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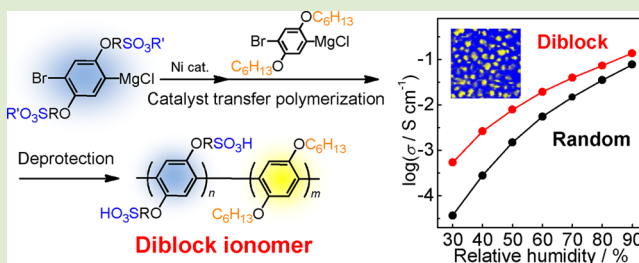
Synthesis of Hydrophilic–Hydrophobic Block Copolymer Ionomers Based on Polyphenylenes

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S Supporting Information

ABSTRACT: Hydrophilic–hydrophobic block copolymer ionomers based on polyphenylenes with controlled the block lengths were synthesized for the first time by a catalyst-transfer polycondensation of a dibromo phenylene derivative having a neopentyl ester protected sulfonic acid group, followed by the polycondensation of hydrophobic dibromo hexyloxybenzene. The diblock copolymer ionomers were obtained by the removal of neopentyl groups, resulting in clear phase separation dependent on the block lengths. The well-developed microphase separation provided controlled water uptake and sufficiently high proton conductivity, especially at low relative humidity conditions. The fine block copolymerization by using catalyst transfer polycondensation is a promising strategy for the development of hydrocarbon ionomers having well-defined ordered structures with reasonable proton conductivity for fuel cell applications.



Polymer electrolyte membranes (PEMs) are one of the most important components of polymer electrolyte fuel cell (PEFC) systems, which are considered to be a promising alternative power generation system for vehicles and stationary use. One of the most promising routes toward the preparation of high-performance proton exchange membranes involves the use of aromatic hydrocarbon units for polymer backbones.^{1–5} Because of the less pronounced ionic/nonionic separation for the hydrocarbon materials suggested by Kreuer,⁶ sulfonated aromatic polymers generally require a much higher ion-exchange capacity (IEC) to obtain a suitable conductivity, resulting in excess water uptake and a drastic loss of mechanical properties. To overcome these drawbacks, block copolymerization of sulfonated aromatic units with hydrophobic aromatic units, leading to an introduction of higher-order structures with phase separated morphology, has been extensively studied.^{7–13} These block copolymers have generally been synthesized by polycondensation; however, a lack of control of block lengths and broad molecular weight distributions leads to deficient phase separation.

Yokozawa et al. and McCullough et al. have independently reported a controlled polycondensation method, called *catalyst-transfer polycondensation*, which functions via a chain-growth polymerization mechanism.^{14,15} For example, chain-growth polymerization of a Grignard thiophene monomer (2-bromo-5-chloromagnesio-3-hexylthiophene) with a Ni(dppp)Cl₂ (dppp = 1,3-bis(diphenylphosphino)propane) catalyst yielded head-to-tail poly(3-hexylthiophene)s with narrow polydispersities and molecular weights that are controlled by the feed ratio of the monomer to the Ni catalyst. To date, there have been many reports relating to the synthesis of various π -conjugated polymers, such as polythiophene,^{16–22} polyphenylene,²³ polypyrrole,²⁴ and polyfluorene^{25,26} derivatives, via

catalyst-transfer polycondensation. In addition, various diblock copolymers composed of π -conjugated polymers have also been synthesized.^{27,28} However, the reports are generally limited to π -conjugated polymers with electron-donating substituents. There are only a few reports relating to the synthesis of polyphenylenes with the exception of alkoxy-substituted polyphenylenes.^{29,30} Among the aromatic hydrocarbon electrolytes, sulfonated polyphenylenes have been considered as potential membrane materials because the rigid rod backbones of polyphenylenes not only provide a sufficient mechanical properties but also induce the segregation into hydrophilic and hydrophobic domains.^{31,32} In this study, we demonstrate that Ni-catalyzed polycondensation of 1,4-dibromo-2,5-di[4-(2,2-dimethylpropoxysulfonyl)phenyl]butoxybenzene (**1**) proceeds by a chain-transfer mechanism to afford a polyphenylene derivative having acid functionalized groups with a narrow polydispersity. Furthermore, we report the first synthesis and fundamental properties of hydrophilic–hydrophobic polyphenylene-based block copolymer ionomers with well-defined block lengths and distributions.

For this study, a hydrophilic monomer (**1**) and hydrophobic monomer, 1,4-dibromo-2,5-dihexyloxybenzene (**2**), were selected. Treatment of **1** with 0.9 equiv of ⁱPrMgCl·LiCl in tetrahydrofuran (THF) at 40 °C for 5 h gave a Grignard-type monomer (**G1**) via a magnesium–bromine exchange reaction. In general, the reaction of the monomer with 1.0 equiv of ⁱPrMgCl·LiCl is carried out at room temperature, and as a consequence, unreacted ⁱPrMgCl·LiCl stops the polymerization

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by end-capping the propagating species. It causes the formation of oligomeric byproducts, which is a disadvantage of the synthesis of block copolymers. To reduce the amount of unreacted $^i\text{PrMgCl}\cdot\text{LiCl}$, the Grignard reaction was performed with 0.9 equiv of $^i\text{PrMgCl}\cdot\text{LiCl}$ at 40 °C. Polymerization was carried out by an addition of $\text{Ni}(\text{dppe})\text{Cl}_2$ (dppe = 1,2-bis(diphenylphosphino) ethane) to the reaction mixture to provide **P1** (Scheme 1). As shown in Figure 1, when

Scheme 1. Synthesis of P1 and P2

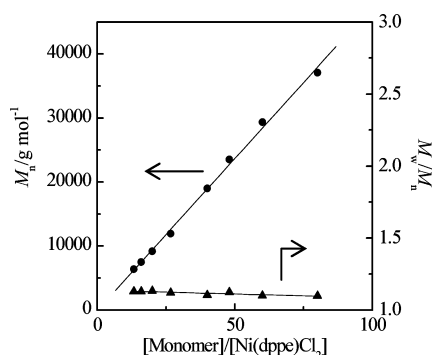
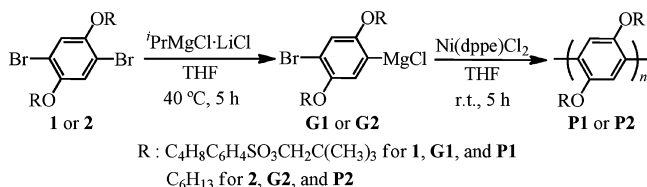
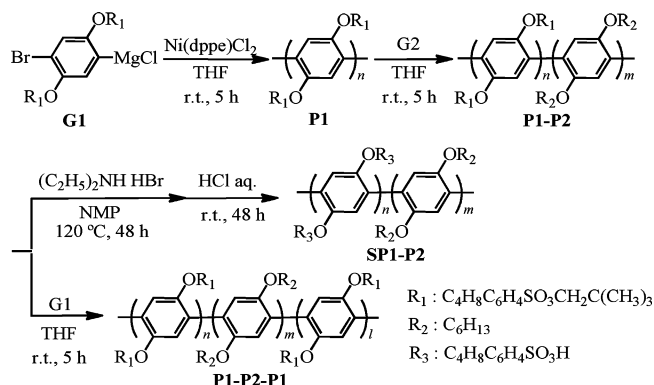


Figure 1. M_n and M_w/M_n values of **P1** obtained with **G1** and $\text{Ni}(\text{dppe})\text{Cl}_2$ in THF, as a function of the feed ratio of monomer to $\text{Ni}(\text{dppe})\text{Cl}_2$ ($[\text{G1}]_0 = 45.5 \text{ mM}$, $[\text{Ni}(\text{dppe})\text{Cl}_2]_0 = 2.30\text{--}17.0 \text{ mM}$).

polymerization of **G1** was carried out with various feed ratios of **G1** to $\text{Ni}(\text{dppe})\text{Cl}_2$, a linear relationship between the M_n value of **P1** and the feed ratio was observed. Here, the molecular weights were determined by gel permeation chromatography (GPC) with THF eluent. After 5 h, M_n of **P1** reached 70% of theoretical value. The M_w/M_n ratios were less than 1.13 under all conditions. The crude products contained a small amount of the unreacted monomer that was easily washed out with acetone.

The chain-growth nature of this polymerization was examined by means of another monomer addition experiments. The monomer **2**, which had previously been successfully applied to the catalyst-transfer polycondensation method, was selected as a typical hydrophobic monomer, and hydrophilic–hydrophobic polyphenylene-based block copolymers were synthesized via successive catalyst-transfer polycondensation of **P1** with this hydrophobic monomer (Scheme 2). After **1** was polymerized in the presence of 2.5 mol % of $\text{Ni}(\text{dppe})\text{Cl}_2$ in THF at room temperature for 5 h to afford well-defined **P1** ($M_n = 14\,900$, $M_w/M_n = 1.09$), 1.0 equiv of **G2** was added to the reaction mixture, and the second polymerization was conducted at room temperature for 5 h to afford well-defined diblock copolymer **P1–P2** ($M_n = 25\,900$, $M_w/M_n = 1.11$). This result indicates that the added monomer **G2** was polymerized from the propagating end of prepolymer **P1** owing to the chain-growth nature of the polymerization and that the diblock copolymers composed of hydrophilic polymers having acid functionalized groups could be synthesized. It was also possible

Scheme 2. Synthesis of SP1–P2 and P1–P2–P1



to obtain triblock copolymer, **P1–P2–P1** ($M_n = 34\,900$, $M_w/M_n = 1.15$), by means of a further addition of 1.0 equiv of **G1** to **P1–P2** at room temperature for 5 h. From the first polymerization to the second one and from the second polymerization to the third one, the GPC elution curves shifted toward the higher-molecular weight region, while retaining a narrow molecular weight distribution (Figure 2a). When

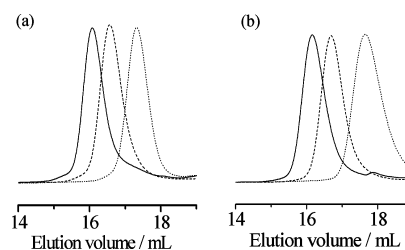


Figure 2. GPC profiles of the polymers obtained by triblock copolymerization. (a) **P1** as a prepolymer (dotted line, $M_n = 14\,900$, $M_w/M_n = 1.09$), **P1–P2** (broken line, $M_n = 25\,900$, $M_w/M_n = 1.11$), and **P1–P2–P1** (solid line, $M_n = 34\,900$, $M_w/M_n = 1.15$). (b) **P2** as a prepolymer (dotted line, $M_n = 9500$, $M_w/M_n = 1.19$), **P2–P1** (broken line, $M_n = 22\,600$, $M_w/M_n = 1.15$), and **P2–P1–P2** (solid line, $M_n = 35\,200$, $M_w/M_n = 1.10$).

diblock copolymers composed of different π -conjugated polymers are synthesized via catalyst-transfer polycondensation, the polymerization order is important because the Ni catalyst-transfer reaction, referred to as *ring-walking*,³³ occurs more readily for π -conjugated polymers having stronger electron-donating ability than for those having electron-accepting properties.¹⁰ In this study, we also tried to synthesize triblock copolymers, **P2–P1–P2**, reversing the polymerization order of **P1–P2–P1**. A diblock copolymer ($M_n = 22\,600$, $M_w/M_n = 1.15$) and a triblock copolymer ($M_n = 35\,200$, $M_w/M_n = 1.10$) were obtained by successive addition of **1** and **2** to prepolymer **P2** ($M_n = 9500$, $M_w/M_n = 1.19$) in the presence of 2.5 mol % of $\text{Ni}(\text{dppe})\text{Cl}_2$ in THF. As shown in Figure 2b, the GPC elution curves also shifted toward the higher-molecular weight region going from the first polymerization to the second and third, while retaining a narrow molecular weight distribution as achieved for the synthesis of **P1–P2–P1**. The successful synthesis of triblock copolymers with good control of the molecular weights of each block suggested that multiblock copolymers composed of hydrophobic and hydrophilic components could be synthesized.

To evaluate the application of these polymers to proton conducting membranes, we prepared three types of diblock

copolymers, **P1–P2**, with relatively high molecular weights that were sufficient to form homogeneous free-standing films. Table 1 shows the molecular weights of **P1–P2**(*n–m*) having

Table 1. Molecular Weights and IECs of Diblock Polymers, P1–P2

	M_n^a	M_w/M_n^a	IEC ^b	IEC ^c	λ (H ₂ O/SO ₃ H) ^d
P1(28)	17800	1.07			
P1–P2(28–262)	68100	1.32	0.96	0.84	2.1
P1(44)	27700	1.07			
P1–P2(44–178)	66300	1.19	1.69	1.77	3.3
P1(74)	43600	1.14			
P1–P2(74–164)	82600	1.15	2.42	2.20	5.8

^aEstimated by GPC based on polystyrene standards (eluent: THF).

^bThe ion exchange capacity (IEC, meq g^{−1}) was calculated from elemental analyses after deprotection of neopentyl groups. ^cIEC determined by back-titration. ^dNumber of absorbed water molecules per a sulfonic acid group of polymers at 80 °C, 90% RH.

different block lengths. The *n* and *m* refer to the number of repeating hydrophilic **P1** and hydrophobic **P2** units, which were estimated by GPC data. A desired M_n up to about 82 600, which was sufficient for film formation, was obtained, and M_w/M_n ratios were all less than 1.19 with the exception of **P1–P2**(28–262). The neopentyl protecting group used in the synthesis of these diblock copolymers was cleaved with an *N*-methylpyrrolidone solution of diethylamine hydrobromide at 120 °C for 48 h to obtain the acid form of the copolymer (**SP1–P2**; Scheme 2). The deprotection was confirmed by ¹H NMR and Fourier transform infrared (FT-IR), and the IEC, determined by elemental analysis, was in the range of 0.96–2.42 meq g^{−1}, which was comparable to the IEC determined by back-titration (Table 1). A number of absorbed water molecules per a sulfonic acid group (λ : [H₂O]/[SO₃H]) at 80 °C, 90% RH of these polymers was about 2–6, which was lower than that (λ = 6.5, IEC = 2.81 meq g^{−1}) of similar sulfonated poly(4-phenoxybenzoyl-1,4-phenylene).³⁴ Figure 3 shows the AFM phase and current images of **SP1–P2** membranes taken at 20 °C and 50% RH. A clear phase separation was observed for all of the films. In the current images, the dark blue regions represent the proton conducting domains, and the bright regions represent the nonconducting domains. **SP1–P2** (74–164) membranes showed sphere-like hydrophobic aggregates surrounded by connected hydrophilic conducting domains. In contrast, larger hydrophobic aggregates and connected hydrophilic domains were observed for **SP1–P2**(28–262) and (44–178). Figure 4 shows the proton conductivity of the **SP1–P2** membranes at 80 °C as a function of relative humidity (RH). Here, a random copolymer, **SP1-*r*-P2**, with M_n = 79 100, M_w/M_n = 1.32, and IEC^b = 2.46 meq g^{−1}, was also investigated for a comparison. For diblock copolymers, proton conductivity increased with increasing RH and almost depended on the IEC except for **SP1–P2**(28–262) and (44–178) at 30–50% RH. The proton conductivity of **SP1–P2**(74–164) was much higher than that of **SP1-*r*-P2** especially at low RH regions although their IEC values are almost the same value. In addition, **SP1–P2**(28–262) (0.96 meq g^{−1}) having much lower IEC than **SP1-*r*-P2** showed higher conductivity than **SP1-*r*-P2** at low RH. These results indicate that the microphase separation induced by the precise control of diblock lengths and compositions successfully developed the

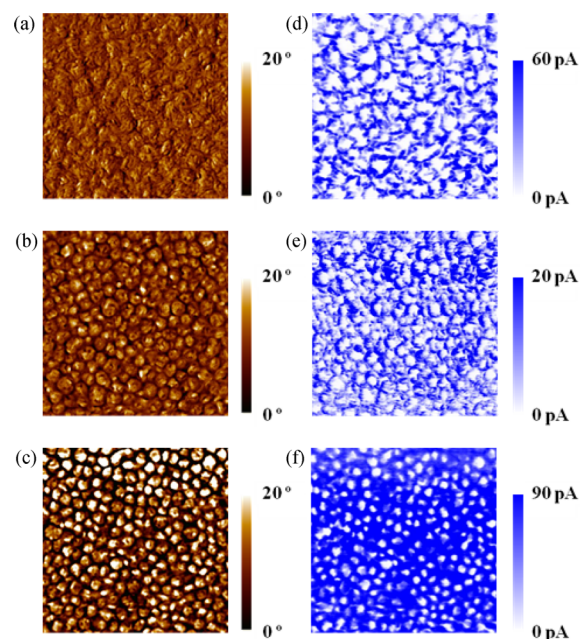


Figure 3. AFM phase (a–c) and current (d–f) images (1 × 1 μm) of polymer membranes: (a, d) **SP1–P2**(28–262), (b, e) **SP1–P2**(44–178), and (c, f) **SP1–P2**(74–164) at 20 °C and 50% RH.

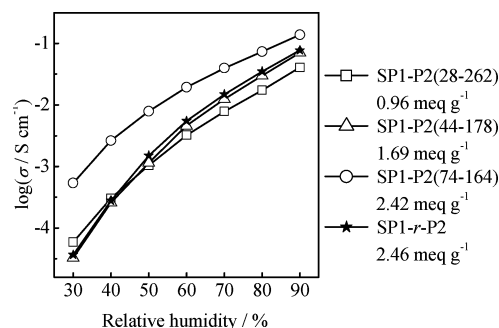


Figure 4. Proton conductivity for **SP1–P2** and **SP1-*r*-P2** membranes at 80 °C and 30–90% RH.

favorable proton transport paths, which provide high proton conductivity with less λ values.

In conclusion, we have demonstrated that catalyst-transfer polymerization is applicable to the synthesis of well-defined polyphenylene block copolymers having acid functionalized groups. These diblock and triblock copolymers composed of the hydrophobic and hydrophilic polyphenylene derivatives having controlled molecular weights could be synthesized. The fine block copolymerization by using catalyst-transfer polycondensation is not only a promising strategy for the development of high proton conducting membranes at low RH conditions but also provides model ionomers to investigate the relationships between highly ordered structures and properties. Further these investigations are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Polymer synthesis and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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