nafion.

This is in support to the AFM images (Figure 5) which show the formation of cocontinuous phase-separated morphological structure with increasing block lengths. Thus establishing connectivity between the hydrophilic domains decreases the morphological barrier for transport.

Figure 6 shows a plot of proton conductivity as a function of relative humidity at 80 °C for Nafion and the multiblock copolymers with varying block lengths. At higher hydration levels, proton transport is facilitated through water assisted percolated hydrophilic domains. Under partially hydrated conditions, however, there is an insufficient amount of water to develop these domains, resulting in an increase in the morphological barrier for proton transport. Consequently, if one can develop cocontinuous morphological structure, proton transport can be achieved under partially hydrated con-

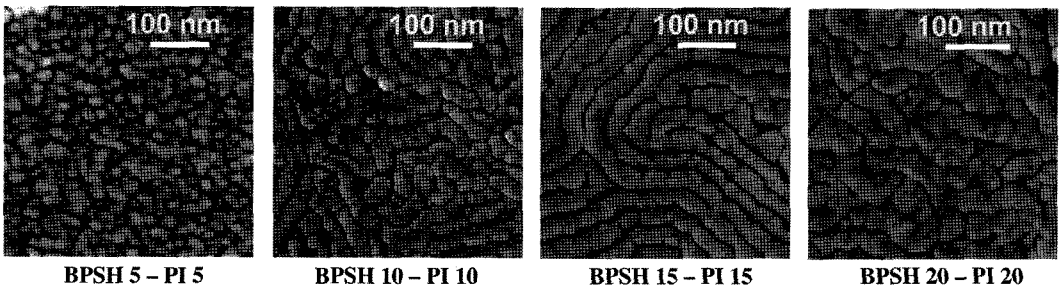

Figure 5. AFM phase images of BPSH-x-PI-x multiblock copolymer series. Setpoint ratios = 0.98, 0.90, 0.98, 0.98.

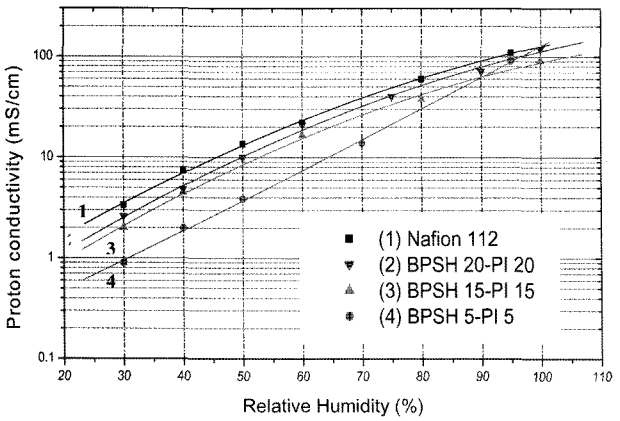

Figure 6. Proton conductivity as function of relative humidity at 80 °C.

ditions. The diffusion coefficient and AFM results indicate the formation of cocontinuous hydrophobic and hydrophilic morphological structure with increasing block lengths. This is reflected in the behavior of proton conductivity under partially hydrated conditions as a function of block lengths, in which proton conductivity is lowest for the less nano-phase developed BPSH-5-PI-5 multiblock copolymer. The value increases with increasing block lengths. The increased connectivity between the hydrophilic domains at higher block lengths facilitates proton transport under low RH and is comparable to that of Nafion.

Hydrolytic Stability. The hydrolytic stability of these multi-block copolymer membranes was tested by methods previously published elsewhere.[15] The acid-form membranes were placed in deionized water at 80 °C until they became brittle. The loss of mechanical strength was determined when the membranes broke after being slightly bent. In addition to the mechanical property test, the IV and IEC value of the copolymers were recorded before and after the hydrolytic stability test. All of the multiblock copolymers were still flexible after a 1,000 h test but their IV and IEC values displayed a slight decrease after the test (Table III). Based on the data, we may conclude that random chain scission reactions due to acid catalyzed hydrolysis occurred during the test but the extent of the degradation on the copolymers were limited due to the phase separated morphology in the membranes. This was much better than the random system.[5]

Conclusions

The controlled molecular weight hydrophilic and hydrophobic blocks with primary amine and anhydride end groups were successfully synthesized. A series of segmented sulfonated poly(arylene ether)-*b*-polyimide multiblock copolymers having various block lengths was synthesized via coupling reactions between amine moieties on hydrophilic blocks and anhydride moieties on hydrophobic blocks. Successful imidization reactions require an NMP + *m*-cresol mixed solvent system and catalysts were essential. All copolymers give flexible and resilient films when cast from a NMP solution. The transport properties of the BPSH-PI multiblock copolymers were studied over a range of different block lengths and IECs. Under fully hydrated conditions all the multiblock copolymers showed similar proton conductivity. However under partially hydrated conditions the proton conductivity was found to be a function of block lengths. This was attributed to the decreasing morphological barrier to the transport with increasing block length, as studied from diffusion coefficient measurements and AFM images. Thus in multiblock copolymers, the hydrophilic domains provide a pathway for water and proton transport whereas the hydrophobic domains maintains the mechanical and hydrolytic stability.

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Table III. A Summary of Hydrolytic Stability Test of Multiblock Copolymers

	Original IV (dL/g)	IV after Test (dL/g)	Original IEC (meq/g)	IEC after Test (meq/g)	Mechanical Properties
BPSH 5-PI 5	0.49	0.40	1.69	1.60	Flexible @ 1,000 h
BPSH 10-PI 10	0.71	0.6	1.57	1.39	Flexible @ 1,000 h
BPSH 15-PI 15	0.67	0.51	1.55	1.30	Flexible @ 1,000 h
BPSH 20-PI 20	0.74	0.58	1.22	0.90	Flexible @ 1,000 h

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