

**Preparation and Characterization of Fluorine-containing
Aromatic Condensation Polymers VIII.
Aromatic Polyether and Copolyethers
from 2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane,
2,2-Bis(4-hydroxyphenyl)propane, or both
and Bis(4-fluorophenyl)phenylphosphine Oxide**

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ABSTRACT: A series of hexafluoroisopropylidene group-containing aromatic polyether and copolyethers with a wide range of unit ratios were synthesized by high-temperature solution polycondensation of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**1a**), 2,2-bis(4-hydroxyphenyl)propane (**1b**), or both with bis(4-fluorophenyl)phenylphosphine oxide, and the effect of fluorine substitution on the properties of these polymers is discussed in relation to the fluorine contents. High- to moderate-molecular-weight polyethers with reduced viscosities of 0.39–0.55 dL g⁻¹ were obtained in high yields by using anhydrous potassium carbonate as a base and *N,N*-dimethylacetamide as a medium at 160 °C for 48 h. Regardless of the fluorine contents, these polymers all were soluble in various organic solvents, including benzene, chloroform, and tetrahydrofuran, and afforded colorless, transparent, and tough films by solution casting. The contact angles of the films to water increased significantly with increasing fluorine content. The glass transition temperatures also increased monotonously with the increase of fluorine content, whereas the temperatures of 5% weight loss and 10% weight loss under nitrogen were scarcely affected by fluorine substitution. These films with and without fluorine exhibited a very sharp cutoff at a wavelength shorter than 290 nm and are colorless. Optically estimated dielectric constant of **1a**-based homopolyether was 2.79, which was remarkably lower than the value of **1b**-based homopolyether, 2.97. [DOI 10.1295/polymj.37.399]

KEY WORDS Fluorine-containing Polymer / Phosphorous-containing Polymer / Aromatic Polyether / 2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane / 2,2-Bis(4-hydroxyphenyl)propane / Bis(4-fluorophenyl)phenylphosphine Oxide / Hexafluoroisopropylidene Group /

Aromatic polyethers are characterized as high-performance film and plastic materials with a favorable balance of physical, chemical, and mechanical properties. A wide variety of aromatic polyethers have so far been synthesized, and the relationship between their primary structures and polymer properties has been studied extensively.¹ However, the synthesis of aromatic polyethers containing fluorine has been reported only sparingly to date. In 1967, Johnson *et al.*² reported on the synthesis of hexafluoroisopropylidene (HFIP) group-containing polyether-ketone from 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**1a**) and 4,4'-difluorobenzophenone. Gerbi *et al.*³ synthesized tetrafluoro-1,4-phenylene unit-containing polyether from 2,2-bis(4-hydroxyphenyl)propane (**1b**) and hexafluorobenzene. No detailed properties, except thermal one, of both the polymers has been disclosed. In 1987, Shimizu *et al.*⁴ reported on the synthesis and characterization of four 2,5-difluoroisophthalonitrile unit-containing polyethers from various bisphenols and tetrafluoroisophthalonitrile. Tullos *et al.*⁵ synthe-

sized and characterized four HFIP group-containing polyether-ketones from **1a** and/or 2,2-bis[4-(4-fluorobenzoyl)phenyl]-1,1,1,3,3,3-hexafluoropropane. These polymers have been identified to have excellent potential for the use in perselective membranes and composite materials.

Much effort has been directed toward the synthesis and characterization of fluorine-containing condensation polymers.^{6,7} A series of our studies on the synthesis, characterization, and evaluation of fluorine-containing aromatic condensation polymers has revealed that HFIP group-containing polymers, such as polycarbonates,⁸ polyformals,⁹ polyketones,¹⁰ polyazomethines,¹¹ polybenzimidazoles,¹² polybenzothiazoles,¹³ polyacetals,¹⁴ and/or their respective copolymers, have unique properties such as good solubility in organic solvents, low inflammability, water and oil repellency, toughness and flexibility at low temperatures, smaller refractive index, lower dielectric constant, higher optical transparency, and high thermal stability in addition to the prominent characteristics

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inherent in the corresponding polymers without fluorine. Thus, the introduction of HFIP groups into existing aromatic condensation polymers can not only make them soluble or processable but also give them several additional characteristics.

In this study, a series of HFIP group-containing aromatic polyether (**3a**) and copolyethers (**3b–3g**) with a wide range of unit ratios were synthesized by high-temperature solution polycondensation of bisphenols **1a**, **1b**, or both with bis(4-fluorophenyl)phenylphosphine oxide¹⁵ (**2**), and the effect of fluorine substitution on the properties of these polymers is discussed in relation to the fluorine contents. Hirose *et al.*,¹⁵ McGrath *et al.*,¹⁶ and Cassidy *et al.*¹⁷ synthesized and characterized triphenylphosphine oxide unit-containing polyethers from difluoride **2** and various bisphenols including **1a** and/or **1b**. These polymers have been reported to be an interesting advanced material for the electronic and aerospace industries.

EXPERIMENTAL

Materials

2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**1a**), provided by Central Glass Co., Ltd. (Tokyo, Japan), was used after two recrystallizations from benzene and had a melting point of 158–159.5 °C (Lit.¹⁴ 162–163 °C). Commercial 2,2-bis(4-hydroxyphenyl)propane (**1b**) was recrystallized twice from benzene and had a melting point of 156–156.5 °C (Lit.¹⁴ 155–156 °C). Bis(4-fluorophenyl)phenylphosphine oxide (**2**), prepared according to the procedure of Hirose *et al.*¹⁵ in two steps starting from 4-fluorobromobenzene, was purified by two repeated vacuum distillations; it had a boiling point of 226–228 °C at 3 mmHg and a melting point of 124–125 °C (Lit.¹⁵ 127–128 °C). Solvents such as *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), *N*-methyl-2-pyrrolidinone (NMP), and tetramethylene sulfone (TMS) were vacuum distilled under nitrogen. Diphenyl sulfone (DPS) was recrystallized from methanol. Special grade anhydrous potassium carbonate was dried at 200 °C *in vacuo*.

Fluorine-containing Polyether (**3a**) from **1a** and **2**

Into a dry 30-mL three-necked flask were charged bisphenol **1a** (0.336 g, 1 mmol), difluoride **2** (0.314 g, 1 mmol), finely pulverized anhydrous potassium carbonate (0.276 g, 2 mmol), and DMAc (5 mL). The mixture was heated to 160 °C under nitrogen and then stirred at that temperature for 48 h. After cooling to ambient temperature, the resulting viscous solution was diluted with DMAc (10 mL) and then poured into methanol (300 mL) to create a white fibrous polymer,

which was filtered off and subjected successively to hot water and hot methanol rinses. The polymer was further purified by repeated reprecipitations with a DMAc–methanol system. The yield after two reprecipitations was 0.549 g (90%). The reduced viscosity in NMP was 0.47 dL g⁻¹, measured at a polymer concentration of 0.5 g dL⁻¹ at 30 °C. IR (film): 1590, 1490 (phenyl and phenylene), 1245 (C–O–C), 1180 cm⁻¹ (P=O). *Anal.* Calcd. for (C₃₃H₂₁F₆O₃P)_n (610.5)_n: C, 64.92%; H, 3.47%. Found: C, 64.29%; H, 3.24%.

Polyether (**3g**) from **1b**

IR (film): 1590, 1490 (phenyl and phenylene), 1240 (C–O–C), 1180 cm⁻¹ (P=O). *Anal.* Calcd. for (C₃₃H₂₇O₃P)_n (502.5)_n: C, 78.87%; H, 5.42%. Found: C, 78.35%; H, 5.13%.

Measurements

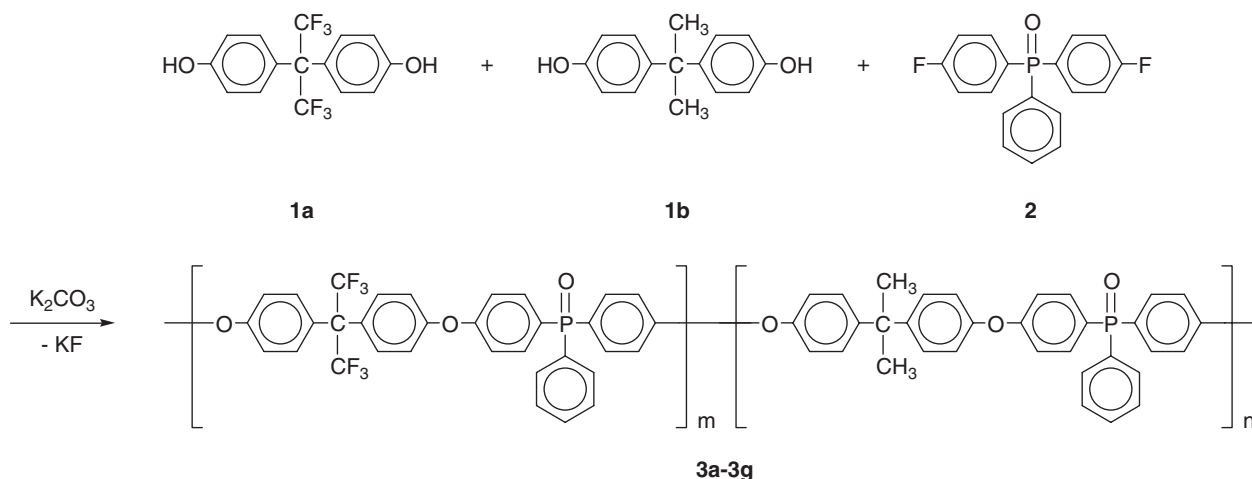
IR spectra were recorded on a Jasco FT/IR-460 spectrophotometer as films. Contact angles (θ_w 's) to water on film surfaces were measured with an Erma G-I contact anglemeter at 22 °C in air. Tensile properties were determined from stress-strain curves obtained with an Orientec STA-1150 at an elongation rate of 10% min⁻¹ with film specimens (3 mm wide, 20 mm long, *ca.* 0.1 mm thick). Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on powder specimens with Seiko DSC 6200 and TG/DTA 6200, respectively, under nitrogen at a heating rate of 10 K min⁻¹. UV–vis spectra of the polymer films were recorded on a Shimadzu UV-2400 PC spectrophotometer. Refractive indices of the polymer films were measured by an Atago Abbe refractometer 4T at ambient temperature in air. The measurements were made at a wavelength of 590 nm.

RESULTS AND DISCUSSION

Polymer Synthesis

The conventional aromatic nucleophilic substitution polymerization technique was applied for the synthesis of aromatic polyethers (**3a–3g**) from 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**1a**), 2,2-bis(4-hydroxyphenyl)propane (**1b**), or both and bis(4-fluorophenyl)phenylphosphine oxide (**2**):

The polycondensation was carried out at an elevated temperature of 160 or 250 °C in a polar medium in the presence of anhydrous potassium carbonate.^{18,19} The effect of reaction media was first investigated on the reaction of bisphenol **1a** with difluoride **2** (Table I). Among six solvents tried, DMAc was found to be the most suitable medium, affording polyether **3a** with the highest reduced viscosity of 0.27 dL g⁻¹ in a high yield of 83% at 160 °C for 20 h, and was selected for further polymerizations. The polymerization



Scheme 1.

Table I. Synthesis of polyether **3a** in various conditions

Solvent ^b	Reaction Conditions ^a		Polymer	
	Temperature (°C)	Time (h)	Yield (%)	η_{red} (dL g ⁻¹) ^c
DMAc (3)	160	48	92	0.45
DMAc (5)	160	20	83	0.27
DMAc (5)	160	48	90	0.47
DMAc (5)	160	72	92	0.46
DMAc (7)	160	48	82	0.39
DMSO (5)	160	20	20	—
HMPA (5)	160	20	69	0.20
NMP (5)	160	20	68	0.25
TMS (5)	250	5	36	—
DPS ^d (5)	250	5	36	—

^aPolymerization was carried out with **1a** (1 mmol) and **2** (1 mmol) in the solvent in the presence of anhydrous potassium carbonate (2 mmol). ^bThe volume of the medium given in parentheses was used. ^cReduced viscosity was measured at a polymer concentration of 0.5 g dL⁻¹ in NMP at 30 °C. ^d5 g of DPS was used.

was almost completed within 48 h, and 5 mL of DMAc were found to be enough for the reaction on a 1 mmol scale (Table I). The highest reduced viscosity of polymer **3a** thus attained was 0.47 dL g⁻¹.

Under the preferable conditions, *i.e.*, in 5 mL of DMAc at 160 °C for 48 h on a 1 mmol scale of monomers, a series of copolyethers **3b–3f** and homopolyether **3g** were synthesized by the reaction of **1a/1b** mixtures at feed ratios of 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 with **2** (Table II). These polyethers were obtained with relatively high reduced viscosities ranging from 0.39 to 0.55 dL g⁻¹ and in high yields.

Polymer Characterization

The formation of polyethers was confirmed by IR spectroscopy, elemental analysis, or both. The IR spectra of all the polymers indicated a very strong and broad absorption characteristic of C–O–C stretching of aryl ether group at around 1240 cm⁻¹. The elemental analysis for both homopolymers **3a** and **3g**

Table II. Synthesis and surface and thermal properties of polyethers **3a–3g**^a

Bisphenol 1a/1b	Polymer			Surface and Thermal Properties				
	Code	Yield ^b (%)	η_{red} (dL g ⁻¹) ^c	θ_w ^d (°)	T_g ^e (°C)	DT ₅ ^f (°C)	DT ₁₀ ^g (°C)	RW ₆₀₀ ^h (%)
100/0	3a	90	0.47	72	210	521	532	66
80/20	3b	90	0.53	70	209	520	529	61
60/40	3c	98	0.49	68	205	517	526	48
50/50	3d	90	0.55	69	205	523	536	46
40/60	3e	92	0.39	65	203	512	529	42
20/80	3f	87	0.44	65	200	521	527	46
0/100	3g	94	0.42	49	198	516	524	36

^aPolymerization was carried out with **1** (1 mmol) and **2** (1 mmol) in DMAc (5 mL) in the presence of anhydrous potassium carbonate (2 mmol) at 160 °C for 48 h. ^bThe yield was calculated on the basis of the theoretical structure. ^cMeasured at a polymer concentration of 0.5 g dL⁻¹ in NMP at 30 °C. ^dContact angle by water was measured at 22 °C in air. ^eGlass transition temperature determined by DSC at a scan rate of 10 K min⁻¹ under nitrogen. ^fTemperature at which 5% weight loss was recorded by TG at a heating rate of 10 K min⁻¹ under nitrogen. ^gTemperature at which 10% weight loss was recorded. ^hResidual weight at 600 °C.

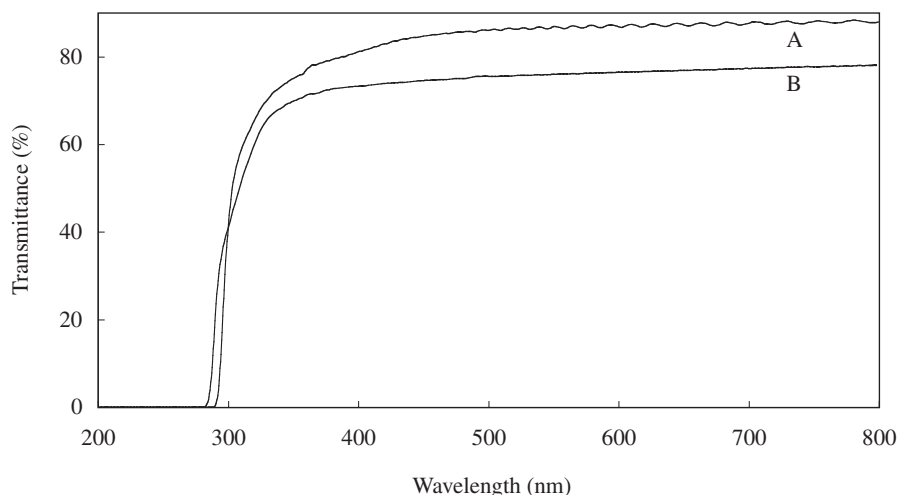


Figure 1. UV-vis spectra of polyether films. (A) **3a**, (B) **3g**.

supports the formation of the expected polyethers.

Regardless of the fluorine contents, these polymers all dissolved in a wide variety of organic solvents such as DMAc, NMP, benzene, nitrobenzene, *m*-cresol, *o*-chlorophenol, dichloromethane, chloroform, *sym*-tetrachloroethane, tetrahydrofuran, and dioxane. All the polymers gave colorless, transparent, and tough films when cast from the NMP solutions. The films self-extinguished as soon as the flame was removed.

The θ_w 's, a measure of wettability, of the films to water ranged from 49–72° (Table II). This result indicates that the introduction of fluorine imparts a remarkable effect on the film surface properties. Namely, the ability to repel water is effectively improved by introducing fluorine and increased exceedingly with increasing fluorine content. The increasing θ_w 's with the increase of fluorine content may be due to the concentration of lower surface energy groups or hydrophobic trifluoromethyl groups on the surfaces of the film.

The tensile properties of the films of two typical polyethers **3a** and **3g** were as follows: the tensile strength, elongation at break, and tensile moduli were 77 MPa, 3%, and 4.2 GPa for **3a** and 59 MPa, 3%, and 2.9 GPa for **3g**. The mechanical properties of both the films are excellent as indicated by the high tensile strength and tensile moduli.

The glass transition temperature (T_g) has been reported to be 197 °C for homopolymer **3g**.¹⁵ The T_g of homopolymer **3a** was 210 °C, which is higher than that of **3g** obtained here by 12 K (Table II). The T_g 's of the copolymers tended to increase monotonously between those of the two homopolymers as the fluorine content was increased (Table II). The presence of bulky and distorted HFIP groups increases the chain rigidity along the polymer backbone, consequently increasing the T_g 's. The TG curves of the

polyethers showed a 5% weight loss (DT_5) at 512–523 °C, a 10% weight loss (DT_{10}) at 524–536 °C, and residual weight at 600 °C (RW_{600}) of 36–66%, respectively, under nitrogen (Table II). Thus, these polyethers with and without fluorine exhibited good resistance to thermal degradation up to *ca.* 500 °C. It is noteworthy that the RW_{600} for homopolymer **3a** is 30% higher than that for homopolymer **3g** and 66% weight is retained even at 600 °C.

The transmission UV-vis spectra of two representative polyether films of **3a** and **3g** are shown in Figure 1. Both the films with and without fluorine exhibited a very sharp cutoff at a wavelength shorter than 290 nm and are colorless. This excellent transparency will enable application of the polyethers in the optoelectric industry.

The averaged refractive indices of polyethers **3a** and **3g** were in the order 1.594 and 1.643, and the dielectric constants that were estimated from the values according to the modified Maxwell equation²⁰ were 2.79 and 2.97, respectively. This result indicates that the incorporation of HFIP groups into the polymer backbone is very effective for the depression of dielectric constant.

CONCLUSIONS

A series of hexafluoroisopropylidene group-containing aromatic polyether and copolyethers with a wide range of unit ratios were synthesized through fluorine displacement polymerization of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, 2,2-bis(4-hydroxyphenyl)propane, or both and bis(4-fluorophenyl)phenylphosphine oxide. The introduction of hexafluoroisopropylidene groups successfully brought about decreases in the wettability and dielectric constant and an increase in the glass transition tempera-

ture of the polymers. These polyethers are considered to be promising soluble or processable high-temperature film and plastic materials.

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