Synthesis of Novel Phosphinic Acid-Containing Polymers

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ABSTRACT: Three arylene difluoride monomers containing phosphine oxide (**1**), phosphinic acid (**2**), or phosphinate ester (**3**) groups were prepared and polymerized with bisphenol A to give novel poly-(arylene ether)s (**4**, **5**, and **6**). The polymers obtained had moderate molecular weights (η_{inh}: 0.14–0.30 dL g^{-1} in *N*-methylpyrrolidinone) and glass-transition temperatures (T_g: 102–200 °C), depending on the phosphine group in the main chain. Using bis(4-fluorophenyl)sulfone as a comonomer improved the polymerization to give copolymers with higher solution viscosities. The stoichiometric investigation revealed that 7 mol % excess of fluoride monomer gave the highest molecular weight copolymer **8** with η_{inh} of 0.78 dL g^{-1}, which had a T_g of 176 °C, a $T_{d_{10\%}}$ of 432 °C, and formed a hard film by casting from solution. © 2001 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 39: 1854–1859, 2001

Keywords: poly-(arylene ether); polymer electrolytes; phosphine oxide; phosphinic acid; phosphinate ester

INTRODUCTION

Solid polymer electrolytes (SPEs) having ionic conductivity are becoming important materials for the application of electronic devices such as batteries, sensors, fuel cells, and electrochromic displays.[1,2] Because of their good processability, light weight, and mechanical strength, SPEs are potentially advantageous over traditional inorganic materials. Considerable effort has been consumed with developing SPE materials for this purpose. SPEs are generally classified into two types: (1) polymers containing ionic substituents (ionomers)[3] and (2) mixtures (or composite) of polymer and small ionic molecules such as acids or salts.[4] In reference to the proton-conducting SPEs,[5] the best-known examples are crosslinked poly(styrenesulfonic acid), poly(perfluorosulfonic acid) (Nafion) or poly(perfluorocarboxylic acid) (Flemion), and polyacrylic acid doped with sulfonic or phosphonic acid. Because of its excellent thermal and chemical stability, Nafion has been preferrably used.[6] The high cost, however, is a serious drawback, and there are still great demands for new lower cost SPEs.

One of the main methods to produce thermally and oxidatively stable proton-conducting SPEs is to introduce strong acid substituents onto aromatic polymers. Sulfonated poly(arylene sulfone)s,[7] ethers,[8] or sulfides[9] have been reported, for example. Despite their potential usefulness, phosphonic and/or phosphinic acid-containing polymers have not been well studied because of the rather limited synthetic procedures available for their preparation compared with sulfonic acid derivatives. High acidity has been noted for benzenephosphonic acid monomethyl ester (pK_a 2.97 in water) and diphenylphosphinic acid (pK_a 2.32 in 7% EtOH).[10] To the best of our knowledge, there has been no research on aromatic polymers having phosphinic acid groups in the main chain. In the present article, we describe our successful synthesis of phosphinic acid-containing poly-(arylene ether)s. The traditional nucleophilic sub-

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stitution polymerization of bis(4-fluorophenyl)-phosphinic acid with bisphenol A (BPA) gave the title compound. The reaction behaviors, including copolymerization with bis(4-fluorophenyl)sulfone and the thermal properties of the polymers, are described.

EXPERIMENTAL

Materials

All the solvents used for the monomer synthesis and polymerization were distilled before use. The commercial reagents, 1-fluoro-4-iodobenzene, diethyl phosphite, magnesium, 30% hydrogen peroxide, butyl iodide, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), and potassium carbonate, were purchased from Aldrich Chemical Co. and used as received. Bis(4-fluorophenyl)sulfone was purified by crystallization twice from ethanol. BPA bis(propylcarbamate) was prepared as reported in the literature.[11]

Measurements

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Mercury 300 or 400 spectrometer. The NMR chemical shifts were calibrated with tetramethylsilane (0 ppm for ^{1}H and ^{13}C) or trifluoroacetic acid (-77.0 ppm for ^{19}F) as the internal standard. Mass spectra were measured on a Kratos MS25RFA at the ionization energy of 70 eV. The inherent viscosity of the polymers was measured in *N*-methylpyrrolidinone (NMP) solution at a concentration of 0.2 dL g^{-1} at 27.0 °C using an Ubbelohde viscometer. DSC was carried out on a Seiko DSC220 thermal analyzer at a heating rate of 20 °C min^{-1} under nitrogen at a flow rate of 150 mL min^{-1}. Thermogravimetric (TG) and differential thermal analyses (DTA) were performed simultaneously on a Seiko TG/DTA220 at a heating rate of 20 °C min^{-1} under nitrogen at a flow rate of 300 mL min^{-1}.

Synthesis of bis(4-Fluorophenyl)phosphine Oxide (1)

The previously reported procedure[12] has been modified as follows. To the suspension of magnesium (0.15 mol) in 30 mL of diethyl ether, 1-fluoro-4-iodobenzene (0.15 mol) in 30 mL of diethyl ether was added dropwise over a period of 30 min under nitrogen atmosphere on cooling with ice. Then the mixture was heated to reflux for 1 h. A solution of diethyl phosphite (63 mmol) in 30 mL of diethyl ether was added dropwise over a period of 1 h on cooling with ice. The mixture was heated to reflux for 30 min to complete the reaction. The reaction was quenched by the dropwise addition of 50 mL of 25% H_2SO_4. The crude product was extracted with 300 mL of CH_2Cl_2. The organic solution was washed with water and 15% K_2CO_3 aqueous solution, dried over $MgSO_4$, and crystallized from benzene/hexane to obtain the pure product **1** in 100% yield.

Thin layer chromatography (TLC) Rf: 0.32 ($CHCl_3$/EtOAc = 1/1). mp 113 °C (by DTA). Mass spectrometry (MS) *m/z*: 238 (M^+), 219 (M^+–F). ^{1}H NMR ($CDCl_3$) δ 7.19–7.27 (m, 4H), 7.29, 8.90 (d, J_{PH} = 484.7 Hz, 1H), 7.66–7.75 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 116.56 (q, $^2J_{CF}$ = 21.59 Hz, $^3J_{CP}$ = 14.11 Hz), 126.92 (q, $^4J_{CF}$ = 3.46 Hz, $^1J_{CP}$ = 105.09 Hz), 133.28 (q, $^3J_{CF}$ = 9.21 Hz, $^2J_{CP}$ = 13.24 Hz), 165.54 (q, $^1J_{CF}$ = 254.51 Hz, $^4J_{CP}$ = 3.46 Hz). ^{19}F NMR ($CDCl_3$) δ -104.66 (d, $^5J_{PF}$ = 321.04 Hz).

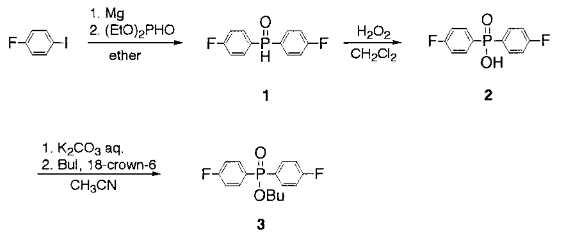
Synthesis of bis(4-Fluorophenyl)phosphinic Acid (2)

A solution of bis(4-fluorophenyl)phosphine oxide (63 mmol) in 100 mL of CH_2Cl_2 was reacted with 60 mL of 30% H_2O_2 aqueous solution for 1 h at 0 °C and 20 h at 20 °C. The mixture was made alkaline with 200 mL of 2.0 *N* NaOH. The aqueous layer was acidified with concentrated HCl to precipitate a white powder. The product was washed with water and dried to obtain bis(4-fluorophenyl)phosphinic (**2**) acid in 44% yield.

TLC Rf: 0.28 (MeOH/EtOAc = 1/2). mp 118 °C (by DTA, lit.[13] 116–118 °C). MS *m/z*: 254 (M^+), 235 (M^+–F). ^{1}H NMR ($CDCl_3$) δ 7.00–7.05 (m, 4H), 7.64–7.70 (m, 4H), 13.25 (br, 1H). ^{13}C NMR ($CDCl_3$) δ 115.72 (q, $^2J_{CF}$ = 21.59 Hz, $^3J_{CP}$ = 14.68 Hz), 128.40 (q, $^4J_{CF}$ = 3.46 Hz, $^1J_{CP}$ = 145.40 Hz), 133.75 (q, $^3J_{CF}$ = 8.64 Hz, $^2J_{CP}$ = 12.09 Hz), 165.06 (q, $^1J_{CF}$ = 253.36 Hz, $^4J_{CP}$ = 4.03 Hz). ^{19}F NMR ($CDCl_3$) δ -107.42 (br).

Synthesis of *n*-Butyl bis(4-Fluorophenyl)phosphinate (3)

A solution of bis(4-fluorophenyl)phosphinic acid (12 mmol) and potassium carbonate (6 mmol) in 30 mL of H_2O was heated at 80 °C for 1 h to give a white slurry. The mixture was evaporated and dried in vacuum at 120 °C over P_2O_5 overnight.



Scheme 1

The resulting white solid of dry potassium bis(4-fluorophenyl)phosphinate was dissolved in 100 mL of CH_3CN containing *n*-butyl iodide (50 mmol) and 18-crown-6 (1 mmol). The mixture was heated to reflux for 20 h and then evaporated to dryness. The crude product was dissolved in 200 mL of benzene and washed with water several times. Evaporation of the organic layer gave a light yellow oil of pure *n*-butyl bis(4-fluorophenyl)phosphinate (**3**) in 74% yield.

TLC Rf: 0.64 ($CHCl_3$/EtOAc = 1/1). MS (*m/z*): 310 (M^+), 253 (M^+–*n*-Bu). ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.42 Hz, 3H), 1.44 (m, 2H), 1.70 (m, 2H), 4.03 (m, 2H), 7.13–7.18 (m, 4H), 7.78–7.84 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 13.79, 19.04, 32.72 (d, $^3J_{CP}$ = 6.34 Hz), 65.09 (d, $^2J_{CP}$ = 6.33 Hz), 116.17 (q, $^2J_{CF}$ = 21.59 Hz, $^3J_{CP}$ = 14.11 Hz), 127.77 (q, $^4J_{CF}$ = 3.46 Hz, $^1J_{CP}$ = 140.65 Hz), 134.33 (q, $^3J_{CF}$ = 8.93 Hz, $^2J_{CP}$ = 11.23 Hz), 165.40 (q, $^1J_{CF}$ = 253.36 Hz, $^4J_{CP}$ = 3.46 Hz). ^{19}F NMR ($CDCl_3$) δ −105.87 (d, $^5J_{PF}$ = 382.47 Hz).

Polymerization

A typical procedure includes the following: The mixture of bis(4-fluorophenyl)phosphinic acid (0.5 mmol), bis(4-fluorophenyl)sulfone (0.57 mmol), BPA bis(*n*-propylcarbamate) (1 mmol), and potassium carbonate (2.5 mmol) was dissolved in 4.5 mL of DMSO. The solution was heated at 160 °C under nitrogen atmosphere for 20 h. The viscous mixture was poured into 300 mL of methanol containing 5 vol % hydrochloric acid. The precipitated off-white powder was filtered, washed with water and methanol, and dried in vacuum to obtain the copolymer **8** (p = 0.5) in 70% yield.

^1H NMR ($CDCl_3$) δ 1.65 (s, 3H), 1.69 (s, 3H), 6.76 (d, J = 8.60 Hz, 2H), 6.91 (d, J = 8.99 Hz, 2H), 6.94 (d, J = 8.60 Hz, 2H), 7.00 (d, J = 8.99 Hz, 2H), 7.09 (d, J = 8.60 Hz, 2H), 7.24 (d, J = 8.60 Hz, 2H), 7.837 (d, J = 8.99 Hz, 2H), 7.844 (d, J = 8.99 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 31.1, 31.2, 42.3, 42.6, 115.1, 117.9, 120.0, 120.1, 125.7, 128.0, 128.1, 128.7, 129.9, 135.4, 147.4, 152.7, 153.0, 162.2.

RESULTS AND DISCUSSION

Synthesis of Monomers

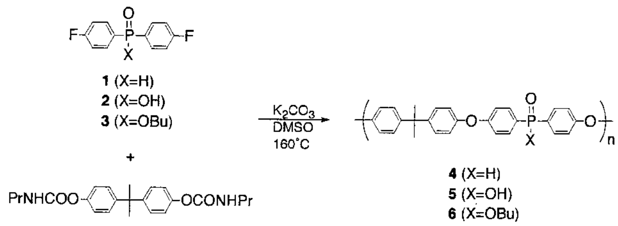
The synthesis of bis(4-fluorophenyl)phosphine oxide (**1**), bis(4-fluorophenyl)phosphinic acid (**2**), and *n*-butyl bis(4-fluorophenyl)phosphinate (**3**) was carried out as depicted in Scheme 1. The previously reported Grignard reaction of an aryl halide with diethyl phosphite[12] was modified for *p*-fluoro-iodobenzene to obtain **1** in 100% yield. The oxidation of **1** using 30% H_2O_2[14] and the following butylation reaction using a phase-transfer catalyst (18-crown-6)[15] was successful to give **2** (44%) and **3** (74%), respectively. All these monomers were pure, indicated by the TLC analyses in which a single spot was observed for each compound [Rf: 0.32 (**1**, $CHCl_3$/AcOEt = 1/1), 0.28 (**2**, MeOH/AcOEt = 1/2), 0.64 (**3**, $CHCl_3$/AcOEt = 1/1)]. The monomers were characterized by ^1H, ^{13}C, ^{19}F NMR, and MS as well as the mps.

The reactivity of the monomers in nucleophilic substitution reactions was estimated from the ^{13}C and ^{19}F NMR experiments[16] (Table I). The ^{13}C NMR chemical shifts of the carbon atoms *ipso* to the fluorine group were in the short range between 165.06 and 165.54 ppm, comparable to that of phenyl bis(4-fluorophenyl)phosphine oxide (165.37 ppm). The latter compound is well known to polymerize with many kinds of biphenol monomers to give high molecular weight poly-(arylene ether)s.[17] The susceptivity was predicted in the order of **1** (165.54 ppm) > **3** (165.40 ppm) > bis(4-fluorophenyl)phosphine oxide (165.37 ppm) > **2** (165.06 ppm). However, the chemical shifts are so close that the differences in the reactivity could be

Table I. ^{13}C NMR[a] and ^{19}F NMR Chemical Shifts of the Monomers

Compound	^{13}C NMR Chemical Shift (ppm)	^{19}F NMR Chemical Shift (ppm)
1	165.54	−104.66
2	165.06	−107.42
3	165.40	−105.87
(4-FPh)$_2$PhPHO	165.37	−105.82

[a] ^{13}C NMR chemical shift of the carbon *ipso* to the fluorine group.



Scheme 2

assumed to be small. The ^{19}F NMR chemical shifts of the compounds (from −104.66 to −107.42 ppm) gave the same conclusions.

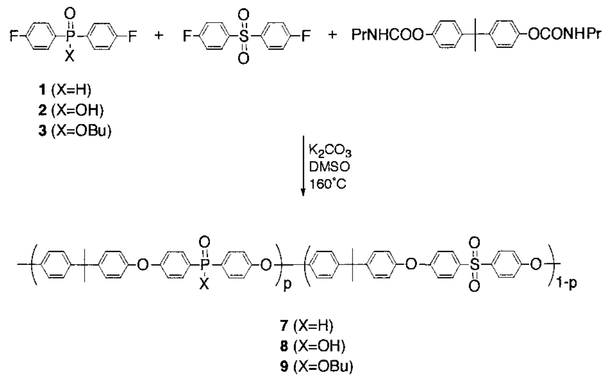
Polymerization of 1, 2, or 3 with BPA

The aforementioned three difluoro monomers were polymerized with BPA under basic conditions at 160 °C in dimethyl sulfoxide (DMSO) to produce the corresponding poly-(arylene ether)s (Scheme 2). Because the carbamoyl-masking groups improve these kinds of nucleophilic-substitution polymerization reactions,[11] BPA bis(propylcarbamate) was used. During the polymerization, compounds **1** and **2** reacted with K_2CO_3 to form the potassium salts. The salts were not soluble in the solvent; therefore, the mixture suddenly became a heterogeneous slurry on heating. After 20 h of polymerization of **1** with BPA, polymer **4** was obtained as a white powder in 52% yield (Table II). Gel permeation chromatographic (GPC) analysis was not possible because there is a strong interaction between our phenogel GPC columns and the phosphine-containing polymers (the polymers stuck on the columns). The solution viscosity of **4** was determined to be 0.24 dL g^{-1} in NMP by using an Ubbelohde viscometer. Compound **2** gave a lower molecular weight polymer **5** (η_{inh} = 0.14 dL g^{-1}) in only 25% yield. Polymer **5** with phosphinic acid groups in the main chain was very soluble in polar organic solvents (dimethylformamide, DMSO, NMP), slightly soluble in chloroform, but not soluble in water. The polymerization of **3** with BPA gave the highest molecular weight polymer **6** (η_{inh} = 0.30 dL g^{-1}) in 78% yield. Polymer **6** was soluble in many organic solvents like benzene, chloroform, tetrahydrofuran, and dimethylformamide. The lower molecular weight products were even soluble in methanol. This accounts for the low yield of the polymers because they were isolated by precipation in methanol. The film obtained by casting from solution was brittle and not self-supporting. DSC analysis showed that **6** has a glass-transition temperature (T_g) of 125 °C. The flexible *n*-butyl groups made the T_g of **6** 75 °C lower than that of **4**. Polymer **6** began to decompose at about 300 °C ($T_{d_{10\%}}$: 325 °C) under nitrogen as a result of the degradation of butyl phosphinate ester groups. Polymers **4** and **5** are more thermally stable and do not decompose up to 400 °C. Although several trials for the hydrolysis of **6** to produce **5** were made, the *n*-butyl phosphinate ester groups were intact even after the treatment with KOH aqueous/DMSO (at 80 °C) or HCl aqueous/chloroform (at 60 °C).

Table II. Synthesis of Polymers **4, 5,** and **6**

Polymer	Yield (%)	η_{inh} (dL g^{-1})^a	T_g (°C)	$T_{d_{10\%}}$ (°C)^b
4	52	0.24	200	477
5	25	0.14	102	422
6	78	0.30	125	325

^{a} In NMP at 27°C.
^{b} Temperature for 10% weight loss under nitrogen.



Scheme 3

Copolymerization of 1, 2, or 3 and bis(4-Fluorophenyl)sulfone with BPA

To produce higher molecular weight polymers, copolymerization with bis(4-fluorophenyl)sulfone was investigated (Scheme 3). The copolymerization was successful and gave polymers (**7**, **8**, or **9**) with a higher solution viscosity (up to 0.39 dL g^{-1} in NMP) than that of the corresponding homopolymers (**4**, **5**, or **6**) (Table III). Because the copolymers were more soluble than the homopolymers and even somewhat soluble in methanol, the isolated yields were not quantitative. However,

Table III. Synthesis of Copolymers **7, 8,** and **9**

Polymer	p	Yield (%)	η_{inh} (dL g^{-1})[a]	T_g (°C)	$T_{d_{10\%}}$ (°C)[b]
7	0.5	78	0.32	202	432
7[c]	0.5	65	0.39	225	454
8	0.1	85	0.33	191	490
8	0.2	67	0.37	183	452
8	0.3	59	0.14	184	465
8	0.5	31	0.14	157	428
9	0.2	91	0.19	175	445
9	0.4	81	0.11	183	401

[a] In NMP at 27°C.
[b] Temperature for 10% weight loss under nitrogen.
[c] Polymerization run in *N*,*N*-dimethylacetamide.

the copolymer compositions were consistent with the monomer feed ratio, which was confirmed by the integration ratio in the ^{1}H NMR spectra. A typical ^{1}H NMR spectrum of copolymer (**8**, $p = 0.2$) is shown in Figure 1 where two kinds of methyl groups of the isopropylidene moieties attached to arylphosphinic acid and arylsulfone groups were observed at 1.65 and 1.69 ppm. All the aromatic protons were well assigned to the proposed structure. The ^{13}C NMR spectrum showed 2 sets of isopropylidene carbons and 16 aromatic carbons, supporting the formation of the copolymer (Fig. 2).

If water is present in the reaction, the hydrolysis of fluoride groups could occur to give phenoxide ions, thus upsetting the stoichiometry. On the assumption that it would be difficult to remove all the water formed by the reaction of **2** and potassium carbonate because the salt formed would be expected to be very hydrophilic, we carried out the reaction using a small excess of **2** in the copolymerization of **2** (50 mol %) and bis(4-fluorophenyl)sulfone (50 mol %) with BPA (Table IV). The highest molecular weight copolymer **8** (η_{inh}: 0.78 dL g^{-1}) was obtained in 70% yield when 7 mol % excess of **2** was used. The polymer was obtained as a white fibrous material and gave a hard and transparent film by casting from chloroform solution. The thermal analysis of the polymer showed a high T_g of 176 °C and a $T_{d_{10\%}}$ of 432 °C, comparable to that of poly(perfluorosulfonic acid) (Nafion; T_g 104 °C, $T_{d_{10\%}}$ 429 °C). Although the polymer film does not swell in pure water, it does swell in aqueous solution containing a small amount (ca. 3 vol %) of DMSO or NMP. These thermal and hydrophilic properties should make

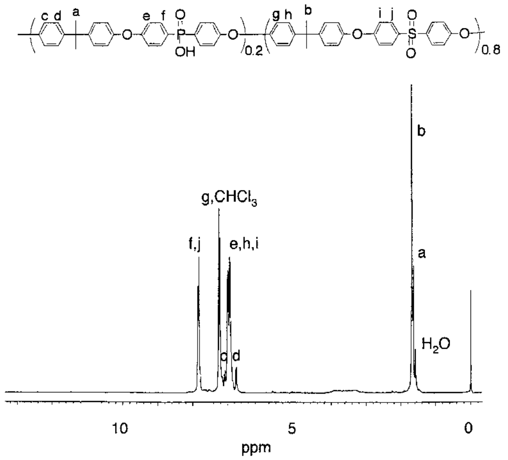


Figure 1. ^{1}H NMR spectrum of copolymer **8** ($p = 0.2$).

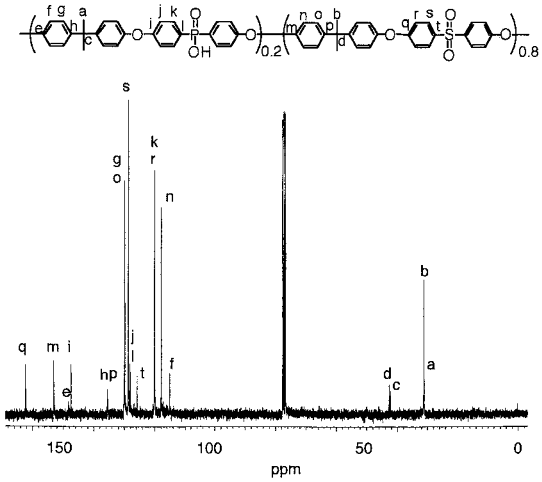


Figure 2. ^{13}C NMR spectrum of copolymer **8** ($p = 0.2$).

Table IV. Stoichiometry Effect on the Copolymerization of **2** and bis(4-Fluorophenyl)-sulfone with BPA

Excess of **2**	Yield (%)	η_{inh} (dL g^{-1})[a]	T_g (°C)	$T_{d_{10\%}}$ (°C)[b]
0	31	0.14	157	428
0.013	35	0.34	164	432
0.05	42	0.25	156	433
0.07	70	0.78	176	432
0.07[c]	45	0.16	171	422
0.1	48	0.29	169	439

[a] In NMP at 27°C.
[b] Temperature for 10% weight loss under nitrogen.
[c] Polymerization run at 200°C in NMP.

the polymer potentially useful as a high-temperature-operating cation exchange resin or a polymer electrolyte for fuel cells.

In light of the results listed in Table IV, the polymerization of **2** and BPA bis(propylcarbamate) was carried out using 7 mol % excess of **2**. A higher molecular weight polymer **5** (η_{inh}: 0.26 dL g^{-1}) was obtained in a higher yield (80%) than that produced from the equimolar amount of monomers (η_{inh}: 0.14 dL g^{-1}, 25% yield, see Table II).

CONCLUSION

Phosphine-containing aromatic difluorides **1**, **2**, and **3** were synthesized by the Grignard reaction of 1-fluoro-4-iodobenzene with diethyl phosphite, followed by oxidation and esterification. Both the ^{13}C and ^{19}F NMR analyses suggested that these difluoride monomers should be almost as reactive as phenyl bis(4-fluorophenyl)phenylphosphine oxide in the nucleophilic displacement reactions. Although the polymerization of **1**, **2**, or **3** with propyl-carbamoyl-masked BPA did not give very high molecular weight polymers, the application of bis(4-fluorophenyl)sulfone as a comonomer gave polymers with a higher solution viscosity up to 0.78 dL g^{-1} in NMP. From the stoichiometric investigations, it was found that trace amounts of water are crucial and hydrolize the fluoride monomers. A 7 mol % excess of difluoride monomer was necessary to obtain the highest molecular weight copolymer. Copolymer **8** was soluble in many organic solvents and gave a film by casting from solution. A high thermal stability (T_g: 176 °C, $T_{d_{10\%}}$: 432 °C) was observed. The polymers did not have high hydrophilicity; however, small amounts of polar organic solvents helped them to swell in water.

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