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Synthesis of Fluorinated Poly(Aryl Ether)s Containing 1,4-Naphthalene Moieties

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8.1. INTRODUCTION

Linear aromatic polymers have long been known for their usefulness in meeting the high-performance requirements for structural resins, polymer films, and coating materials needed by the aerospace and electronics industries. Aromatic polyimides[1,2] and poly(aryl ether ketone)s[3-6] are the polymers of choice for these applications because of their unique combination of chemical, physical, and mechanical properties. Poly(aryl ether ketone)s are especially desirable because they are economically accessible by both nucleophilic and electrophilic routes. In addition, because of the flexibilizing ether and ketone groups present in the polymer backbone, poly(aryl ether ketone)s are generally more easily processed than polyimides. In recent years, poly(aryl ether ketone)s have been prepared containing 2,6-naphthalene and 1,5-naphthalene units. Ohno[4] and Hergenrother[5] reported that polyetherketones containing naphthalene moieties in the main chain possess higher T_g's but low solubility in ordinary organic solvents.

    Considerable attention has also been devoted to the preparation of fluorine-containing polymers because of their unique properties and high-temperature

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performance. Among the high-performance fluorinated polymers being studied for use in aerospace and electronics applications are the fluorinated aromatic poly-ethers prepared containing hexafluoroisopropylidene (HFIP) units.[7] Polymers containing HFIP units have been studied for applications as films, coatings for optical and microelectronics devices, gas separation membranes, and as a matrix resin in fiber-reinforced composites. Frequently the incorporation of HFIP units into the polymer backbone leads to polymers with increased solubility, flame resistance, thermal stability, and glass transition temperature, while also resulting in decreased color, crystallinity, dielectric constant, and moisture absorption.

Recently the synthesis and characterization of novel fluorinated poly(aryl ether)s containing perfluorophenylene moieties[8–10] was also reported. These fluorinated polyethers were prepared by reaction of decafluorobiphenyl with bisphenols. These polymers exhibit low dielectric constants, low moisture absorp-tion, and excellent thermal and mechanical properties. Tough, transparent films of the polymers were prepared by solution-casting or compression-molding. The fluorinated poly(aryl ether)s containing perfluorophenylene moieties are good candidates for use as coatings in microelectronics applications.

As part of an effort to develop high-performance, high-temperature-resistant polymers for microelectronics applications, we also recently described a series of both partially fluorinated and nonfluorinated poly(aryl ether ketone)s containing amide, amide–imide, cyano oxadizole, or pyridazine groups and characterized their thermal and electrical properties.[11]

On the basis of the above studies reported thus far, we have designed and synthesized a series of novel poly(aryl ether)s containing both hexafluoroisopro-pylidene and 1,4-naphthalene moieties. We found these new polyarylethers to have good solubility, high T_g's, and excellent thermal stability. We report herein the synthesis and characterization of these poly(aryl ether)s containing fluorinated 1,4-naphthalene moieties.

8.2. EXPERIMENTAL

8.2.1. Starting Materials

N,N-Dimethylacetamide (DMAc), 4-fluorobenzoic acid, 4-fluorobenzoyl chloride, aluminum chloride, 1-bromonaphthalene, nitrobenzene, ferric chloride, dimethyl sulfone, 4,4′-dihydroxybiphenyl (DHB), and potassium carbonate were obtained from Aldrich and used without purification. 4,4-(Hexafluoroiso-propylidene)-diphenol (6F-BPA), 9,9-bis(4-hydroxyphenyl)fluorene (HPF), and 1,1-bis(4-hydroxyphenyl)-1-phenylethane (Bisphenol AP) were obtained from Ken Seika Corporation and used without purification. 4,4′-Dihydroxydiphenyl sulfone (DHDS) was obtained from Nachem Incorporated and used without purification.

8.2.1.1. 2,2-Bis[4-(1-Naphthoxy)Phenyl]Hexafluoropropane (**1**)

A 500-ml three-neck round-bottom flask equipped with nitrogen inlet, thermometer, overhead stirrer, and condenser was charged with 6F-BPA (24.5 g, 0.073 mol), 1-bromonaphthalene (31.0 g, 0.15 mol), potassium carbonate (21.9 g, 0.162 mol), copper (I) iodide (0.8g), and DMAc (250ml). The reaction mixture was purged with nitrogen for 10 min and then heated, with stirring, at about 150°C under nitrogen for 5 days. The mixture was allowed to cool to room temperature and poured slowly into 500ml of water, resulting in the formation of a water-insoluble oil. The water/DMAc mixture was carefully decanted from the oil. The oil was dissolved in 200 ml of a 25/75 (by volume) mixture of hexane/toluene and was washed once with 100 ml of 5 wt% NaOH in water and twice with 100 ml of water. The hexane/toluene mixture was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield a brown oil (38.4 g), which partially crystallized on standing overnight at room temperature. The product was suspended in a 50150 (by weight) mixture of ethanol/methanol- and filtered to yield an off-white crystalline solid (m.p. 94–95°C). The yield was 34.2 g (79%). GC/MS m^+/e = 588. Calculated for $C_{49}H_{28}O_4F_8$: C, 71.43; H, 3.77; F, 19.37. Found: C, 71.54; H, 3.63; F, 19.51.

8.2.1.2. 2,2-Bis[4-(4-{4-Fluorobenzoyl}-1-Naphthoxy)Phenyl]Hexafluoropropane (**2**)

This compound was prepared as depicted in Scheme 1 using the following procedure: To a 250-ml round-bottom flask was added 10.00g (0.0170mol) of 2,2-bis[4-(1-naphthoxy)phenyl]hexafluoropropane (**1**), 5.71 g (0.0360 mol) of 4-fluorobenzoyl chloride, 2.3 g (0.0246 mol) of dimethyl sulfone, and 132 g of dichloromethane. The mixture was stirred under nitrogen until the solids dissolved, then cooled in an ice bath, and 14.5 g (0.109 mol) of aluminum chloride was added. The mixture was stirred for 1 h at ice-bath temperature, 24 h at room temperature, and 1 h at reflux. The mixture was allowed to cool to room temperature and poured into methanol. The resulting solid was filtered, washed with methanol and water, dried, and recrystallized from DMAc to yield 11.6 g (82% yield). m.p. = 261–263°C. Calculated for $C_{49}H_{28}O_4F_8$: C, 70.67; H, 3.39; F, 18.25. Found: C, 70.74; H, 3.36; F, 18.54.

8.2.2. Polymerizations

8.2.2.1. Homopolymerization of **1**: Preparation of 6FNE

As depicted in Scheme 2, homopolymerization of **1** to form the aromatic poly(aryl ether) 6FNE utilized the Scholl reaction in nitrobenzene with anhydrous ferric chloride at room temperature. A 100-ml round-bottom flask was charged

with **1** (3.6 g, 0.0061 mol) and dry nitrobenzene (25 ml). Anhydrous ferric chloride (2.96 g, 0.0183 mol) was added portionwise with stirring over 15 min. The mixture was stirred under nitrogen for 6 h. The mixture was poured into 300ml of methanol acidified with 1 ml of concentrated HCl. The precipitate was collected by filtration, washed three times with methanol and once with deionized water, and dried to yield 3.2 g (89%) of a tan powder.

8.2.2.2. Poly(Aryl Ether Ketone) Synthesis

Aromatic poly(aryl ether ketone)s containing 1,4-naphthalene moieties were prepared by the reaction of a bisphenol and **2** in the presence of potassium carbonate in DMAc at 160°C as depicted in Scheme 3. A typical polymerization was carried out as follows: To a 100-ml round-bottom flask was added 8.32 g (0.010 mol) of 2, 3.36 g (0.010 mol) of 4,4′-(hexafluoroisopropylidene) diphenol, 51.2 g of DMAc, and 3.1 g (0.022 mol) of potassium carbonate. The mixture was heated to 160°C with stirring under nitrogen for 18 h. The mixture was allowed to cool to room temperature. The polymer was precipitated by pouring the reaction mixture into a blender containing about 100 ml of water, filtered, washed three times with water and dried to yield 8.1 g (92% yield) as a white powder.

8.2.3. Polymer Films

6FNE was spin-coated from diethylbenzene at 17 wt% solids onto glass substrates. Solutions of polymers 3–7 (15–20 wt% solids) in xylene/NMP mixture (1 : 4 by weight) were spin-coated onto glass substrates. All the coatings were dried for 1 h at 100°C and for 45 min at 200°C. The films, about 10 µm thick, were released from the glass substrates by placing the substrate in deionized water after cooling to room temperature. All six poly(aryl ether)s yielded tough, flexible, creasable films.

8.2.4. Measurements

Dielectric constants were measured using the previously described fluid displacement method.[12] The capacitance of the films was measured using circular gold electrodes (1 in. diameter) mounted in a brass dielectric cell held to a constant 25°C and a GenRad Precision LC Digibridge (Model 1688) at 10KHz. Percent relative humidity was measured using a General Eastern dew-point hygrometer (System 1 100DP). Glass transition temperatures (T_g) reported in this chapter were determined in air using differential scanning calorimetry (DSC) with a heating rate of 10°C/min. Thermal gravimetric analyses (TGA)

were determined in air using a heating rate of 20°C/min Both DSC and TGA were performed on a Seiko SSC 5200 System DSC 220C TGA/DTA 320. IR spectral analysis was performed on a Bio-Rad FTS-60A FTIR.

The molecular-weight distributions were measured using a Waters GPC in the dual-detector mode (DRI and UV). The UV detector was operated at 254 nm. The samples were prepared by dissolving 2 mg of polymer in 10 ml of THE The injection volume was 200 µl. Separations were effected using two Polymer Labs 10-µm PL mixed-B columns. THF was used as the mobile phase. The molecular-weight distributions were calculated relative to narrow polystyrene standards ranging from 10^2 to 4 x 10^6 M_W.

Proton-decoupled ^{13}C-NMR spectra were recorded on a Varian XL-300 operating at 75.4 MHz. Approximately 250 mg of the sample was dissolved in 3 ml of deuterated chloroform. [13]C chemical shifts were referenced internally to $CDCl_3$ (77 ppm). A delay of 200s was used to ensure relaxation of all the carbon nuclei and 1000 transients were collected to assure a good signal-to-noise ratio.

Low-temperature dynamic mechanical analysis (DMA) studies were carried out on a Perkin-Elmer DMA7 operating in the penetration mode. Samples were scanned at 3°C/min and 1 Hz between –140°C and ambient temperature. The temperature was calibrated using high-purity indium and *n*-octane standards. Above ambient temperature studies were carried out using a Rheometric Scientific DMTA Mk II operating in dual-cantilever bending mode. Samples were scanned from ambient, through the glass transition, at 2°C/min over the frequency range 0.1–30Hz. Samples were prepared by pressing together solvent cast films at 300°C. The principal parameter determined was tan δ.
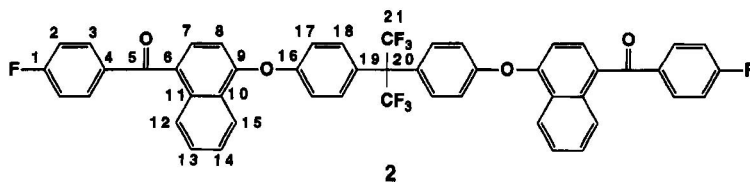
8.3. RESULTS AND DISCUSSION

The syntheses of **1** utilized the Ullmann ether synthesis.[13] Reaction of 2 mol of 1-bromonaphthalene with 4,4-(hexafluoroisopropylidene)diphenol afforded the desired product **1.** The reaction was carried out in DMAc at 160°C in the presence of potassium carbonate as the base and copper (I) iodine as the reaction catalyst to yield **1,** as depicted in Scheme 1. The reaction proceeded slowly but in good yield with easy isolation of the desired compound. Acylation of **1** with 4-fluorobenzoyl chloride to prepare **2** was carried out under modified Friedel–Crafts reaction conditions[14] using dimethyl-sulfone as catalyst moderator. Both **1** and **2** were easily recrystallized to yield high-purity monomers suitable for polymerizations.
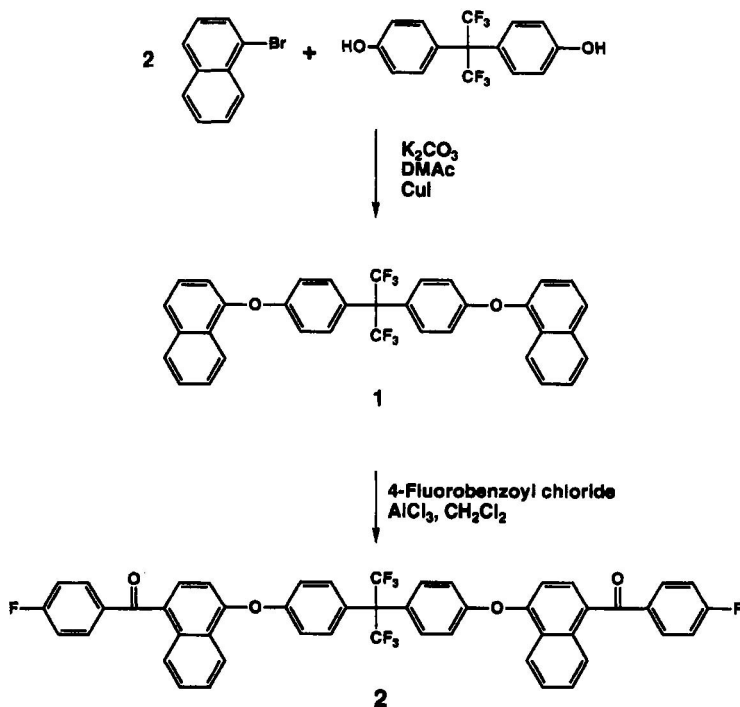
Scheme 1. Synthesis of monomer **2.**

Compounds **1** and **2** were identified by FTIR and ^{13}C-NMR. The ^{13}C proton decoupled spectra for **1** and **2** are dominated by signals ranging from 62 to 195 ppm. The ^{13}C chemical shift assignments were made based on comparisons with 4,4′-(hexafluoroisopropylidene)diphenol and from calculations based on substituted benzenes and naphthalenes.[15] The ^{13}C-NMR spectrum clearly showed that the Friedel–Crafts acylation of **1** by 4-fluorobenzoyl chloride yielded the 1,4-addition product exclusively. The ^{13}C chemical shifts for **2** are listed in Table 8.1. The key structural features in the FTIR spectrum of **2** include the following absorptions: aromatic C–H, 3074 cm^{-1}, ketone C=O, 1658 cm^{-1}, aromatic ether Ar—O—Ar, 1245 cm^{-1}, and C—F, 1175 cm^{-1}.

The homopolymerization of **1** consists of a room-temperature reaction of the monomer dissolved in nitrobenzene in the presence of anhydrous ferric chloride. Polymerizations were carried out under a stream of dry nitrogen. As depicted in Scheme 2, the homopolymerization of **1** to form 6FNE takes place by means of the Scholl reaction. The mechanism of the Scholl reaction was assumed to proceed through a radical-cation intermediate derived from the single-electron oxidation of the monomer and its subsequent electrophilic addition to the nucleophilic monomer. The reaction releases two hydrogens, both as protons, to form the

Table 8.1. ^{13}C Chemical Shifts (ppm) of 2,2-Bis[4-(4-{4-Fluorobenzoyl}-1-Naphthoxy)-Phenyl]Hexafluoropropane (**2**)

2

C1 = (167.4, 164.1)	C11 = 134.8
C2 = 115.7	C12 = 129.0
C3 = 132.0	C13 = 132.8
C4 = 133.0	C14 = 126.6
C5 = 195.6	C15 = 132.0
C6 = 131.6	C16 = 157.3
C7 = 128.3	C17 = 118.6
C8 = 115.4	C18 = 132.9
C9 = 155.1	C19 = 128.6
C10 = 126.8	C20 = (64.6, 64.3, 64.0, 63.7, 63.4, 63.1, 62.8)
	C21 = (118.6, 115.4, 122.2, 125.8)

1

Nitrobenzene
Ferric Chloride

6FNE
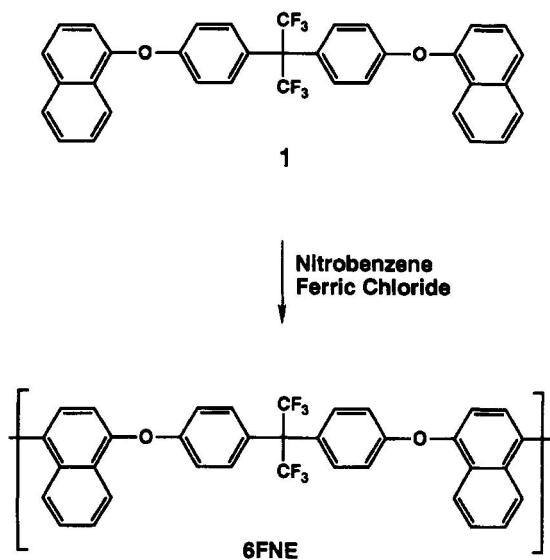
Scheme 2. Homopolymerization of **1**.

neutral polymer.[16] More recently, Percec[17] described the use of the Scholl reaction to prepare poly(ether ketone)s and poly(ether su1fone)s containing 4,4′-disubsti-tuted-1,1′-dinaphthyl units.

The homopolymerization of **1** was performed with a molar ratio of [FeCl3]/[monomer] equal to 3. The isolated polymer was thoroughly washed with methanol and water to remove the residual nitrobenzene and iron salts. 6FNE was soluble in a broad range of solvents, including NMP, DMAc, xylene, and THF 6FNE displayed a T_g of 247°C and a TGA onset of decomposition in air at 523°C. Films of 6FNE were tough, flexible, and creasable. The dielectric constant of 6FNE was 2.72 at 0% relative humidity (RH) and rose to only 2.79 at 83% RH. The FTIR spectrum of **3** is shown in Figure 8.1.

Figure 8.2 shows the a-relaxation of 6FNE, which is related to the glass transition process. In the first scan, a low-temperature shoulder is present on the main peak. Similar peaks have been observed in other rigid amorphous poly-mers.[18] It is claimed that this is not a true relaxation, but is due rather to the presence of defects that collapse on heating.[19] The peak is indeed diminished on the second scan, which suggests that it may be related to the thermal history of the glassy polymer. The T_g of 6FNE, defined at the temperature corresponding to the peak maximum, increases from 242°C on the first scan to 247ºC on the second. In addition, the intensity of the α-peak increases significantly. An analysis of the frequency dependence of the T_g, using an Arrhenius equation, shows that the apparent activation energy remains constant on both the first and second scans, at
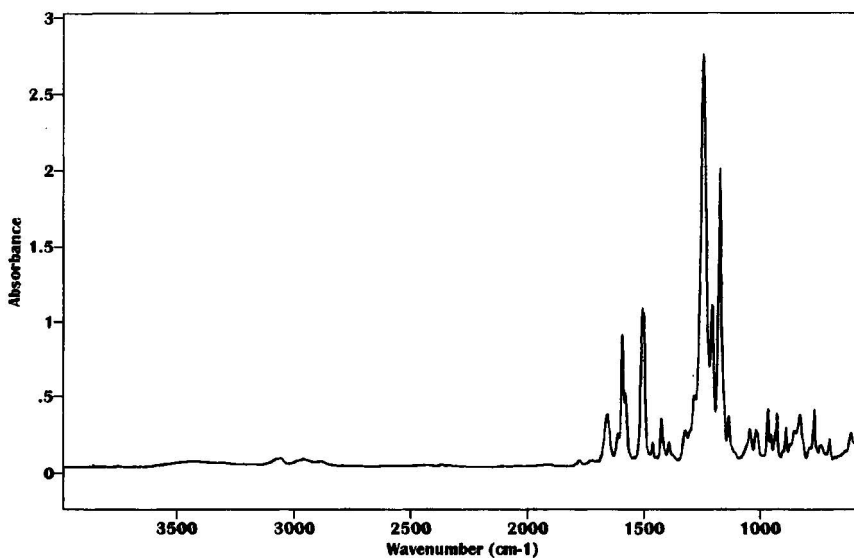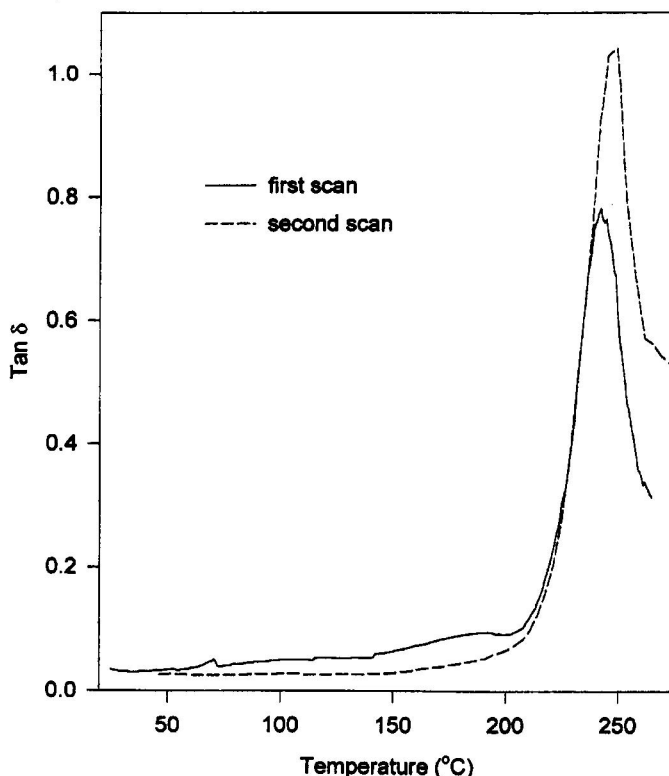

Figure 8.1 The FTIR spectra of **3**.

Figure 8.2. Temperature dependence on tan δ at 1 Hz in the α-relaxation region for 6FNE.

800 kJ/mol. This high value of the activation energy is a reflection of the rigid chain structure of 6FNE.

Figure 8.3 shows the temperature dependence of tan δ in the β-relaxation region of 6FNE. The β-peak is typically broad (centered around $-80°$C) and weak and arises from the localized motions of the polymer chains. The origins of secondary relaxations in rigid aromatic polymers have been attributed to superpositions of two motional processes: a low-temperature component reflecting local intrachain motions and a high-temperature cooperative component attributed to the local motions in ordered amorphous regions.[20] The mechanism of the process is suggested to be flips of the phenyl rings. The β-process is known to be sensitive to water content, aging history, and morphology.

Polycondensation reactions of **2** with diphenols were carried out in DMAc at 160°C using an excess of potassium carbonate to yield viscous solutions of the desired poly(aryl ether ketone)s. Judging by the viscosity increase, the polymerization reaction was near completion after only about 8 h at 160°C. Aqueous

workup of the reaction mixture yielded the 1,4-naphthalene-containing polymers as white powders. The isolated polymers were thoroughly washed with water to remove the residual DMAc and potassium salts.

2

HO-R-OH
DMAc, K$_2$CO$_3$
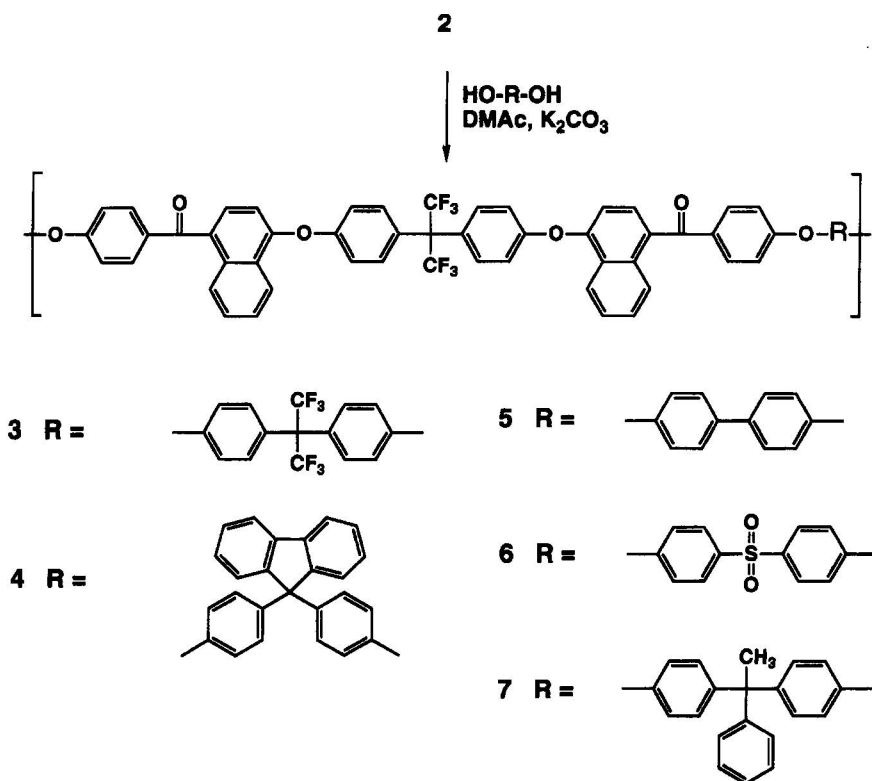
Scheme 3. synthesis of fluorinated poly (aryl ether ketone)s 3–7

Poly(ether ketone)s **3, 4, 5, 6,** and **7** were soluble in polar aprotic solvents such as DMAc and NMP and in chlorinated solvents such as chloroform. The improved solubility of these fluorinated poly(ether ketone)s can be explained by the presence of both the flexible hexafluoroisopropylidene groups and the bulky 1,4-naphthalene moieties, which inhibit polymer crystallization and facilitate the penetration of solvent molecules between the polymer chains.

The T_g's for the poly(ether ketone)s prepared from **2** and 6F-BPA, HPF, DHB, DHS, and Bisphenol AP were 194, 230, 200, 205 and 198ºC, respectively. The T_g for **3** is higher than for the fluorinated polyetherketone **8,** reported to be 175°C by R. N. Johnson *et al.*[21] The higher T_g of **3** compared to **8** is attributed to the presence of the bulky 1,4-naphthalene moieties in **3.** The high T_g of **4** is
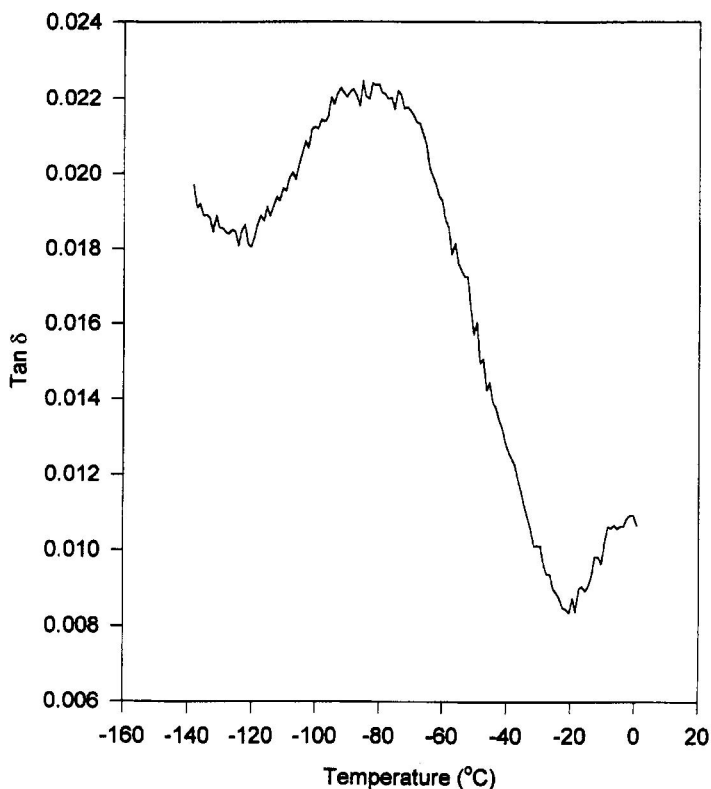
Figure 8.3. Temperature dependence on tan δ at **1 Hz** in the β-relaxation region for 6FNE.

attributed to the incorporation of the cardo group from the 4,4′-dihydroxyphenyl-fluorene. Korshak *et al.*[22] previously reported that the incorporation of cardo groups in polyarylates endows them with enhanced glass transition temperatures, improved thermal stability, and increased solubility. TGA of **3, 4, 5 ,6,** nd **7** reveals that the polymers exhibit initial weight loss in air at about 500°C (scan rate = 20°C/min). The broad temperature range between the T_g and the thermal decomposition temperature makes these polymers attractive for thermoforming processes. Table 8.2 presents the characterization data of the poly(ether ketone)s.

At 0% RH, **3, 4, 5, 6,** and **7** display dielectric constants (measured at 10 KHz) of 3.32, 3.23, 3.36, 3.63, and 3.32, respectively. At about 80% RH, the dielectric constants of **3, 4, 5, 6,** and **7** increased to 3.88, 3.52, 3.87, 4.18, and 3.47, respectively. The relationships of dielectrics constant to relative humidity for polymers **3, 4, 5, 6,** and **7** are depicted graphically in Figure 8.4. For comparison, the fluorinated poly(aryl ether ketone) **8,** made by the reaction of 6F-BPA and 4,4′-

difluorobenzophenone, displayed a dielectric constant of 2.94 at 0% RH and increased to 3.25 at 58% RH.
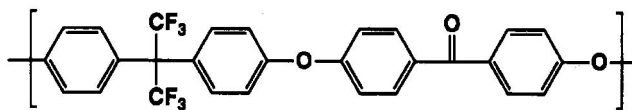
8

All of the poly(ether ketone)s containing 1,4-naphthalene moieties described in this chapter have dielectric constants greater than that of **8.** Since the dielectric constant of a polymer is a function of the polymer's total polarizability, α_T [23,24] the higher dielectric constants of the poly(ether ketone)s **3, 4, 5, 6,** and **7,** compared to that of **8,** are attributed to the more polar nature of the naphthalene moieties present in **3, 4, 5, 6,** and **7.** In addition, polymer **6** displays the highest dielectric constant of the poly(ether ketone)s described in this chapter. The higher dielectric constant observed in **6** is attributed to the presence of the polarizable sulfone groups in the polymer. Polymer **6** also displays the greatest increase in dielectric constant with increasing relative humidity. The larger increase in the dielectric constant of **6** with increasing relative humidity, compared to **3, 4, 5,** and **7,** is attributed to higher levels of moisture absorption facilitated by hydrogen-bonding of water to the sulfone moiety in **6.**

Size-exclusion chromatography of **3–7** showed that the polymers were of high molecular weight and displayed very high polydispersity. A low-molecular-weight fraction, which we attribute to cyclic oligomers, was observed for all five polymers tested. However, the presence of the oligomeric species did not have an especially negative effect on the polymer properties since all the polymers yielded flexible, creasable films showing good mechanical integrity. Molecular-weight

Table 8.2. Properties of Fluorinated Poly(Aryl Ether)s Containing 1,4-Naphthalene Moieties

Polymer	Diphenol	T_g (°C) (DSC)	T_g (°C) onset[a]	Dielectric constant		Molecular weight	
				0%RH	80% RH	M_n	M_w
6FNE	—	247	523	2.72	2.79	18,100	52,800
3	6F-BPA	194	524	3.32	3.88	6,900	51,000
4	HPF	230	513	3.23	3.52	6,200	45,700
5	DHB	200	510	3.36	3.87	13,800	58,500
6	DHDS	205	502	3.63	4.18	6,700	34,300
7	Bisphenol AP	198	503	3.32	3.74	5,900	38,600

[a]Onset of decomposition characterized by 5% wt loss in air.
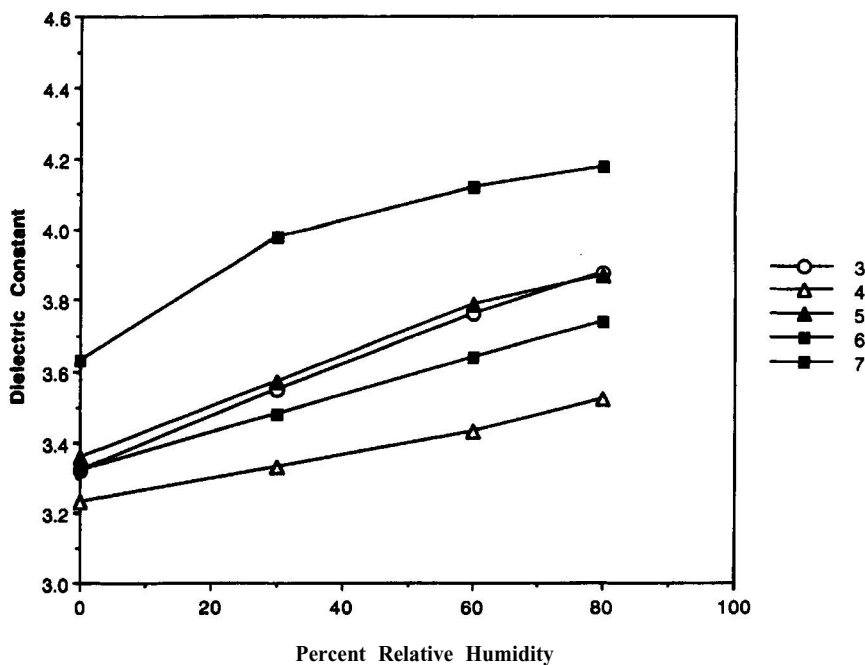
Figure 8.4. Effect of humidity on the dielectric constant of polyetherketones **3–7.**

distributions for **3** and **7** are depicted in Figure 8.5 and GPC results for **3–7** are tabulated in Table 8.2.

8.4. CONCLUSIONS

Six novel fluorinated poly(aryl ether)s containing 1,4-naphthalene moieties were synthesized in high yield using 2,2-bis[4-(1-naphthoxy)phenyl]hexafluoropropane (**1**). Oxidative coupling of **1** yielded a polymer with high T_g, low moisture absorption, and low dielectric constant that could be cast into flexible films. The low dielectric constant and low moisture absorption of 6FNE may make it useful as a dielectric insulator in microelectronics applications.

Reaction of **1** with 4-fluorobenzoyl chloride yielded the difluoro-containing monomer **2,** which is readily polymerized with a bisphenol using potassium carbonate in *N,N*-dimethylacetamide to yield poly(ether ketone)s. The five poly-(ether ketone)s prepared were soluble in polar aprotic solvents and were cast into flexible, creasable films showing good thermal stability. We have demonstrated that 1-phenoxy-substituted naphthalene moieties undergo a Friedel–Crafts acyla-
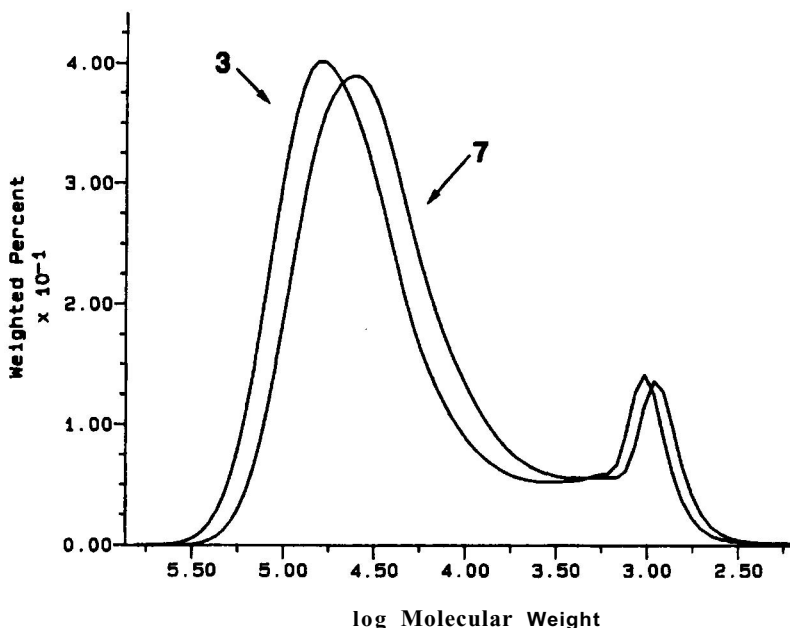
Figure 8.5. Molecular weight distributions for **3** and **7.**

tion reaction at the 4-position when reacted with 4-fluorobenzyl chloride to yield the 1,4-substituted product in high yield. The appropriately substituted monomers were easily prepared and subjected to displacement polymerizations with various bisphenols to yield polymeric products. High molecular weight was readily achieved, and structural variety was introduced by selection of the appropriate bisphenol.

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