Synthesis and Properties of Novel Sulfonated Arylene Ether/Fluorinated Alkane Copolymers

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ABSTRACT: The polymerization of 2,3,5,6-tetraphenylhydroquinone (or 2,2′,3,3′,5,5′-hexaphenyl-4,4′-dihydroxybiphenyl) with α,ω-tetrahydroperfluoroalkanediol and decafluorobiphenyl was carried out to synthesize a series of copolymers **III** (M_w = 49 100−80 900). The copolymers **III** are composed of arylene ether (10−30 mol %) and fluorinated alkane (90−70 mol %) moieties. The reaction of **III** with chlorosulfonic acid gave sulfonated polymers **IV**, which are soluble in polar organic solvents and form flexible and transparent films by casting from solution. The polymers **IV** have glass transition temperatures of 109−155 °C and decomposition temperatures of ca. 300 °C. The hydrated polymers show protonic conductivity (3.4×10^{-3} S cm^{-1}), which does not decrease at temperatures up to 170 °C.

Introduction

Polymer electrolytes bearing strong acid groups have been developed and utilized mainly as cation-exchange resins for more than half a century.[1] Since protons can migrate through their membranes under wet conditions in an electric field, these polymers are attracting increased interest as solid electrolytes for fuel cells especially for transportation and portable applications to provide high power density.[2] Among the many kinds of proton conducting polymer electrolytes that have been made, poly(perfluoroalkylsulfonic acid) (Nafion) produced by Du Pont, is most preferable from the standpoint of chemical, thermal stability, and physical and conducting properties.[3] However its high cost is a serious drawback for large-scale practical use.

Much effort has been expended in the development of new proton conducting polymers. The major approach has been the attachment of sulfonic and/or phosphonic acid groups onto highly stable aromatic polymers, such as poly(ether ether ketone) (PEEK),[4] polysulfone (PSF),[5] and poly(phenylene sulfide).[6] Although these polymers are very stable structural materials, fuel cells made from these membranes generally fail in a relatively short time, presumably by a combination of hydrolytic and oxidative degradation.[7] Hydrolysis of ether and sulfide linkages would be expected to be enhanced by the introduction of sulfonic acid groups which would contribute to the lower stability since the electron withdrawing groups would increase the ease of nucleophilic displacement reactions. The polymers have much higher glass transition temperature (T_g > 200 °C)[8] than that of Nafion (115 °C), due to the stiffness of the main chain. The high T_g's result in low mobility of ions through the membranes.

To produce a polymer electrolyte to meet the requirements for fuel cells, we have designed aromatic copolymers containing sulfonated tetraphenylphenylene (or hexaphenylbiphenylene), fluorinated alkane and perfluorobiphenylene moieties. The sulfonic acid substituents attached onto the pendant phenyl groups would be expected to be more stable than those on main chains. The other component of the copolymers, fluorinated alkanes, makes them soluble in organic solvents. It is possible to tailor the ionic density (or equivalent weight per acid group) and thermal transitions by changing the copolymer ratio. The synthesis, characterization, thermal, and proton conducting properties of these copolymers are described.

Experimental Section

Materials. 2,3,5,6-Tetraphenylhydroquinone[9] and 2,2′,3,3′,5,5′-hexaphenyl-4,4′-dihydroxybiphenyl[10] were synthesized as described in the literature. Commercial reagents 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-1,10-decanediol, decafluorobiphenyl, and chlorosulfonic acid were purchased from Aldrich Co., Inc., and used as received. Solvents were distilled prior to use. Nafion NR50 (beads, 10−35 mesh, EW 1250, Aldrich Co., Inc.) was used for thermal analysis, and a 5 wt % solution of Nafion 117 in a mixture of lower aliphatic alcohols and water (EW 1100, Aldrich Co., Inc.) was used for proton conductivity measurements.

Measurement. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Mercury 300 or 400 spectrometer using $CDCl_3$, acetone-d_6, or DMSO-d_6 as a solvent and tetramethylsilane (^{1}H and ^{13}C) or CF_3COOH (^{19}F) as a reference. IR spectra were obtained as a KBr pellet on a Jasco FT/IR-5300 spectrometer. Matrix assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectra were recorded on a Kratos Kompact MALDI−III TOF mass spectrometer with the instrument set in the positive reflection mode. Lithium bromide and dithranol were used as cationization reagent and matrix, respectively. Thermal analysis was performed by thermogravimetry (TG) using a Seiko TG/DTA 220 instrument and by differential scanning calorimetry (DSC) using a Seiko DSC 220 instrument at a heating rate of 20 °C/min under nitrogen. Molecular weight measurements were done by gel permeation chromatography (GPC) using a Waters 510 system equipped with a UV detector set at 254 nm. Chloroform or THF was used as eluent. Calibration was made with polystyrene standards.

Surface conductivity measurements were conducted on hydrated film samples using a HP 4194A impedance/gain-phase analyzer over the frequency range from 100 Hz to 40

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MHz. The cell assembly was comprised of a 15 mm diameter, 40 μm thickness film cast on a gold electrode. One drop of methanol was applied onto the surface of a film, which was then soaked in double-distilled deionized water for 30 min. The hydrated sample was sandwiched with another gold electrode. Light pressure was applied on the electrodes by means of a clamp, which was tightened until a constant meter reading was obtained to ensure the best interfacial contact. The ac protonic conductivity was calculated from the complex impedance plot with a computer curve-fitting technique.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluoro-1,10-bis(trimethylsilyloxy)decane [1b (R = TMS)]. To a solution of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-1,10-decanediol (4 mmol) in 10 mL of THF was added hexamethyldisilazane (8 mmol) dropwise over a period of 10 min under nitrogen. The mixture was heated at reflux for 6 h. The colorless solution was added to 100 mL of $CHCl_3$ and washed with three portions of 200 mL of water. The organic layer was dried over $MgSO_4$ and evaporated to dryness to obtain a colorless oil of pure product. Yield: 92%. ^{1}H NMR ($CDCl_3$): δ 0.16−0.18 (m, 18H), 4.05 (t, J = 3.72 Hz, 4H).

1,4-Bis(propylcarbamoyl)-2,3,5,6-tetraphenylbenzene [2a (R = PrNHCO)]. A solution of 2,3,5,6-tetraphenylhydroquinone (0.03 mol), *n*-propylisocyanate (15 mL), and triethylamine (2 mL) in 300 mL of toluene was heated at 110 °C for 10 h. The mixture was evaporated to dryness to obtain a crude product. Crystallization twice from CH_2Cl_2/hexane gave pure 1,4-bis(propylcarbamoyl)-2,3,5,6-tetraphenylbenzene. Yield: 86%. MALDI−TOF−MS: 590.9 (M + Li^+). ^{1}H NMR ($CDCl_3$): δ 0.60 (t, J = 7.43 Hz, 6H), 1.05−1.11 (m, 4H), 2.73−2.78 (m, 4H), 4.33 (t, J = 5.86 Hz, 2H), 7.11 (d, J = 2.35 Hz, 8H), 7.13−7.27 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 10.9, 22.7, 43.0, 126.6, 127.3, 130.6, 136.0, 136.1, 143.9, 154.0. Mp: 299 °C dec.

2,3,5,6-Tetraphenylbenzene-1,4-bis(methanesulfonate) [2a (R = Ms)]. To a solution of 2,3,5,6-tetraphenylhydroquinone (3.4 mmol) and triethylamine (17 mmol) in 50 mL of THF was added methanesulfonyl chloride (20 mmol) in 5 mL of THF dropwise over a period of 10 min under nitrogen. The mixture was stirred at 25 °C for 20 h. The white suspension was poured into 300 mL of water. The crude product, a white powder, was crystallized from $CHCl_3$/ethanol to obtain pure 2,3,5,6-tetraphenylbenzene-1,4-bis(methanesulfonate). Yield: 80%. MALDI−TOF−MS: 577.8 (M + Li^+). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 6H), 7.09−7.22 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 40.1, 127.9, 128.1, 128.6, 131.1, 131.5, 135.3. Mp: 380 °C dec.

2,2′,3,3′,5,5′-Hexaphenyl-4,4′-bis(propylcarbamoyl)biphenyl [2b (R = PrNHCO)]. A solution of 2,2′,3,3′,5,5′-hexaphenyl-4,4′-dihydroxybiphenyl (0.03 mol), *n*-propylisocyanate (15 mL), and triethylamine (1 mL) in 200 mL of toluene was heated at 110 °C for 17 h. The mixture was evaporated to dryness to obtain a crude product. Crystallization twice from $CHCl_3$/hexane gave pure 2,2′,3,3′,5,5′,-hexaphenyl-4,4′-bis(propylcarbamoyl)biphenyl. Yield: 79%. MALDI−TOF−MS: 819.9 (M + Li^+). ^{1}H NMR ($CDCl_3$): δ 0.61 (t, J = 7.42 Hz, 6H), 1.04−1.10 (m, 4H), 2.74−2.79 (m, 4H), 4.38 (d, J = 5.44 Hz, 2H), 6.94 (br, 6H), 6.98−7.03 (m, 12H), 7.27−7.32 (m, 14H). ^{13}C NMR ($CDCl_3$): δ 10.9, 22.9, 43.1, 126.0, 126.4, 127.1, 127.3, 128.5, 129.3, 131.0, 131.9, 133.6, 134.4, 136.2, 137.0, 138.1, 138.2, 138.7, 141.0, 144.6, 154.1. Mp: 316 °C dec.

Polymer I. A typical polymerization procedure is as follows. To a solution of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (0.8 mmol) and decafluorobiphenyl (0.8 mmol) in 4 mL of *N*,*N*-dimethylacetamide was added sodium hydride (2 mmol) at 0 °C under nitrogen. The mixture was then allowed to warm to 25 °C within 1 h. After 20 h, the mixture was poured into 80 mL of 3% hydrochloric acid to precipitate a white fiber. The product was purified by precipitation from THF/methanol. Yield: 90%. ^{1}H NMR (DMSO-d_6): δ 4.95 (t, J = 11.72 Hz, 4H). ^{19}F NMR (DMSO-d_6): δ −122.5 (br, 4F), −126.7 (br, 2F), −141.9 (br, 4F). −157.0 (br, 4F).

Polymer II. A typical procedure is as follows. A mixture of 1,4-bis(propylcarbamoyl)-2,3,5,6-tetraphenylbenzene, **2a** (R = PrNHCO), (0.9 mmol), decafluorobiphenyl (0.9 mmol), potassium carbonate (1.35 mmol), and 10 mL of *N*,*N*-dimethylacetamide was heated at 160 °C under nitrogen. After 20 h, the mixture was added to 300 mL of 5% hydrochloric acid to precipitate a pale brown powder. The crude product was purified by precipitation from THF/methanol/water (1/20/20 by volume) to obtain the polymer **IIa** as a white powder; yield 97%. ^{1}H NMR ($CDCl_3$): δ 7.04 (d, J = 6.45 Hz, 8H), 7.07 (br, 12H). ^{19}F NMR ($CDCl_3$): δ −142.6 (d, J = 17.84 Hz, 4F), −157.0 (d, J = 17.84 Hz, 4F).

Polymer III. A typical procedure is as follows. To a solution of 1,4-bis(propylcarbamoyl)-2,3,5,6-tetraphenylbenzene, **2a** (R = PrNHCO), (0.1 mmol), 2,2,3,3,4,4-hexafluoro-1,5-pentane-1,5-diol (0.9 mmol), and decafluorobiphenyl (1 mmol) in 3 mL of *N*,*N*-dimethylacetamide was slowly added sodium hydride (2.5 mmol) over a period of 30 min at 0 °C under nitrogen. The mixture was allowed to warm to 25 °C within 1 h. After 20 h, the mixture was further reacted at 160 °C for 20 h. Adding the mixture to 150 mL of 5% hydrochloric acid gave a pale brown fiber. The crude product was purified by precipitation from THF/methanol/water (1/20/20 by volume) to obtain a white polymer **IIIa** (p = 0.1). Yield: 98%. ^{1}H NMR ($CDCl_3$): δ 4.78 (t, J = 13.48 Hz, 3.6H), 7.08 (d, J = 7.03 Hz, 0.8H), 7.13 (br, 0.8H), 7.26 (br, 0.4H). ^{19}F NMR ($CDCl_3$): δ −122.4 (s, 3.6F), −126.8 (s, 1.8F), −139.6 (s, 3.6F), −140.0 (s, 0.4F), −156.9 (s, 3.6F), −157.4 (s, 4F). IR (KBr): 2969, 2928 (ν_{CH}), 1652, 1506, 1436 ($\nu_{C=C}$), 1163, 1112 (ν_{COC}), 983, 725, 668 (ν_{CF}), 751, 699 (δ_{CH}) cm^{-1}.

2,3,5,6-Tetrakis(4-chlorosulfonylphenyl)hydroquinone (3). Into 5 mL of chlorosulfonic acid was added 2,3,5,6-tetraphenylhydroquinone slowly over a period of 30 min under cooling with dry ice. The brown solution was stirred at −30 °C for 30 min, 0 °C for 30 min, and then 25 °C for 5 h. The mixture was poured into 200 mL of crushed ice to precipitate a white powder of 2,3,5,6-tetrakis(4-chlorosulfonylphenyl)-hydroquinone (**3**). Yield: 100%. ^{1}H NMR (acetone-d_6): δ 4.61 (br, 2H), 7.44 (d, J = 10.36 Hz, 8H), 7.74 (d, J = 10.36, 8H). ^{13}C NMR (acetone-d_6): δ 127.1, 129.8, 132.9, 136.2, 139.8, 142.1.

Polymer IV. A typical procedure is as follows. To a solution of polymer **IIIa** (p = 0.1) (0.2 mmol) in 5 mL of methylene chloride were added three drops of chlorosulfonic acid at 25 °C. After 1 h, the light brown precipitate was filtered and washed with hexane. The product was dissolved in 5 mL of DMSO, added to 100 mL of 3% potassium hydroxide aqueous solution, and left for 6 h. The solution was acidified with concentrated hydrochloric acid and concentrated to ca. 20 mL by evaporation. The pale brown product was filtered, washed with water and dried to obtain polymer **IVa** (p = 0.1). Yield: 98%. ^{1}H NMR (DMSO-d_6): δ 5.14 (br, 3.6H), 7.09 (br, 0.8H), 7.34 (br, 0.8H). ^{19}F NMR (DMSO-d_6): δ −122.3 (s, 3.6F), −126.5 (s, 1.8F), −141.7 (br, 4F), −156.9 (br, 4F). IR (KBr): 2969, 2930 (ν_{CH}), 1653, 1506, 1436 ($\nu_{C=C}$), 1238 ($\nu_{S=O}$), 1161, 1114 (ν_{COC}), 983, 725, 668 (ν_{CF}), 827 (δ_{CH}) cm^{-1}.

Results and Discussion

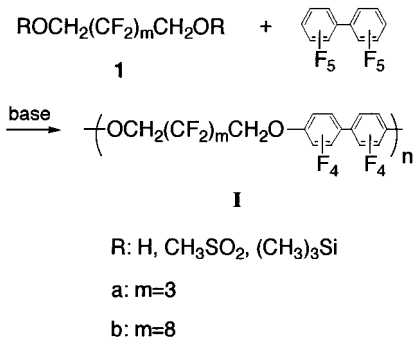
Polymerization of Fluorinated Alkanediol with Decafluorobiphenyl. To synthesize high-molecular-weight copolymers **III**, we first investigated the polymerization behavior of each component (fluorinated alkanediol and phenylated arenediol). The polymerization of fluorinated alkanediols, **1**, with decafluorobiphenyl was previously reported in the literature,[11] in which they claim an almost linear (4,4′-biphenylene) structure of the fractionated product. The solvent (mixture of THF and sulfolane) and the base (NaH three times molar amount of diol monomer) were fixed and not examined. We therefore looked into the effect of base, masking group, solvent and temperature on the polymerization of decafluorobiphenyl with 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluoro-1,10-decanediol (**1b**) (Scheme 1; Table 1). The polymerization in *N*,*N*-dimethylacetamide (DMAc) or DMSO does not take place

Table 1. Polymerization of α,ω-Tetrahydroperfluoroalkanediol with Decafluorobiphenyl (Scheme 1)

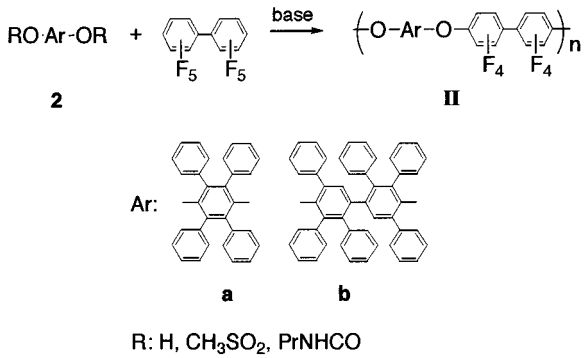
m	R	base	solvent	temp (°C)	yield (%)	M_w	M_n	T_g (°C)	T_m (°C)	$T_{d5\%}$ (°C)[a]
3	H	NaH[b]	DMAc	25	90	59 500	31 500	31	159	405
8	H	K_2CO_3[b]	DMAc	160	0					
8	H	KOH[b]	DMSO	160	59	*c*	*c*	*d*	*d*	356
8	H	NaH[b]	THF/sulfolane[e]	25	85	9700	3200	61	197	398
8	H	NaH[b]	DMAc	25	95	12 500	5600	64	205	403
8	H	NaH[f]	DMAc	25	89	*c*	*c*	145	*d*	391
8	Ms	NaH[b]	DMAc	25	0					
8	TMS	CsF[g]	DMF	50	80	10 800[h]	7700[h]	89	177	368

[a] Temperature for 5% weight loss under nitrogen. [b] Base used was 2.5 times the molar quantity of the monomer. [c] Insoluble in THF. [d] No clear transition was observed. [e] Mixture of THF/sulfolane (9/1 by volume). [f] Base used was 3 times the molar quantity of the monomer. [g] Catalyst 5% of the molar quantity of the monomer was used. [h] Partially soluble in THF.

Scheme 1



Scheme 2



with potassium carbonate and potassium hydroxide and requires a stronger base, e.g., sodium hydride. A white fibrous polymer (**Ib**, $m = 8$) with $M_w = 12\,500$ and $M_n = 5600$ was obtained in 95% yield. The polymer is soluble in THF, DMSO and sulfolane and has a T_g at 64 °C, T_m at 205 °C and $T_{d5\%}$ at 403 °C. The solvent mixture of THF/sulfolane (9/1 by volume), which was used in the literature[11] gave a polymer with lower molecular weight ($M_w = 9700$, $M_n = 1500$). Addition of more NaH (more than three times that of the monomer) produces the polymer insoluble in the solvents. The higher T_g at 145 °C for the product would suggest a cross-linked structure. The mesyl (methanesulfonyl) masking group has been used to improve some kinds of nucleophilic substitution reactions;[12] however, it did not work out in this polymerization. The polymerization of the bis(trimethylsilyloxy)fluorinated alkane **1b** (R = TMS), with decafluorobiphenyl catalyzed by CsF[13] gave a product only partially soluble in THF. A diol monomer with a smaller alkane chain (2,2,3,3,4,4-hexafluoro-1,5-pentanediol, **1a**) gave higher molecular weight polymer (**Ia**, $m = 3$; $M_w = 59\,500$, $M_n = 31\,500$). The polymer has a lower glass transition temperature (T_g at 31 °C and T_m at 159 °C) than polymer **Ib** ($m = 8$).The polymers **I** were characterized by NMR spectroscopy. In the ^{1}H NMR spectrum of **Ia**, only a triplet peak attributed to the methylene groups was observed at 4.95 ppm. The hydroxy end groups could not be confirmed in a reasonable *S*/*N* ratio. The ^{19}F NMR spectrum shows four peaks at −122.5 (CF_2CH_2), −126.7 (CF_2), −141.9, and −157.0 (aromatic CF) ppm, consistent with the reported data for the linear polymer.[11] These spectra do not show any evidence for structural defects such as cross-linking or branching.

Polymerization of Tetraphenylhydroquinone with Decafluorobiphenyl. We reported previously on the polymerization of 2,3,5,6-tetraphenylhydroquinone with bis(4-fluorophenyl)sulfone or 4,4′-difluorobenzophenone.[9] The polymerization proceeds under basic conditions (K_2CO_3 in NMP at 180 °C). Since the products are highly insoluble and precipitate out from the solution during the polymerization, it is difficult to obtain high-molecular-weight polymers. Using decafluorobiphenyl, which is more reactive in nucleophilic substitution reactions and makes the polymer more soluble than the above two fluoride monomers, allows the polymerization to take place at lower temperatures (<160 °C) in a homogeneous solution (Scheme 2). Although the polymerization does not proceed at 25 °C with NaH as base, moderately high molecular weight polymer **IIa** (M_w = 31 000, M_n = 12 000) was obtained in 65% yield by heating at 160 °C (Table 2). However, the polymer obtained is lightly brown colored. The disodium salt of the monomer is poorly soluble in the solvent and oxidation reactions with a trace amount of oxygen in the system was inevitable which could account for the color. Masking the hydroquinone greatly improves the polymerization reaction. The mesyl group is not effective, however, the propylcarbamoyl-masked monomer[14] gave the highest molecular weight polymer (M_w = 166 000, M_n = 36 000). The white powder product was soluble in many organic solvents such as acetone, $CHCl_3$, and THF and gave a transparent and flexible film by casting from solution. The ^{1}H NMR spectrum of **IIa** shows two peaks at 7.04 (d) and 7.07 (br) ppm assigned to the pendant phenyl groups. The propylcarbamoyl groups were not observed. The ^{19}F NMR spectrum shows two sets of doublet peaks at −142.6 and −157.0 ppm, indicating the predominant formation of the 1,4-phenylene structure. T_g at 268 °C and $T_{d5\%}$ at 502 °C were measured by DSC and TGA analyses. The polymer is completely amorphous, and no T_m was observed even after annealing at 250 °C for 2 h. Hexaphenylbiphenol bis(propylcarbamate), **2b** (R = PrNHCO), could also be polymerized with decafluorobiphenyl under the same conditions, however the molecular weight of the obtained polymer **IIb** is lower (M_w = 50 800, M_n = 21 900) than that of **IIa** due to the lower solubility of **IIb** (polymer **IIb** is partly soluble in $CHCl_3$

Table 2. Synthesis of Polymers II

polymer	R	base	solvent	temp (°C)	yield (%)	M_w	M_n	T_g (°C)	$T_{d5\%}$ (°C)[a]
IIa	H	NaH[b]	DMAc	25	0				
IIa	H	NaH[b]	DMAc	100	52	3600	2600	197	451
IIa	H	NaH[b]	DMAc	160	65	31 000	12 000	242	504
IIa	H	K_2CO_3[c]	DMAc	160	95	23 000	4100	239	497
IIa	Ms	Cs_2CO_3[c]	DMSO	100	0				
IIa	PrNHCO	NaH[b]	DMAc	160	98	11 700	2800	195	432
IIa	PrNHCO	K_2CO_3[c]	DMAc	160	97	166 000	36 000	268	502
IIb	PrNHCO	K_2CO_3[c]	DMAc	160	93	50 800[d]	21 900[d]	274	544

[a] Temperature for 5% weight loss under nitrogen. [b] Base used was 2.5 times the molar quantity of the monomer. [c] Base used was 1.5 times the molar quantity of the monomer. [d] Partially soluble in chloroform.

Scheme 3

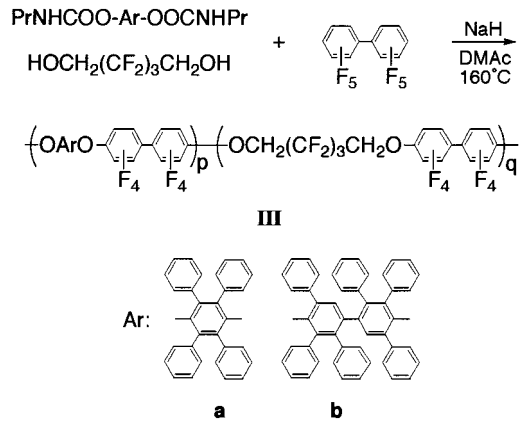


Table 3. Synthesis and Thermal Properties of Copolymers III

polymer	p	yield (%)	M_w	M_n	T_g (°C)	T_d (°C)[a]
IIIa	0.1	98	71 700	23 500	61	390
	0.2	99	58 000	22 000	79	393
	0.3	98	80 900	10 800	109	391
IIIb	0.1	99	49 100	18 000	68	393
	0.2	99	70 300	25 000	107	390
	0.3	99	59 800	14 600	139	389

[a] Temperature at which polymer begins to decompose under nitrogen.

and DMAc). T_g and $T_{d5\%}$ of **IIb** are 6 and 42 °C higher than those of polymer **IIa**.

Synthesis of Copolymers III. The polymerization conditions for the synthesis of copolymers **III** were summarized in Tables 1 and 2, and the reaction is shown in Scheme 3 (NaH as base, DMAc as solvent, at 160 °C, use of propylcarbamoyl-masked monomer). The polymerization started at 0 °C with slow addition of the base to avoid vigorous exothermic reactions and continued at 25 °C for 20 h, followed by heating at 160 °C for another 20 h. The copolymers with different proportions ranging from 10 to 30 mol % of tetraphenylphenylene ether (**IIIa**) or hexaphenylbiphenylene ether (**IIIb**) were obtained as white fibers in quantitative yields (>98%) (Table 3).The products were analyzed by IR, ^{1}H NMR, and ^{19}F NMR spectroscopies. In the IR spectrum of **IIIa** (p = 0.1), the existence of ether bonds (ν_{COC}: 1163, 1112 cm^{-1}), pendant aromatic rings (δ_{CH}: 751, 699 cm^{-1}) and fluorocarbon groups (ν_{CF}: 983, 725, 668 cm^{-1}) was confirmed, indicating the formation of a copolymer. In the ^{1}H NMR spectrum, a triplet peak of methylene protons (4.78 ppm) and four peaks of aromatic protons (7.08 (d), 7.13, 7.26 ppm) are well-assigned to the structure (Figure 1). The integration ratio of these peaks corresponds to the proposed molar ratio of each component (e.g., feed molar ratio of monomers) of the copolymer. Propylcarbamate or hydroxy end groups could not be detected. No extra peaks were observed, confirming the absence of structural defects such as branching or cross-linking. The ^{19}F NMR spectrum further supports the structure.

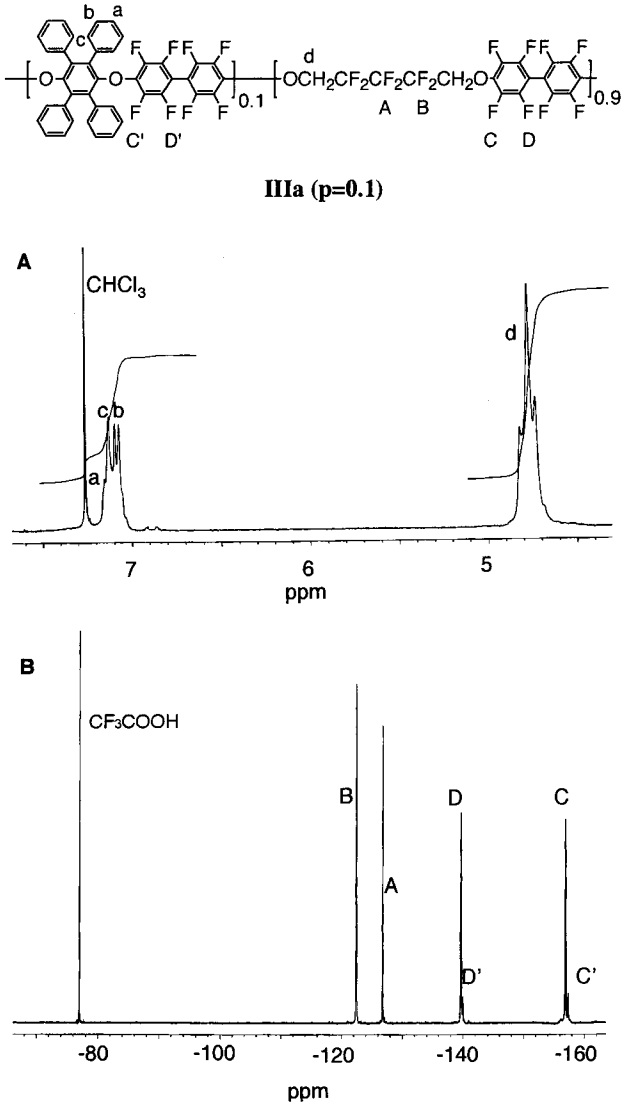
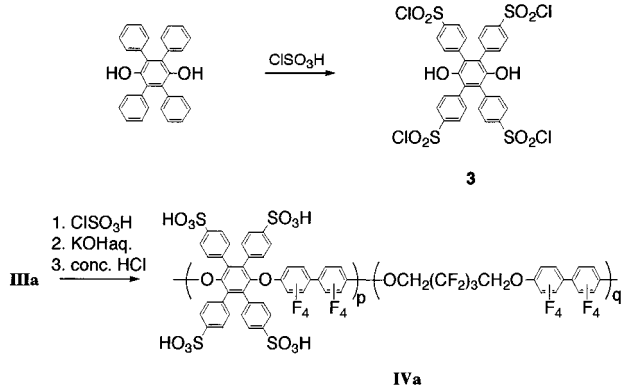


Figure 1. ^{1}H (A) and ^{19}F (B) NMR spectra of polymer **IIIa** (p = 0.1).

The copolymers **IIIa** and **IIIb** with compositions up to 30 mol % of aryleneether moieties have very good solubility in organic solvents. They are soluble in acetone, $CHCl_3$, THF, and DMF. The GPC analyses show that the polymers are high-molecular weight (M_w: 41 900−80 900, M_n: 10 800−25 000). The elution curves are unimodal, excluding the possibility of mixtures of each homopolymer. The polymers show a single

Scheme 4

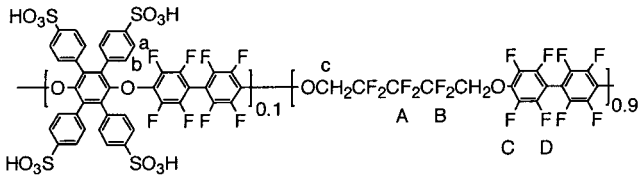


glass transition temperature between those of **I** (31 °C) and **IIa** (268 °C) or **IIb** (274 °C), suggesting the formation of random copolymers without micro phase separation. The T_g can be controlled simply by changing the copolymer proportions. No thermal decomposition was observed for all the copolymers up to 390 °C under nitrogen, at which temperature the fluorinated alkane ether segments degrade as shown in Table 3.

Synthesis of Sulfonated Copolymers IV. The sulfonation of the monomer (2,3,5,6-tetraphenylhydroquinone) was examined first (Scheme 4). The reaction was conducted in neat chlorosulfonic acid. A careful control of the reaction temperature (at −30 °C for 30 min, at 0 °C for 30 min, and at 25 °C for 5 h) resulted in the selective chlorosulfonation at the *para* position of each pendant phenyl group. The product, tetrakis(4-chlorosulfonylphenyl)hydroquione (**3**) was characterized by the ^{1}H NMR spectrum, where two sets of doublet peaks of aromatic protons indicate a 1,4-disubstituted phenylene structure. The ^{13}C NMR spectrum also confirms the 4-chlorosulfonated phenylene structure.

In the chlorosulfonation reaction of the copolymers **III**, methylene chloride was used as solvent. The reaction was completed within a few minutes to give a light brown precipitate of the product. The chlorosulfonated polymers were hydrolyzed in aqueous KOH with a small amount of DMSO, followed by acidification with concentrated HCl to obtain sulfonated copolymers **IV** in the protonic form. The IR spectra of polymers **IV** were compared with those of **III**. The absorption bands at 699 and 751 cm^{-1} attributed to the CH out-of-plane deformation vibration (δ_{CH}) of pendant phenyl groups observed in the parent polymers **III** disappeared after the sulfonation. Instead, an absorption of δ_{CH} of 1,4-disubstituted benzene was observed at 827 cm^{-1} for polymers **IV**. A typical absorption peak of sulfonic acid groups is observed at 1238 cm^{-1}. In the ^{1}H NMR spectrum of polymer **IVa** (p = 0.1) (Figure 2), two broad aromatic peaks at 7.09 and 7.34 ppm correspond to the sulfophenylene groups of the proposed structure. The integration ratio of aromatic to methylene protons indicates a quantitative sulfonation reaction. The combination of ^{1}H and ^{19}F NMR spectra does not show any evidences of structural changes in the polymer main chain after the sulfonation reaction. The degree of sulfonation was also confirmed by titration and back-titration in H_2O/methanol using 0.1 N NaOH, 0.1 N HCl, and methyl red indicator.

Stability, Thermal, and Proton Conducting Properties of Copolymers IV. The sulfonated copolymers **IV** are insoluble in water, $CHCl_3$, and toluene. They are



IVa (p=0.1)

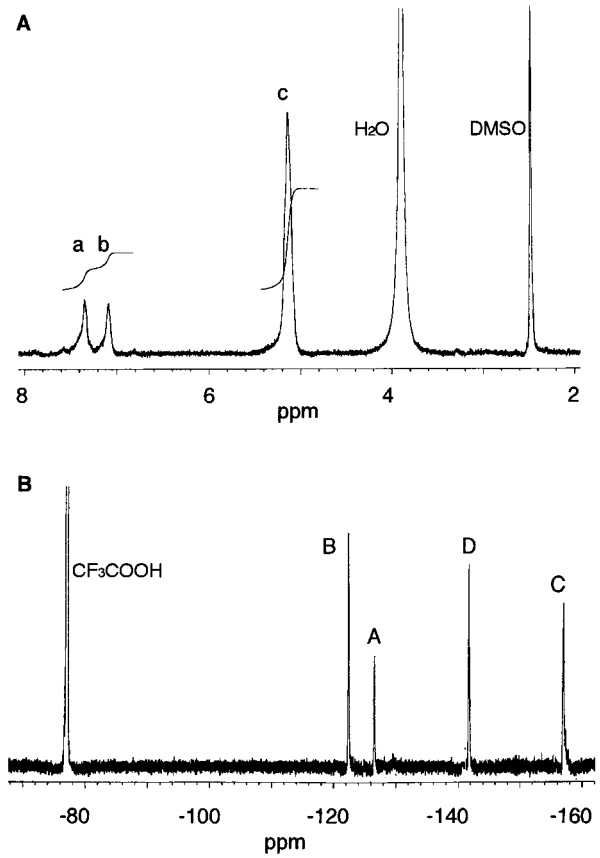


Figure 2. ^{1}H (A) and ^{19}F (B) NMR spectra of polymer **IVa** (p = 0.1).

Table 4. Properties of Sulfonated Copolymers IV

polymer	p	T_g (°C)	T_d (°C)[a]	σ (10^{-3} S cm^{-1})[b]	EW[c]
IVa	0.1	109	299	0.1	1396
	0.2	155	311	2.1	763
	0.3	152	290	0.2	552
IVb	0.1	110	315	1.3	995
	0.2	149	296	0.9	574
	0.3	148	284	0.5	433

[a] Temperature at which polymer begins to decompose under nitrogen. [b] Proton conductivity of hydrated sample at 30 °C. [c] Theoretical equivalent weight per sulfonic acid group.

soluble in DMF, DMSO, and 2-methoxyethanol and swell in methanol and THF. A self-supporting, flexible, and transparent film was obtained by casting from 2-methoxyethanol solution. The T_g of **IV** is higher than that of the corresponding parent polymer **III** due to the hydrogen bonding among sulfonic acid groups (Table 4). The T_g increases with increasing proportion of sulfonated moieties, however, there are no further differences between p = 0.2 and 0.3. The polymers **IV** are thermally stable up to 300 °C under nitrogen atmosphere. The thermogravimetric curve of **IVa** (p = 0.1) is shown in Figure 3 together with those of **IIIa** (p = 0.1) and Nafion (EW 1250). The polymer **IVa** begins to

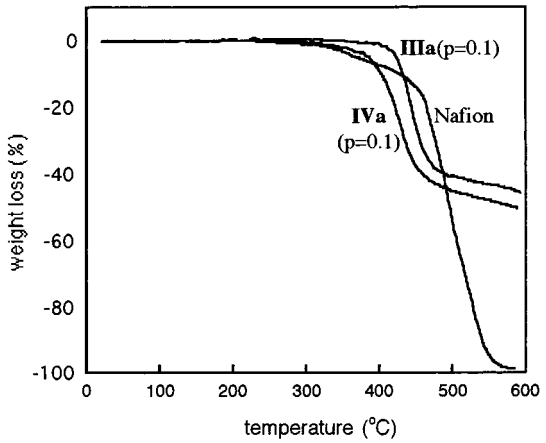


Figure 3. TGA curves of **IIIa** ($p = 0.1$), **IVa** ($p = 0.1$), and Nafion.

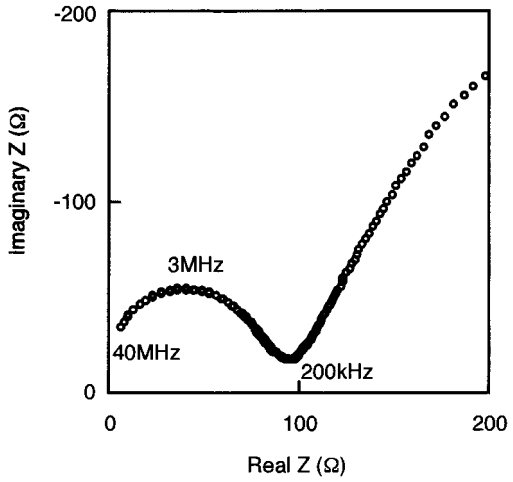


Figure 4. Typical complex impedance plot for hydrated polymer **IV** with gold electrodes.

decompose at 299 °C, the same temperature as Nafion, due to the loss of sulfonic acid groups. The ash left at 600 °C is 53% for **IVa** and only 2% for Nafion.

The stability of polymer **IV** to hydrolysis and oxidation was investigated. A film sample of polymer **IVb** ($p = 0.2$) with a thickness of 100 μm was heated in boiling water. The film kept its form after this treatment for more than 7 days, indicating no serious hydrolysis. The film was also soaked in Fenton's reagent (30 ppm Fe_2SO_4 in 30% H_2O_2) at 25 °C. It took more than 4 h before the film started to break into pieces and 6 h before it disappeared into solution.

The film of polymers **IV** absorbed 4.6−5.1 wt % of water when left under saturated humidity or soaked in water. More than 30 wt % of water could be absorbed by activating the surface of a film with a small amount of methanol before being soaked in water. The proton conductivity of the hydrated samples was evaluated by complex impedance analysis using gold electrodes. A typical complex plane (Cole−Cole) plot for the polymers is shown in Figure 4. The observed frequency dependence approximating a semicircle indicates an equivalent circuit corresponding to proton-blocking gold electrodes. The proton conductivity (σ) for copolymers **IV** at 30 °C calculated from the radius of the semicircle was on the order of 10^{-3}−10^{-4} S cm^{-1} (Table 4), comparable to that of hydrated Nafion 117 (EW 1100) (2.3×10^{-3} S cm^{-1}). From the proton conductivity standpoint, the preferable equivalent weight per sulfonic acid group (EW) of

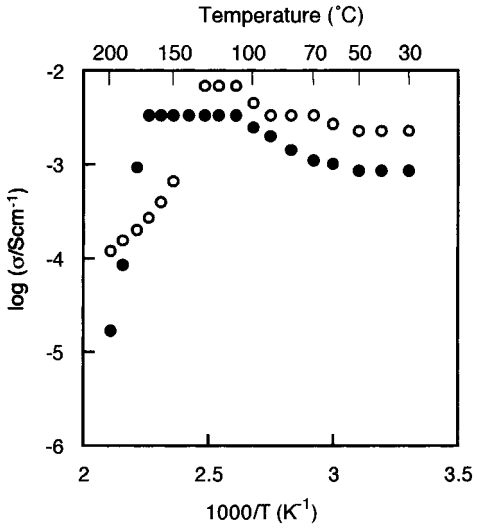


Figure 5. Temperature dependence of the proton conductivity of hydrated **IVb** ($p = 0.2$) (●) and Nafion (○).

polymers is about 700−1000 [**IVa** ($p = 0.2$) and **IVb** ($p = 0.1$)]. The higher EW [**IVa** ($p = 0.1$)] results in a lower carrier (proton) concentration, therefore, a lower proton conductivity. The lower conductivity with lower EW [**IVa** ($p = 0.3$) and **IVb** ($p = 0.2, 0.3$)] might be caused by insufficient diffusion of carriers. The temperature dependence of the proton conductivity for **IVb** ($p = 0.2$) is shown in Figure 5. The conductivity increases with temperature up to 3.4×10^{-3} S cm^{-1} at 100 °C. It retains almost the same value until 170 °C, above which temperatures the conductivity decreases due to the loss of water. Under the same measurement conditions, although its initial conductivity at 30 °C is slightly higher than **IV**, the hydrated Nafion loses its conductivity beyond 130 °C. Polymer **IV** retains water at higher temperatures than Nafion, that should be potentially advantageous for use in fuel cells operated at higher temperatures.

Conclusions

Novel sulfonated aryl ether/fluoroalkane copolymers were synthesized by the polymerization of decafluorobiphenyl with phenylated arenediols and fluorinated alkanediols followed by a sulfonation reaction. Optimization of each homopolymerization reaction provided preferable copolymerization conditions to obtain high-molecular-weight copolymers **III** ($M_w = 49\,100$−$80\,900$, $M_n = 10800$−25000). As also evidenced from the model reaction using the monomer, tetraphenylhydroquinone, the chlorosulfonation reaction of **III** took place quantitatively and exclusively at the *para* position of each pendant phenyl group. The hydrolysis and acidification of the chlorosulfonated products gave the protonated form of copolymers **IV**, which are soluble in polar organic solvents (DMSO, DMF, 2-methoxyethanol). The glass transition temperature and ionic density (or equivalent weight per sulfonic acid group) of **IV** are controllable by changing the copolymer composition. The polymers are as thermally stable as commercially available perfluorinated sulfonic acid polymer (Nafion) and do not decompose up to ca. 300 °C. Excellent hydrolysis and oxidation stability were confirmed by the treatment with boiling water. The copolymers show proton conductivity on the order of $10^{-3} - 10^{-4}$ S cm^{-1}, which increases with the temperature up to 170 °C. It showed

that better thermal stability can be achieved for polymers with proton conductivity comparable to that of Nafion.

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