New Poly(arylene ether)s with Pendant Phosphonic Acid Groups

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ABSTRACT: Soluble brominated poly(arylene ether)s containing mono- or dibromotetraphenylphenylene ether and octafluorobiphenylene units were synthesized. The polymers were high molecular weight (weight-average molecular weight = 115,100–191,300; number-average molecular weight = 32,300–34,000) and had high glass-transition temperatures (>279 °C) and decomposition temperatures (>472 °C). The brominated polymers were phosphonated with diethylphosphite by a palladium-catalyzed reaction. Quantitative phosphonation was possible when 50 mol % of a catalyst based on bromine was used. The diethylphosphonated polymers were dealkylated by a reaction with bromotrimethylsilane in carbon tetrachloride followed by hydrolysis with hydrochloric acid. The polymers with pendant phosphonic acid groups were soluble in polar solvents such as dimethyl sulfoxide and gave flexible and tough films via casting from solution. The polymers were hygroscopic and swelled in water. They did not decompose at temperatures of up to 260 °C under a nitrogen atmosphere. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 3770–3779, 2001

Keywords: poly(arylene ether); polymer electrolytes; phosphonic acid; phosphonate ester; functionalization of polymers; ionomers; membranes

INTRODUCTION

Acid-containing polymers have attracted much attention as solid electrolyte membranes in batteries and fuel cells.[1] The majority of acid-containing polymers have the sulfonic acid functionality as the proton-exchange site.[2] There have been several reports of phosphonic acid-containing polymers as membranes for fuel-cell applications.[3] They have lower acidity than sulfonic acids;[4] however, their better chemical and thermal stability with respect to corresponding sulfonic acid-functionalized polymers offers potential advantages.[3(c)]

Recently, we synthesized a new series of copolymers containing sulfonated tetraphenylphenylene ether (or hexaphenylbiphenylene ether), perfluorobiphenylene, and fluorinated alkylene moieties.[5] We demonstrated that with sulfonic acid groups attached to the pendant phenyl rings, the resulting aromatic polymers were very stable under heat, hydrolysis, and oxidation. The hydrated polymer membranes showed high proton conductivity (>10^{-3} S cm^{-1}) from 25 to 170 °C. In this article, we describe our successful synthesis of novel aromatic polymers containing phosphonic acid substituents on the pendant phenyl rings. Mono- and dibromotetraphenylhydroquinones were synthesized and polymerized with decafluorobiphenyl to produce the corresponding brominated poly(arylene ether)s. The bromine groups were converted to phosphinic acid groups by palladium-catalyzed phosphonation with diethylphosphite followed by hydrolysis. The synthesis, structure, and some basic properties of these polymers are reported.

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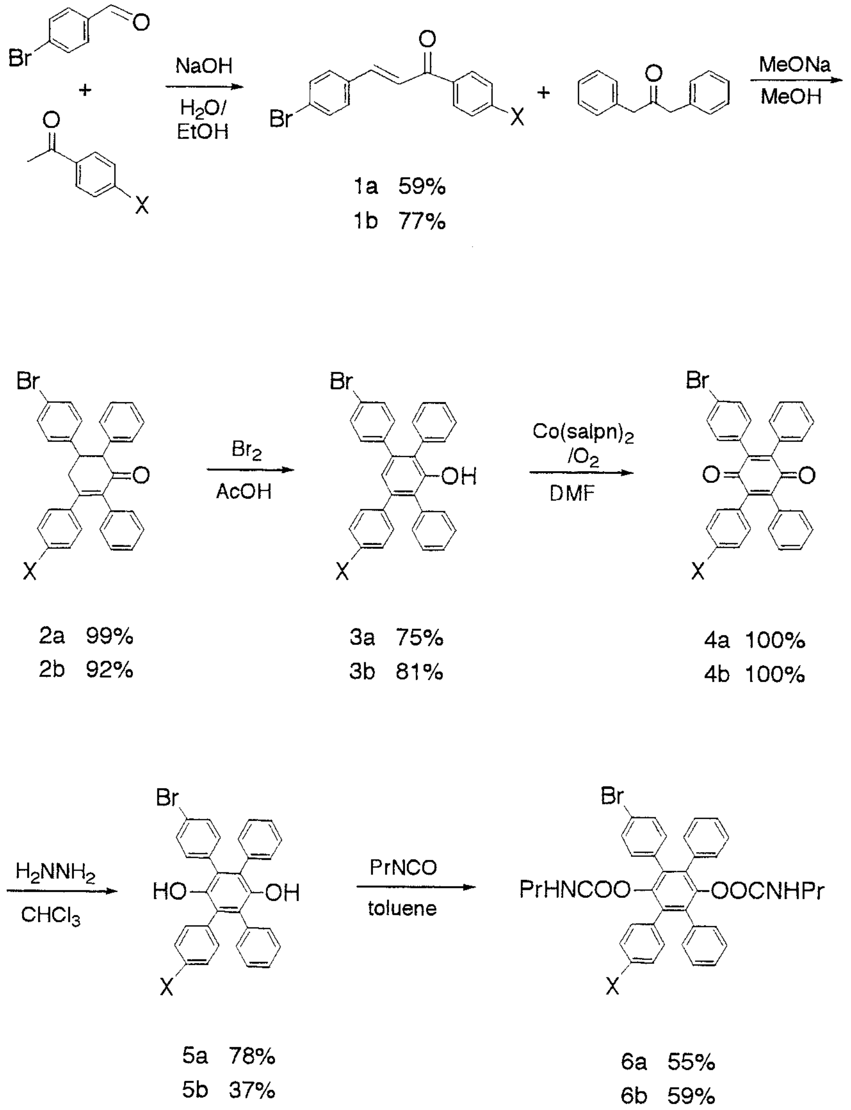


X: H(a), Br(b)

Scheme 1

RESULTS AND DISCUSSION

Synthesis of the Monomers

The synthetic procedures for the synthesis of mono- and dibromotetraphenylhydroquinone (**5a** and **5b**) and their bispropylcarbamate-masked derivatives (**6a** and **6b**) are depicted in Scheme 1. The reactions are similar to those for the synthesis of unsubstituted tetraphenylhydroquinone.[6] Brominated chalcones (benzylideneacetophenone; **1a** and **1b**), prepared from bromobenzaldehyde and acetophenone (or 4-bromoacetophenone), were reacted with 1,3-diphenylacetone under basic conditions to produce the δ-diketone compounds (Michael addition). The same reagent at 60 °C effected the aldolization and dehydration of the diketones to give the tetraphenylcyclohexenones (**2a** and **2b**) in high yields (>92%). The oxidation of **2** with 1 mol equiv of bromine gave the corresponding phenols (**3**). Compounds **3a** and **3b** were further oxidized with oxygen in dimethylformamide (DMF) in the presence of a cobalt catalyst. It should be noted that salcomine [Co(salen)$_2$, or *N,N'*-bis(salicylidene)ethylenediaminocobalt] is not very effective as a catalyst. Oxidation with the phenylene derivative *N,N′*-bis(salicylidene)-1,2-phenylenediaminocobalt [Co(salpn)$_2$] as a catalyst gave a quantitative reaction probably due to its higher oxidizing ability. Brominated tetraphenyl-1,4-benzoquinones **4a** and **4b**, both obtained in 100% yields, were reduced with hydrazine in methylene chloride/chloroform solutions to give the hydroquinones **5a** and **5b**. Because carbamate-masked monomers often give much better results in nucleophilic substitution polymerization reactions than the parent bisphenols,[7] the hydroquinones were reacted with *n*-propylisocyanate to give the corresponding bispropylcarbamoyl compounds **6a** and **6b**. These compounds were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectra and melting temperatures. The monomers were pure enough for the polymerization reactions, as confirmed by high-pressure liquid chromatography (HPLC) analyses.

Polymerization

The polymerization of **6** with arylene difluorides was carried out in *N,N*-dimethylacetamide (DMAc) in the presence of a 50 mol % excess of potassium carbonate. We first examined the polymerization with the commonly used difluoride monomers bis(4-fluorophenyl)sulfone and 4,4′-difluorobenzophenone. However, both were unsuccessful and gave oligomers with a number-average molecular weight (M_n) of less than 5000, even after polymerization for 3 days at 160 °C. Decafluorobiphenyl, a much more reactive difluoride monomer, gave high molecular weight polymers in high yields after polymerization for 20 h (Scheme 2 and Table I). The reaction temperatures should not be higher than 140 °C to prevent some reactions of bromine on pendant phenyl rings. Monobrominated polymer **7a** [weight-average molecular weight (M_w) = 191,300; M_n = 32,300] and dibrominated polymer **7b** (M_w = 115,100; M_n = 34,000) were obtained as white powders.

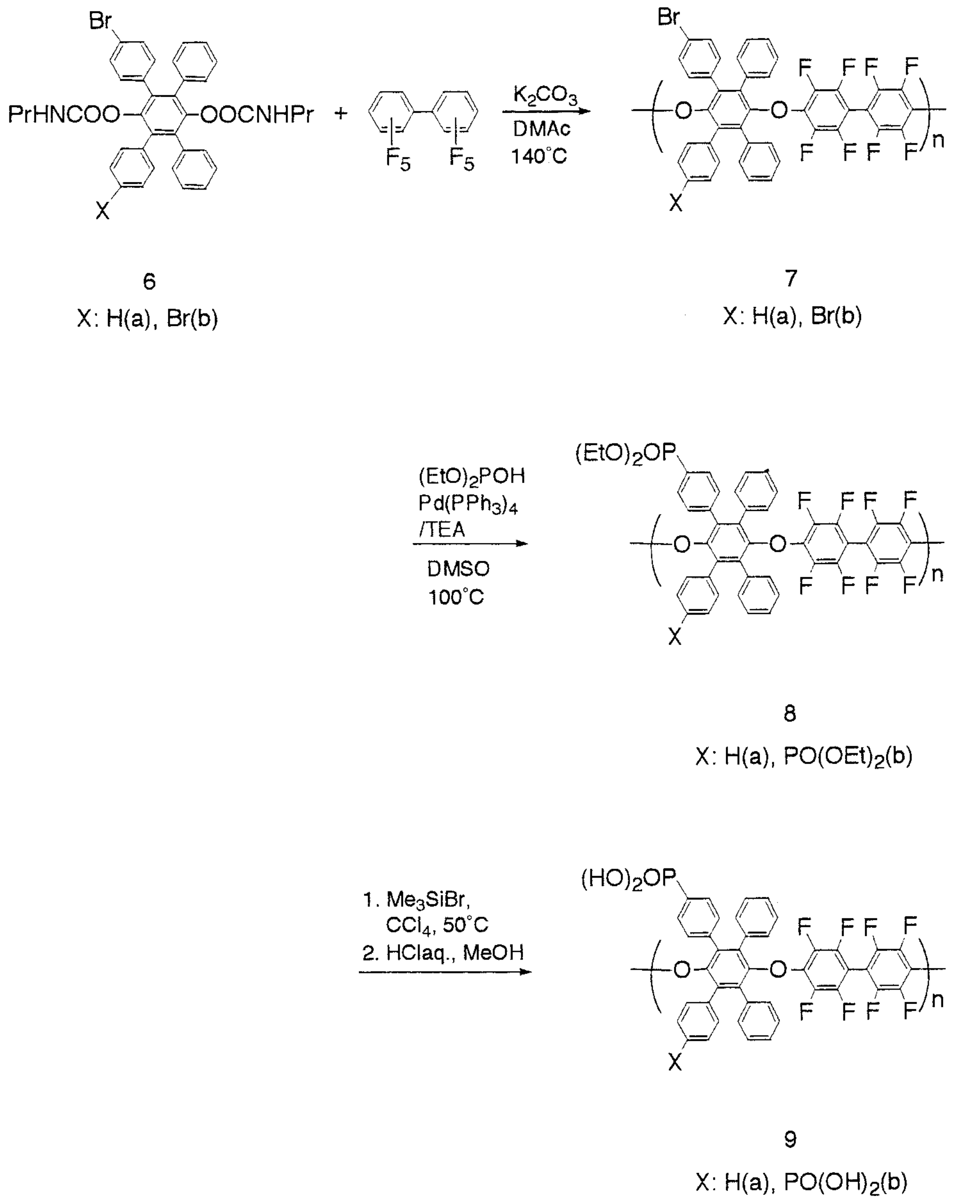
Polymers were characterized with NMR and IR spectroscopies. In the ^{1}H NMR spectrum of **7b**, two sets of doublet peaks assigned to 4-bromophenylene units were observed at 6.96 and 7.20 ppm, indicating that the bromine groups were intact throughout the polymerization reactions. The integration ratio of the doublets to a broad peak of unsubstituted phenyl rings (7.08 ppm) was 8:10, supporting the proposed structure of the polymer. No peaks of propylcarbamoyl groups were detected. The ^{19}F NMR spectrum showed a doublet peak (−141.3 and −141.6 ppm) of fluorines meta to the ether bond and a singlet peak (−156.1 ppm) of fluorides ortho to the ether bond. The results confirmed the structure of the polymer containing perfluoro-4,4′-biphenylene and unsymmetrically substituted tetraphenylphenylene ether units. A random distribution of heads and tails for brominated tetraphenylphenylene units would be expected because the reactivity and steric effect of the hydroxy groups should be similar.

Polymers **7a** and **7b** were soluble in many organic solvents such as acetone, chloroform, toluene, and dimethyl sulfoxide (DMSO) and gave transparent and flexible films via casting from solution. The glass-transition temperatures (T_g's) of the polymers varied with the number of bromines per repeating unit: T_g = 268 °C with no bromine,[5] T_g = 279 °C with one bromine (**7a**), and T_g = 285 °C with two bromines (**7b**). They were thermally stable up to about 470 °C without decomposition under a nitrogen atmosphere, as confirmed by thermogravimetry (TG) analyses.

Phosphonation

There are several methods reported for the preparation of arenephosphonates from aryl bromides.[8] The classical Arbuzov reaction[9] is commonly used, in which triethylphosphite and nickel dichloride as a catalyst are employed. The reaction often requires harsh conditions (160 °C) and suffers from low yields. We chose the palladium-catalyzed reaction[10] for the phosphonation of polymers **7a** and **7b**. The reactions were carried out with diethylphosphite and tetrakis(triphenylphophine)palladium as a catalyst with triethylamine (Scheme 2, Table II). The first-trial phosphonation reaction of the brominated polymer with 5 mol % of the palladium catalyst was unsuccessful, with no reaction occurring, as confirmed by ^{1}H NMR analyses. The addition of more catalyst (35 mol %) and/or dimethylphosphite did not improve the reaction and resulted in conversions lower than 15%. For quantitative reactions, 50 mol % of the palladium catalyst was needed. Polar solvents (DMSO), temperature (100 °C), and time (70 h) were also important factors for obtaining 100% conversion. The polymers **8a** and **8b** were isolated as pale-brown powders.

Polymers **8a** and **8b** were less soluble than the parent brominated polymers but were still soluble in chloroform and DMSO. Molecular weight measurements were not performed because our gel



6
X: H(a), Br(b)

7
X: H(a), Br(b)

8
X: H(a), PO(OEt)$_2$(b)

9
X: H(a), PO(OH)$_2$(b)

Scheme 2

permeation chromatography (GPC) columns absorbed phosphorus-containing polymers. However, both polymers formed films as tough and flexible as those of **7a** and **7b**, implying no degradation in the phosphonation reactions. In the ^{1}H NMR spectrum of **8a** in $CDCl_3$ (Fig. 1), methyl (1.20 ppm) and ethyl (3.98 ppm) protons of diethylphosphonate ester were observed. The aromatic protons could be assigned to the proposed structure, and the integration ratio of the peaks indicated a quantitative phosphonation reaction. No changes were observed in the ^{19}F NMR spectra between **7a** and **8a**, suggesting that perfluorobiphenylene moieties were intact throughout the reaction. A singlet peak attributed to arenedialkylphosphonate was observed at 19.5 ppm in the ^{31}P NMR spectrum. The IR spectrum further confirmed the phosphonation reaction, where a strong absorption band corresponding to the stretching vibration of POC bonds appeared at 1025 cm^{-1}.

Polymer **8a** had a lower T_g at 244 °C than **7a** (T_g = 279 °C) due to the flexible pendant diethylphosphonate groups, whereas **8b** did not show a T_g below its decomposition temperature. The TG profile of polymer **8a** is shown in Figure 2(b) to-

Table I. Synthesis and Properties of Polymers **7, 8,** and **9**

Polymer	Yield (%)	M_w[a]	M_n[a]	T_g (°C)	T_d (°C)[b]	Solubility[c]			
						Acetone	$CHCl_3$	DMSO	H_2O
7a	95	191,300	32,300	279	472	+	+	+	−
7b	100	115,100	34,000	285	478	+	+	+	−
8a	98	—[d]	—[d]	244	284	−	+	+	−
8b	100	—[d]	—[d]	—[e]	257	−	+	+	−
9a	98	—[d]	—[d]	—[e]	263	−	−	+	±[f]
9b	92	—[d]	—[d]	—[e]	257	−	−	±	±[f]

[a] Measured by GPC calibrated with polystyrene standards.
[b] Temperature at which decomposition takes place.
[c] + = soluble; ± = swellable; − = insoluble.
[d] Not available with our GPC columns.
[e] Not detected.
[f] Hot water.

gether with that of **7a**, where **8a** begins to decompose at 284 °C. The weight loss from 284 to 350 °C is about 7 wt %, which almost corresponds to the quantitative loss of two ethyl groups per repeating unit. The results are consistent with a previous report[3(a)] in which it was claimed that diethylphosphonated poly(phenylene oxide) begins to decompose at 270 °C with the evolution of fragments [*m/z* = 27 (C_2H_3)] from ethyl ester groups. The second step of the degradation of **8a**, starting from about 475 °C, should be the degradation of the main chain.

Dealkylation

The dealkylation of polymers **8a** and **8b** was conducted in carbon tetrachloride with an excess of bromotrimethylsilane.[11] The reaction proceeded at 50 °C to give the bistrimethylsilylated product, which was hydrolyzed with hydrochloric acid (HCl) in methanol. Polymers **9a** and **9b** were obtained as pale-brown powders in good yields (>92%) after purification. The dealkylated products were characterized by NMR and IR spectroscopy. In the ^1H NMR spectrum of **9a** in DMSO-d_6 (Fig. 3), no peaks attributed to ethyl groups were observed in the field from 1.0 to 5.0 ppm, indicating the completion of the deethylation reaction. There were no significant changes in the ^{19}F NMR spectra after the reaction, except that the doublet peak of fluorines meta to the ether bond merged into one peak at −140.9 ppm because of the viscosity of the polymer electrolyte solution. In the ^{31}P NMR spectrum, the peak of phosphonate ester at 19.5 ppm disappeared, and a new peak assignable to phosphonic acid appeared at 13.3 ppm. The stretching vibration mode of POC bonds was not detected in the IR spectrum.

Unlike the parent polymers **7** and **8**, polymers **9a** and **9b** were not soluble in less polar solvents

Table II. Palladium-Catalyzed Phosphonation Reaction of Brominated Polymers **7a** and **7b**

Polymer	Pd/Br[a]	Solvent	Temperature (°C)	Time (h)	Conversion (%)[b]
7a	0.05	Toluene	90	20	0
7a	0.35	Toluene	90	20	15
7a	0.50	DMSO	100	70	100
7b[c]	0.35	Toluene	90	50	5
7b	0.50	DMSO	100	45	70
7b	0.50	DMSO	100	70	100

[a] Molar ratio of tetrakis(triphentylphosphine)palladium to bromine.
[b] Calculated from the integration ratio in the ^1H NMR spectra.
[c] Dimethylphosphite was used.

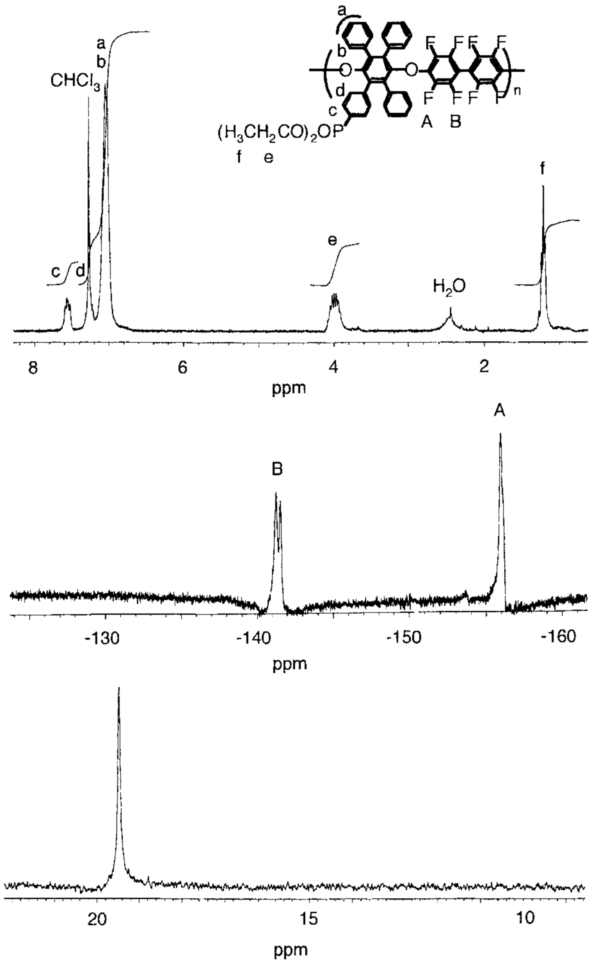


Figure 1. ^{1}H (top), ^{19}F (middle), and ^{31}P (bottom) NMR spectra of **8a**.

such as chloroform and tetrahydrofuran but were soluble in DMSO (polymer **9b** swelled but was not fully soluble in DMSO even at 100 °C). Pale-brown, flexible, and tough films were obtained via casting from DMSO solutions, suggesting no degradation during the dealkylation reaction. Because of the phosphonic acid groups, polymers **9a** and **9b** were hydrophilic and swelled in hot water when soaked for several hours. There were no significant differences in the swelling behaviors of **9a** and **9b**, despite a large difference in the equivalent weight per phosphonic acid group (EW) between them (EW = 789 for **9a**; EW = 434 for **9b**). The polymer films had good hydrolytic stability and did not degrade after treatment in a boiling water for more than 1 week. They did not show T_g's and began to decompose at about 260 °C, as shown in Figure 2(c). The weight loss from 260 to 380 °C for **9a** was about 10 wt %, corresponding to one phosphonic acid group per repeating unit. These TG analyses suggest that the degradation mode of **9a** was based on the loss of phosphonic acid groups and was different from that of **8a**, in which only ethyl groups were eliminated at the first stage of the thermal degradation. The thermal, chemical, and hydrophilic properties of these phosphonic acid-containing poly(arylene ether)s indicate that they may find applications as polymer electrolyte membranes for low-temperature-operating fuel cells.

CONCLUSIONS

Brominated tetraphenylhydroquinones **5a** and **5b** were synthesized from brominated chalcones and diphenylacetone in four steps. The polymerization of bispropylcarbamoyl-masked monomers **6a** and **6b** with bis(4-fluorophenyl)sulfone or 4,4′-difluorobenzophenone was not successful and gave oligomers with $M_n < 5000$. Decafluorobiphenyl was effective in the polymerization reaction to give soluble, high molecular weight poly(arylene ether)s with pendant bromophenyl groups. No reactions of bromine groups occurred when the polymerization was carried out below 140 °C. The T_g's of the polymers depended on the number of bromines per repeating unit: T_g = 268 °C with no bromine, T_g = 279 °C with one bromine, and T_g = 285 °C with two bromines. Polymers **7a** and **7b** were reacted with diethylphosphite in the presence of $Pd(PPh_3)_4$ as a catalyst. A catalyst concentration of 50 mol % per bromine, a highly polar solvent (DMSO), and long reaction times (70 h) were required for the complete phosphonation of

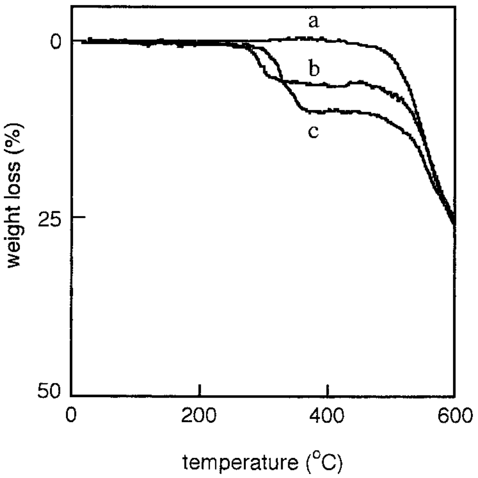


Figure 2. TG thermograms of (a) **7a**, (b) **8a**, and (c) **9a**.

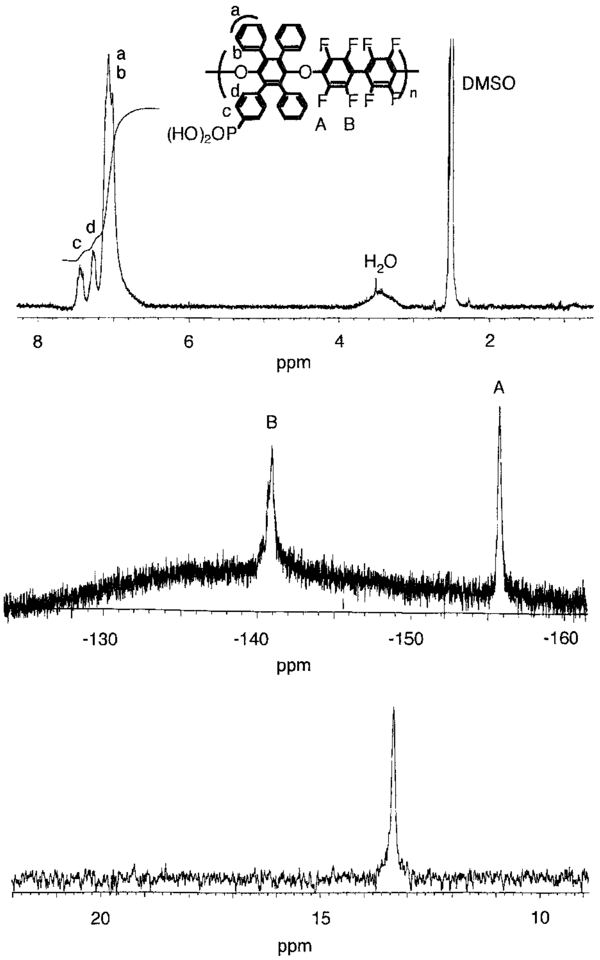


Figure 3. ^{1}H (top), ^{19}F (middle), and ^{31}P (bottom) NMR spectra of **9a**.

the bromine groups. Diethylphosphonated polymers **8a** and **8b** were deethylated by transesterification with bromotrimethylsilane and hydrolysis with HCl. The reaction was completed after 1 day, as confirmed by NMR and IR spectroscopy. The phosphonic acid-containing polymers were soluble in DMSO and gave flexible and tough films via casting from solution, indicating that no chain degradation occurred during phosphonation and deethylation. Hydrophilic properties as well as hydrolytic and thermal stability were confirmed for the polymers, indicating potential applications as polymer electrolyte membranes.

EXPERIMENTAL

Materials

4-Bromobenzaldehyde, acetophenone, 4-bromoacetophenone, 1,3-diphenylacetone, and decafluorobiphenyl were purchased from Aldrich Co., Inc. and were purified by distillation or crystallization. Other reagents for monomer synthesis, polymerization, phosphonation, and dealkylation shown in Schemes 1 and 2 were commercial products from Aldrich or Lancaster Co., Inc. and were used as received. Solvents were distilled before use.

Measurements

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Mercury 300 or 400 spectrometer with $CDCl_3$ 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 KBr pellets on a Jasco FT/IR-5300 spectrometer. Mass spectra were measured on a Kratos MS25RFA at an ionization energy of 70 eV. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF mass spectrometer set in the positive reflection mode. Lithium bromide and dithranol were used as the cationization reagent and matrix, respectively. Thermal analysis was performed via TG with a Seiko TG/DTA 220 instrument and differential scanning calorimetry (DSC) with a Seiko DSC 220 instrument at a heating rate of 20 °C/min under nitrogen. Molecular weight measurements were done via GPC with a Waters 510 system equipped with a UV detector set at 254 nm. Chloroform was used as an eluent. Calibration was performed with polystyrene standards.

4-Bromobenzylideneacetophenone (1a) and 4-Bromobenzylidene-4′-bromoacetophenone (1b)

A procedure similar to that previously reported[12] for the synthesis of benzylideneacetophenone was used. Into a solution of sodium hydroxide (0.065 mol) in 25 mL of water and 12.5 mL of ethanol, acetophenone or 4-bromoacetophenone (0.05 mol) and 4-bromobenzaldehyde (0.05 mol) were added. The temperature of the mixture was set at 25 °C with a water bath during the reaction. The reaction was continued for 2 h until the pale-yellow suspension of the mixture became so thick that magnetic stirring was no longer effective. The mixture was left at 0 °C for 5 h and filtered. The crude product was washed with water and crystallized from ethanol/chloroform to obtain **1a** in a 59% yield or **1b** in a 77% yield.

1a

mp: 127 °C (lit.[13] 125–126 °C). Mass spectrometry (MS): 286, 288 (M^+) *m/z*.

1b

mp: 190 °C (lit.[13] 187–188 °C). MS: 364, 366, 368 (M^+) *m/z*.

2,3,6-Triphenyl-5-(4′-bromophenyl)-2-cyclohexenone (2a) and 2,6-Diphenyl-3,5-bis(4′-bromophenyl)-2-cyclohexenone (2b)

Into a solution of **1** (0.012 mol) and 1,3-diphenylacetone (0.012 mol) in 50 mL of DMF, sodium methoxide (0.012 mol) was added. The mixture was reacted at 60 °C for 1 h under a nitrogen atmosphere. Another portion of sodium methoxide (0.012 mol) with 30 mL of methanol was added, and the reaction was continued for 8 h. The mixture was poured into 300 mL of water to precipitate a white powder. The crude product was filtered and crystallized from benzene/petroleum ether to obtain **2a** in a 99% yield and **2b** in a 92% yield.

2a

MS: 478, 480 (M^+) *m/z*.

2b

MS: 556, 558, 560 (M^+) *m/z*.

2,3,6-Triphenyl-5-(4′-bromophenyl)phenol (3a) and 2,6-Diphenyl-3,5-bis(4′-bromophenyl)phenol (3b)

Into a suspension of **2** (0.0248 mol) in 250 mL of acetic acid, bromine (0.0248 mol) was added. The mixture was reacted at 70 °C for 18 h until a pale-brown product precipitated out of the solution. The mixture was poured into 500 mL of water. The crude product was filtered, washed with water, and crystallized from chloroform/ethanol to obtain **3a** in a 75% yield or **3b** in an 81% yield.

3a

Purity: 99.8% (by HPLC). mp: 239 °C. MS: 476, 478 (M^+) *m/z*. ^{1}H NMR ($CDCl_3$, δ): 5.29 (s, 1H), 7.04 (d, *J* = 8.21 Hz, 2H), 7.11 (s, 1H), 7.17 (br, 6H), 7.25 (m, 11H). ^{13}C NMR ($CDCl_3$, δ): 121.1, 124.1, 126.9, 127.7, 127.8, 128.0, 128.8, 128.9, 129.9, 130.4, 130.8, 131.1, 131.3, 131.6, 132.2, 135.7, 135.8, 140.1, 140.4, 141.0, 141.9, 150.6.

3b

Purity: 99.9% (by HPLC). mp: 179 °C. MS: 554, 556, 558 (M^+) *m/z*. ^{1}H NMR ($CDCl_3$, δ): 5.29 (s, 1H), 7.02 (d, *J* = 8.79 Hz, 4H), 7.05 (s, 1H), 7.23 (d, *J* = 8.21 Hz, 4H), 7.30 (m, 10H). ^{13}C NMR ($CDCl_3$, δ): 121.2, 123.8, 126.6, 127.9, 129.0, 131.19, 131.21, 131.5, 135.5, 139.9, 140.6, 150.7.

2,3,6-Triphenyl-5-(4′-bromophenyl)-1,4-hydroquinone (5a) and 2,6-Diphenyl-3,5-bis(4′-bromophenyl)-1-4-hydroquinone (5b)

A mixture of **3** (0.018 mol) and Co(salpn)$_2$ (6 mmol) in 250 mL of DMF was reacted at 90 °C for 45 h under an oxygen atmosphere. The dark-brown solution of the mixture was poured into 500 mL of water containing 10 vol % of 37% HCl. The dark-brown powder of the product was filtered, washed with diluted HCl and with water, and dried to obtain **4** in a 100% yield. Compound **4** was dissolved in 300 mL of methylene chloride/chloroform (1/1). The mixture was reacted with 10 mL of hydrazine hydrate at 50 °C for 17 h. A pale-brown product was obtained by distillation of the solvent. The crude product was treated with charcoal in methylene chloride/ethanol and crystallized twice from chloroform/hexane to obtain **5a** in a 78% yield or **5b** in a 37% yield.

5a

Purity: 99.7% (by HPLC). mp: 306 °C. MALDI-TOF MS: 494.4 (M^+). ^{1}H NMR ($CDCl_3$, δ): 4.72 (s, 1H), 4.77 (s, 1H), 7.08 (d, *J* = 8.21 Hz, 2H), 7.20 (m, 9H), 7.25 (m, 6H), 7.35 (d, *J* = 8.21 Hz, 2H). ^{13}C NMR ($CDCl_3$, δ): 121.1, 126.6, 127.3, 127.4, 127.6, 127.9, 128.0, 128.3, 128.4, 128.6, 130.7, 130.79, 130.82, 131.1, 132.6, 135.06, 135.14, 135.4, 135.5, 143.5, 143.8.

5b

Purity: 100% (by HPLC). mp: 274 °C. MALDI-TOF MS: 577.4 ($M + Li^+$). ^{1}H NMR ($CDCl_3$, δ): 4.60 (s, 1H), 4.75 (s, 1H), 7.06 (d, *J* = 8.79 Hz, 4H), 7.17 (d, *J* = 8.21 Hz, 4H), 7.25 (m, 6H), 7.37 (d, *J* = 8.21 Hz, 4H). ^{13}C NMR ($CDCl_3$, δ): 121.5, 126.7, 127.5, 128.1, 128.5, 130.7, 131.5, 132.5, 134.5, 135.2, 143.3, 143.9.

1,4-Bis(propylcarbamoyl)-2,3,6-triphenyl-5-(4′-bromophenyl)-1,4-benzene (6a) and 1,4-Bis(propylcarbamoyl)-2,6-diphenyl-3,5-bis(4′-bromophenyl)-1,4-benzene (6b)

To a solution of **5** (0.01 mol) in 150 mL of toluene, 6 mL of *n*-propylisocyanate and 1 mL of triethylamine were added. The mixture was reacted at 110 °C for 21 h to obtain a brown solution. A crude product was recovered by distillation of the solvent, washed with hexane, and crystallized twice from methylene chloride/hexane to obtain **6a** in a 55% yield or **6b** in a 59% yield.

6a

Purity: 100% (by HPLC). mp: 267 °C. MALDI-TOF MS: 669.5 (M + Li^+). ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 0.61 (m, 6H), 1.09 (m, 4H), 2.76 (m, 4H), 4.37 (t, J = 6.25 Hz, 2H), 7.02 (d, J = 7.43 Hz, 2H), 7.12 (br, 15H), 7.26 (d, J = 7.82 Hz, 2H). ^{13}C NMR ($\mathrm{CDCl_3}$, δ): 10.8, 10.9, 22.65, 22.69, 40.4, 42.5, 121.0, 126.7, 126.8, 127.3, 127.5, 130.4, 130.5, 132.3, 134.7, 134.9, 135.5, 135.7, 135.8, 136.1, 136.4, 143.7, 143.9, 153.76, 153.83.

6b

Purity: 100% (by HPLC). mp: 263 °C. MALDI-TOF MS: 748.1 (M + Li^+). ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 0.59 (t, J = 7.43 Hz, 3H), 0.65 (t, J = 7.43 Hz, 3H), 1.06, (m, 2H), 1.14 (m, 2H), 2.74 (m, 2H), 2.81 (m, 2H), 4.33 (t, J = 6.25 Hz, 1H), 4.40 (t, J = 6.25 Hz, 1H), 7.00 (d, J = 7.82 Hz, 4H), 7.12 (br, 4H), 7.15 (br, 6H), 7.28 (br, 4H). ^{13}C NMR ($\mathrm{CDCl_3}$, δ): 11.0, 11.1, 22.9, 23.0, 42.75, 42.82, 121.3, 127.2, 127.8, 130.6, 130.8, 132.4, 135.0, 135.1, 135.6, 136.5, 143.8, 144.2, 153.8, 154.0.

Polymerization

A mixture of **6** (0.6 mmol), decafluorobiphenyl (0.63 mmol), potassium carbonate (0.9 mmol), and 6 mL of DMAc was slowly heated to 140 °C under a nitrogen atmosphere. The reaction was continued at 140 °C for 20 h. The brown, viscous solution was cooled to room temperature, diluted with 20 mL of chloroform, and poured into 400 mL of methanol containing 5 vol % of 37% HCl. The white powder was filtered, washed with water and methanol, reprecipitated from chloroform/methanol, and dried.

7a

Yield: 95%. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 7.02 (br, 11H), 7.08 (br, 6H), 7.22 (d, J = 8.21 Hz, 2H). ^{19}F NMR ($\mathrm{CDCl_3}$, δ): −141.3, −141.6, −156.1. IR (KBr): 3069, 3031 (ν_{CH}), 1649, 1487, 1402 ($\nu_{\mathrm{C{=}C}}$), 1095 (ν_{COC}), 839, 750, 700 (δ_{CH}), 725 (ν_{CF}) $\mathrm{cm^{-1}}$.

7b

Yield: 100%. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 6.96 (d, J = 8.21 Hz, 4H), 7.07 (br, 10H), 7.20 (d, J = 8.21 Hz, 4H). ^{19}F NMR ($\mathrm{CDCl_3}$, δ): −141.7, −142.5, −157.0.

Phosphonation

A typical procedure is as follows. To a solution of diethylphosphite (6 mmol), triethylamine (6 mmol), and tetrakis(triphenylphosphine)palladium (0.15 mmol) in 3 mL of DMSO, polymer **7a** (0.3 mmol) was dissolved under a nitrogen atmosphere. The mixture was reacted at 100 °C for 70 h to obtain a brown suspension. The mixture was poured into 200 mL of methanol containing 5 vol % of 37% HCl. The product was filtered, washed with water and methanol, reprecipitated from chloroform/methanol, and dried to give polymer **8a**.

8a

Yield: 98%. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 1.20 (t, J = 7.03 Hz, 6H), 3.98 (dq, J_{HH} = 7.19 Hz, J_{PH} = 23.84 Hz, 4H), 7.03 (m, 15H), 7.21 (br, 2H), 7.54 (dd, J_{HH} = 6.82 Hz, J_{PH} = 12.90 Hz, 2H). ^{19}F NMR ($\mathrm{CDCl_3}$, δ): −141.3, −141.6, −156.0. ^{31}P NMR ($\mathrm{CDCl_3}$, δ): 19.5. IR (KBr): 3070, 3029, 2964, 2930 (ν_{CH}), 1649, 1485, 1400 ($\nu_{\mathrm{C{=}C}}$), 1095 (ν_{COC}), 1025 (ν_{POC}), 842, 752, 700 (δ_{CH}), 725 (ν_{CF}) $\mathrm{cm^{-1}}$.

8b

Yield: 100%. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 1.17 (t, J = 7.03 Hz, 12H), 3.96 (dq, J_{HH} = 7.62 Hz, J_{PH} = 18.17 Hz, 8H), 7.03 (br, 10H), 7.21 (br, 4H), 7.52 (dd, J_{HH} = 7.03 Hz, J_{PH} = 12.31 Hz, 4H). ^{19}F NMR ($\mathrm{CDCl_3}$, δ): −141.3, −141.4, −156.0. ^{31}P NMR ($\mathrm{CDCl_3}$, δ): 19.1.

Dealkylation

Into a solution of polymer **8** (0.3 mmol) in 20 mL of carbon tetrachloride, bromotrimethylsilane (1.0 mL) was added dropwise at 10 °C under a nitrogen atmosphere. After complete addition, the mixture was allowed to warm to 25 °C over 1 h. The mixture was further reacted at 50 °C for 24 h to obtain a brown suspension. The mixture was poured into 300 mL of methanol containing 5 vol % of 37% HCl. The product was filtered, washed with methanol, reprecipitated from DMSO/1% HCl containing methanol, and dried to give polymer **9**.

9a

Yield: 98%. ^{1}H NMR (DMSO-d_6, δ): 7.02 (br, 6H), 7.07 (br, 9H), 7.27 (br, 2H), 7.44 (br, 2H). ^{19}F NMR (DMSO-d_6, δ): -140.9, -155.7. ^{31}P NMR (DMSO-d_6, δ): 13.3. IR (KBr): 3071, 3028 (ν_{CH}), 1649, 1485, 1402 ($\nu_{C{=}C}$), 1093 (ν_{COC}), 843, 752, 698 (δ_{CH}), 725 (ν_{CF}) cm^{-1}.

9b

Yield: 92%. ^{1}H NMR (DMSO-d_6, δ): 7.11 (br, 10H), 7.20 (br, 4H), 7.38 (br, 4H). ^{19}F NMR (DMSO-d_6, δ): -140.0, -140.9, -155.9. ^{31}P NMR (DMSO-d_6, δ): 13.3.

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