# Polymers Derived from Hexafluoroacetone: 12F-Poly(ether ketone)

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ABSTRACT: The compounds 2,2-bis[4-(4-fluorobenzoyl)phenyl]propane and 2,2-bis[4-(4-fluorobenzoyl)phenyl]hexafluoropropane were synthesized, and each was polymerized with Bisphenol A or Bisphenol AF (155 °C for 3–6 h in *N,N*-dimethylacetamide (DMAc)) to give an homologous series of four, thermally stable, aromatic poly(ether ketones) in yields greater than 90%. Incorporation of hexafluoroisopropylidene (6F) and/or isopropylidene (6H) groups in the poly(ether ketone) backbone greatly enhanced the solubility of these polymers (compared to Victrex PEEK) in common organic solvents. Thermal stabilities by TGA for the polymer series ranged from 485 to 553 °C in air at the point of 10% weight loss. Glass transition temperatures ($T_g$) ranged from 169 to 180 °C by DSC. The synthesis and characterization of poly(ether ketones) containing 6F and 6H groups in the backbone are reported along with a study of the effect that replacing the 6H group with the 6F group has on the properties of the polymers.

## Introduction

Among the high-performance polymers currently being examined for use in aerospace and electronics applications are poly(aryl ether ketones) (PEK's). High strength, toughness, good electrical properties, thermooxidative stability, and solvent resistance make this class of polymers an excellent candidate for advanced materials.

Aromatic poly(ether ketones) are generally prepared by the nucleophilic displacement of activated aromatic dihalides with alkali-metal bisphenolates in polar aprotic solvents[1,2] and to a lesser extent by Friedel–Crafts acylation reactions.[3,4] Considering the many monomers available for the synthesis of PEK's, the study of structure/property relationships in these polymer systems is receiving more attention. Other research has focused on producing soluble, thermally cross-linkable PEK polymers or oligomers, which, when cured, display improved solvent resistance.[5,6] These polymers have shown promise for use as composite materials on aircraft where resistance to aviation fuels and harsh environments is essential.

Victrex PEEK, poly(ether ether ketone), has gained significant commercial success because of its thermal stability, solvent resistance, and ability to be fabricated by conventional extrusion and molding techniques.[7] However, many PEK's including Victrex PEEK have proved difficult to synthesize and process because of their lack of solubility.[8,9] To improve solubility in these and other polymer classes, functional groups are commonly added in or onto the polymer backbone; however, the gain in solubility is frequently accompanied by a loss of thermal stability.[10]

Recent research[11] has shown that incorporation of hexafluoroisopropylidene (HFIP or 6F) groups into polymer backbones enhances polymer solubility without forfeiture of thermal stability. This added solubility is sometimes referred to as the "fluorine effect". The retention of high thermal stability is attributed to the strong C–F bond. Other effects of the 6F group are increased $T_g$ and flame resistance with concomitant decreased crystallinity and water absorption.

It has also been noted[12] that 6F groups prohibit conjugation when placed between aromatic moieties, presumably via interruption of an extended $\pi$-system, resulting in decreased color. Other functional groups that also achieve this effect are ether, sulfide, and alkyl moieties. The bulky 6F groups also serve to increase the free volume of the polymer, thereby improving the electrical insulating properties of polymers. For highly conjugated polymer systems such as polyimides, incorporation of the 6F group into the backbone has enabled the synthesis of soluble, transparent, colorless, fully imidized polymers with outstanding electrical properties.[12,13]

This paper reports the synthesis and characterization of a homologous series of PEK's which contain 6F and/or isopropylidene (6H) groups on the polymer backbone. The effect of 6F versus 6H substitution on the properties of the polymer series is also reported.

## Experimental Section

**Materials.** Bisphenol AF and 2,2-bis(4-carboxyphenyl)hexafluoropropane were supplied by Hoechst Celanese Corp. Bisphenol A was obtained from Aldrich. Both bisphenols were purified by sublimation prior to use. Dry toluene was prepared by distilling from the sodium–benzophenone ketyl. Acetone was dried over Drierite and distilled immediately before use. *N,N*-Dimethylacetamide (DMAc) from Aldrich was distilled prior to use as the polymerization solvent. Commercial-grade *p*-chlorotoluene was dried over calcium chloride and filtered before use. All other materials were used as received.

Melting points were determined using a MEL-TEMP II hotblock melting point apparatus. Thermal analyses were performed on a Du Pont 9900 thermal analyzer at Texas Research Institute, Austin, Inc., in Austin, TX. Values of 10% weight loss for TGA's in air and nitrogen were determined at a heating rate of 20 °C/min. Glass transition temperatures ($T_g$) by DSC were taken as the inflection point on the trace. Gas chromatographic analyses were performed on a Varian Model 3700. An Instron Model TTD universal testing instrument was used to obtain mechanical strength data on thin-film samples (1 mil) cast from chloroform. Inherent viscosities were determined at a concentration of 0.25 g/dL in chloroform at room temperature using a Cannon-Fenske 50-bore viscometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Molecular weight determinations were conducted at the Springborn Testing Institute, Inc., Enfield, CT, and are based on polystyrene standards. Permeation

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tests were performed at the Department of Chemical Engineering, University of Texas at Austin, Austin, TX. Isothermal aging, crystallinity, dielectric, optical transparency, composite, ultraviolet irradiation, and electron irradiation measurements were courtesy of the NASA Langley Research Center, Hampton, VA.

**Synthesis of 2,2-Bis(4-carboxyphenyl)propane (6HDCA).** Using a procedure similar to that outlined by Coscia,[14] a solution of 50 mL (0.42 mol) of *p*-chlorotoluene in 200 mL of anhydrous diethyl ether was stirred in an argon-purged, 500-mL, round-bottomed flask to which was added 5.86 g (0.85 mol) of lithium wire (high sodium). The reaction flask was surrounded with a water bath, and within 2 h a cloudy, yellow mixture was obtained (90% *p*-tolyllithium (I) by gas chromatography (GC)).

The reaction mixture of I was cooled to −78 °C and reacted by dropwise addition with 31 mL (0.42 mol) of acetone. The resultant white reaction mixture was allowed to warm and then was acidified by pouring into a stirred, ice-cold solution of 41.2 g (0.42 mol) of ammonium bromide in 700 mL of water. The organic phase was collected, concentrated, and vacuum-distilled to yield a mixture of 2-hydroxy-2-*p*-tolylpropane (II) and the corresponding dicymene ether compound (III). Both products codistilled at 49–51 °C at 0.1 mmHg to give a clear colorless liquid, 41.5 g (65%), based on II. $^1$H NMR: δ 1.45 (s, 6 H), 2.24 (s, 3 H), 3.06 (s, 1 H), 6.96–7.34 (q, 4 H aromatic).

Compounds II and III were stirred with 100 mL of toluene and cooled to below 5 °C in an ice–water bath. To this was added 70 mL of 12 M HCl over a 10-min period. After an additional 10 min, the organic layer was collected and dried over $CaCl_2$. The solution of 2-chloro-2-*p*-tolylpropane (IV) was used immediately in the preparation of V.

2,2-Di-*p*-tolylpropane (V) was synthesized from the toluene solution of IV under Friedel–Crafts conditions described by Coscia et al.[14] Recrystallization of V from methanol yielded 32.1 g (55%) based on II, large, colorless, plate crystals, mp 77–78 °C. $^1$H NMR: δ 1.59 (s, 6 H), 2.13 (s, 6 H), 6.92–7.21 (q, 8 H aromatic).

A 1-L, round-bottomed flask was filled with 15.0 g (0.067 mol) of V, 13.0 g (0.23 mol) of potassium hydroxide pellets, and 75 mL of pyridine. The contents of the flask were heated to a gentle reflux, and then a solution of 95.1 g (0.60 mol) of $KMnO_4$ in 400 mL of water was cautiously added to the reaction flask over a 1.5-h period. The $KMnO_4$ solution was maintained at 70–80 °C during addition to prevent recrystallization in the addition funnel. After addition, the reaction was allowed to continue for 2 h at reflux, cooled, and filtered (to remove $MnO_2$) to yield a clear, colorless filtrate. Acidification with 250 mL of 6 M HCl gave a white precipitate which was collected by filtration, washed with water, and dried in vacuo to yield 18.5 g (97%) of 2,2-bis(4-carboxyphenyl)propane (6HDCA), mp 315–316 °C (lit.[15] mp 315–316 °C). $^1$H NMR: δ 1.62 (s, 6 H), 7.02–7.95 (m, 8 H aromatic), 10.79 (s, 2 H).

**Synthesis of 2,2-Bis[4-(4-fluorobenzoyl)phenyl]propane (6HBFP).** A 500-mL, round-bottomed flask was charged with 17.0 g (0.06 mol) of 6HDCA, 100 mL of thionyl chloride, and 3 drops of *N,N*-dimethylformamide (DMF) as a reaction catalyst. The reaction mixture was heated to 50–60 °C with stirring for 2 h. The clear, yellow solution which formed was cooled, and excess thionyl chloride was removed from the product via vacuum distillation. To the remaining viscous residue was added 400 mL of hexane. A solid white crystalline mass formed which was dissolved at reflux and filtered hot under aspiration to yield a clear colorless filtrate. Upon recrystallization from isopropyl alcohol, white needle crystals, 17.5 g (91%), of 2,2-bis[4-(chloroformyl)phenyl]propane (6HDAC) were isolated, mp 95–96 °C. $^1$H NMR: δ 1.74 (s, 6 H), 7.26–8.10 (q AA′XX′, 8 H aromatic).

A 500-mL, round-bottomed flask was purged with argon and filled with 15.0 g (0.047 mol) of 6HDAC and 100 mL of fluorobenzene. To this stirred solution was added 17.0 g of $AlCl_3$ in small portions over a 5-min period. The yellow reaction mixture was heated to 50–60 °C for 1.5 h, cooled, and then poured slowly into 700 mL of stirred, ice-cold 1 M HCl. The organic layer was collected and concentrated to a pale yellow residue. The residue was digested in 100 mL of ethanol for 2 h, and the resulting white solid, collected by filtration. Recrystallization from isopropyl alcohol yielded 14.6 g (71%) of the bis(fluorophenyl)-terminated monomer (6HBFP), mp 167–168 °C. $^1$H NMR: δ 1.77 (s, 6 H), 7.02–7.93 (m, 16 H aromatic). Anal. Calcd: C, 79.08; H, 5.03. Found: C, 78.74; H, 4.85.

**Synthesis of 2,2-Bis[4-(4-fluorobenzoyl)phenyl]hexafluoropropane (6FBFP).** This monomer was prepared from 2,2-bis(4-carboxyphenyl)hexafluoropropane (6FDCA) using reaction conditions identical to those employed for the synthesis of 6HBFP. The crude product was recrystallized from isopropyl alcohol to give white needle crystals of 6FBFP in 73% yield, mp 143 °C. $^1$H NMR: δ 7.07–7.98 (m). Anal. Calcd: C, 63.51; H, 2.94. Found: C, 63.73; H, 2.67.

**Polymerizations.** The two bis(fluorophenyl)-terminated monomers, 6HBFP and 6FBFP, were each polymerized with either Bisphenol A or Bisphenol AF to give a series of four polymers. The PEK's were prepared using equimolar amounts of monomers at a concentration of 15–20% (w/v) solids in DMAc with an excess of anhydrous potassium carbonate. All polymerizations involved two reaction steps. First, the dipotassium salt of the desired bisphenol was synthesized by reacting the bisphenol with potassium carbonate at reflux (130 °C) for 2 h in a DMAc/toluene solution. Water was removed from the reaction via the toluene/water azeotrope which was separated using a Dean–Stark trap. Toluene was then removed from the reaction flask by distillation until the reaction temperature reached 155–160 °C. The desired bis(fluorophenyl)-terminated monomer was then added to the reaction flask and stirred at reflux under an inert atmosphere for 3–6 h. The resulting reaction mixtures were diluted with twice the volume of DMAc and then filtered to remove excess potassium salts. The filtrates were slowly poured into water to yield flaky, white precipitates. Purification of the resultant polymers was accomplished by dissolving in chloroform, precipitation into methanol, and drying in vacuo at 110 °C for 24 h. Results of the polymerizations may be found in Table I, and analytical data for the polymers may be found in Table IV.

**Film Casting.** Dried PEK samples (0.35 g) were dissolved in 8 mL of chloroform to give 4.4% (w/v) solutions which were filtered onto 4 in. × 4 in. level glass plates and carefully spread to the edges. The films were allowed to dry slowly under a Petri dish for 24 h and then dried for 2 h in air at 130 °C. The dried films were released from the glass by soaking in water to give colorless, transparent samples (approximately 1 mil thick).

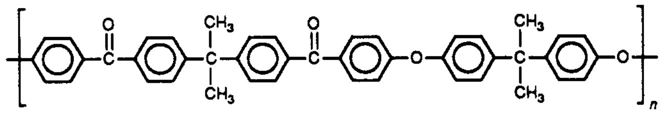
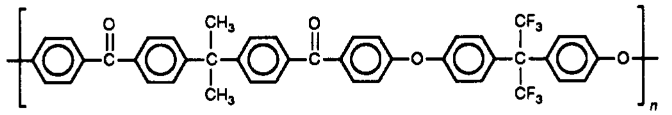
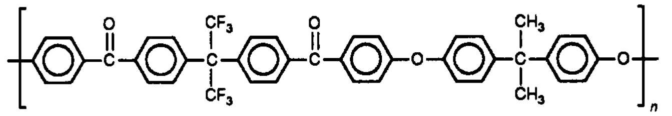
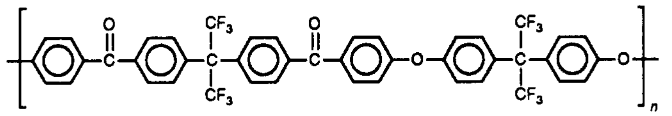
**Thin-Film Mechanical Testing.** Tensile strength and percent elongation values for the polymer series were determined using cast films having dimensions (4 in. × 0.5 in. × 1 mil). The films were pulled at a rate of 0.2 in./min at room temperature, with the initial distance between grips being 1.6 in.

**Ultraviolet Irradiation of 12F-PEK.** Thin films of 12F-PEK (1.0 mil), PEEK (2.0 mil), and Kapton H (0.5 mil) were characterized by UV–visible and infrared spectroscopy before and after exposure to varying doses of UV radiation. For testing, 1-in.-diameter film specimens were mounted in individual sample holders with their own ion pump under a vacuum of $1.3 \times 10^{-5}$ Pa. Spurasil quartz optics were used to transfer and focus the ultraviolet radiation from a 1-kW xenon lamp onto the film specimens which were mounted against a silver reflecting surface. The film specimens were irradiated for 100- and 200-h periods with 1.5 solar constants of UV radiation.

**Electron Irradiation of 12F-PEK.** Thin films of 12F-PEK (1.0 mil), PEEK (2.0 mil), and Kapton H (0.5 mil) were characterized by UV–visible and infrared spectroscopy before and after exposure to varying doses of electron radiation. The thin-film specimens were irradiated with 1-MeV electrons in a clean high-vacuum chamber at a pressure of $2.7 \times 10^{-5}$ Pa. The specimens were mounted to a temperature-controlled aluminum plate which was perpendicular to the electron beam. The samples received doses of $1 \times 10^9$ and $5 \times 10^9$ rad at a rate of $5 \times 10^7$ rad/h. Faraday cups mounted in the electron beam were used to measure the flux levels on the films. The temperature of the film samples did not exceed 30 °C during exposure.

**Composite Laminates of 12F-PEK.** Glass fiber composites of 12F-PEK were produced by applying a 28.5% solution of 12F-PEK in methyl ethyl ketone to S2-glass fibers on a Research Tool Corp. drum winder using a drum rotation of 3 rpm, a transferse rate of 34% full speed, and a die gap of 0.11 in. × 0.03 in. The resulting prepreg was dried until tack-free, cut into 1-in.-long sections, and B-staged in a forced-air oven for 0.5 h at 150 °C. Laminates were prepared in 3 in. × 3 in. stainless steel molds

**Table I**
**Structures and Results of the PEK Series**

| structure | name | yield, % | inherent viscosity, dL/g |
|---|---|---|---|
|  | 12H-PEK | 97 | 0.73 |
|  | 6H6F-PEK | 91 | 0.89 |
|  | 6F6H-PEK | 90 | 1.09 |
|  | 12F-PEK | 93 | 0.71 |

from the prepregs by molding for 1 h at 300 °C and 300 psi. The resulting 8-ply and 16-ply unidirectional laminates were cooled and used in the determination of short-beam shear (SBS) strength, flexural properties, and dielectric constant. The S2-glass fibers have a dielectric constant of 5.0 from 8 to 12 GHz.

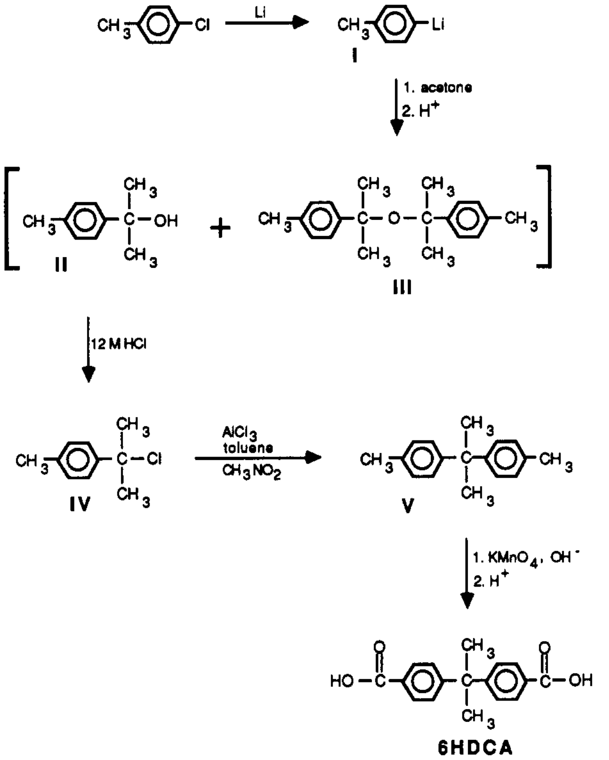


**Figure 1.** Synthesis of 2,2-bis(4-carboxyphenyl)propane (6HDCA).

## Results and Discussion

For many polymer systems, it has been reported[11] that incorporation of 6F groups into the polymer backbone has improved solubility and the electrical and optical properties without a decrease in thermal stability. For the PEK's reported herein, 6F groups were placed in either or both places in the repeating unit (between the ketone or ether linkages) to yield a homologous series of four polymers (Table I) which could be readily evaluated in terms of structure/property relationships.

Introduction of the 6H group between the ketone linkages of the PEK's was accomplished through the synthesis of 6HDCA from V[14] (Figure 1). Treatment of *p*-chlorotoluene with lithium metal gave compound I in high yield. Reaction of I with acetone and then acidification gave a mixture of II and III in good yield. The ratio of II to III will vary depending upon how quickly the lithium salt is decomposed. As much as 98% of III can be obtained in some cases. Treatment with 12 M HCl converted II and III to a single product (IV) which was used to produce V by a Friedel–Crafts reaction with toluene. Chlorocymene (IV) is reported[14] to eliminate HCl readily to yield $\alpha$,*p*-dimethylstyrene; indeed, our attempts to isolate IV by vacuum distillation often resulted in a condensate that rapidly solidified (Coscia[14] identified a similar residue as oligomers of $\alpha$,*p*-dimethylstyrene). As a result, IV was not isolated in subsequent reactions but used immediately. Oxidation of the aromatic methyl groups of V with basic potassium permanganate followed by acidification yielded 6HDCA.

6HDCA and 6FDCA were used to synthesize two new activated bis(fluorophenyl)-terminated monomers as shown in Figure 2. Reaction of 6HDCA and 6FDCA in thionyl chloride with DMF as a catalyst produced 6HDAC and 6FDAC in high yields. Friedel–Crafts acylation of fluorobenzene with 6HDAC and 6FDAC gave the reactive monomers 6HBFP and 6FBFP in good yields.

Condensation of 6HBFP or 6FBFP with either Bisphenol A or Bisphenol AF yielded a homologous series of four aromatic poly(ether ketones) containing 6H and/or 6F groups in the backbone. Polymerizations were typical nucleophilic aromatic displacement reactions conducted in DMAc at 155–160 °C as shown in Figure 3. Reaction times from 3 to 6 h were sufficient to produce high molecular weight polymers as evidenced by solution viscosities. Attempts to synthesize analogous polymers with chlorine[16] as the aromatic leaving group were unsuccessful. A reported order of ease of displacement of activated aromatic halides has been given as F ≫ Cl > Br > I.[1] This reactivity order agrees well with results obtained in our studies using activated chloro and fluoro end-capped monomers. Preparation of polyethers from bis(chloride) monomers has been reported to be successful only when sulfone is the activating group[17] or transition-metal catalysts such as nickel are employed.[18] Table I shows the structures of the polymers and the naming used in

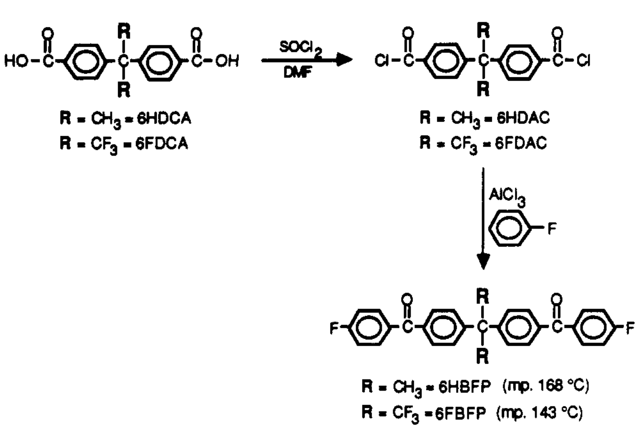


**Figure 2.** Synthesis of 6HBFP and 6FBFP, activated bis(fluorophenyl)-terminated monomers.

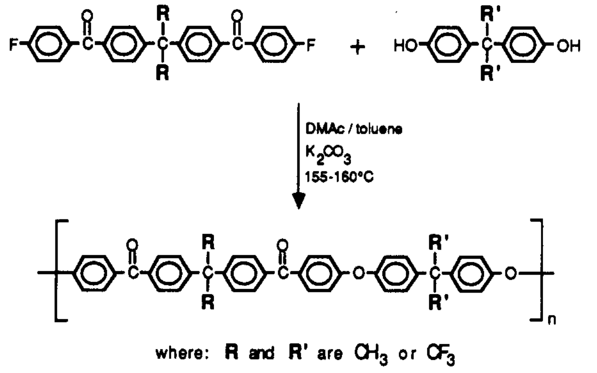


**Figure 3.** General reaction scheme for PEK synthesis.

**Table II**
**Thermal Properties of the PEK Series**

| polymer | $T_g$, °C | TGA,[a] °C air | TGA,[a] °C nitrogen | char yield at 800 °C, % |
|---|---|---|---|---|
| 12H-PEK | 169 | 485 | 536 | 35 |
| 6H6F-PEK | 174 | 553 | 550 | 55 |
| 6F6H-PEK | 172 | 485 | 542 | 53 |
| 12F-PEK | 180 | 537 | 552 | 55 |

[a] Temperature of 10% weight loss at a heating rate of 20 °C/min.

**Table III**
**Mechanical Properties of the PEK Series[a]**

| polymer | tensile strength, psi | elongation, % |
|---|---|---|
| 12H-PEK | 8200 | 99 |
| 6H6F-PEK | 9150 | |
| 6F6H-PEK | 7600 | |
| 12F-PEK | 10600 | 96 |

[a] Thin-film samples.

**Table IV**
**Elemental Analysis of the PEK Series**

| polymer | C, % calcd | C, % found | H, % calcd | H, % found |
|---|---|---|---|---|
| 12H-PEK | 84.05 | 83.86 | 5.77 | 5.49 |
| 6H6F-PEK | 71.74 | 71.86 | 4.10 | 3.90 |
| 6F6H-PEK | 71.74 | 71.87 | 4.10 | 3.78 |
| 12F-PEK | 62.57 | 62.81 | 2.86 | 2.72 |

**Table V**
**Permeability Coefficients for 12F-PEK**

Permeability[a]

| $N_2$ | $O_2$ | $CH_4$ | $H_2$ | He | $CO_2$ |
|---|---|---|---|---|---|
| 0.63 | 3.0 | 0.53 | 24.0 | 31.8 | 13.4 |

Selectivity

| $O_2/N_2$ | $H_2/CH_4$ | $CO_2/CH_4$ |
|---|---|---|
| 4.8 | 45.3 | 25.3 |

[a] Units: cm$^3$ cm/(cm$^2$ s cmHg), 35 °C.

this paper. Some results of the polymerizations are also given. Thermal properties for the PEK series are shown in Table II. Glass transition temperatures ($T_g$) by DSC for the polymer series ranged from 169 to 180 °C. The 12H-PEK displayed the lowest $T_g$ and 12F-PEK the highest, as was expected. Replacement of 6H groups by 6F groups in the polymer backbone led to a corresponding increase in $T_g$, indicating that the bulkier 6F groups inhibit free rotation of the polymer backbone to a greater extent than 6H groups. However, the relative locations of the 6H and 6F groups had no significant effect on $T_g$. When comparing thermal stabilities in air, it was predicted (and confirmed) that all 6H-containing polymers would have a lower TGA value than 12F-PEK (due to the susceptibility of methyl groups to air oxidation), but the 6H6F-PEK (with backbone methyl groups) had a significantly higher thermal stability than the 6F6H analogue. From these data it is evident that the thermooxidative weak link in the polymers is the 6H group located between diphenyl ether linkages. It is believed that the electron-donating ability of the ether functions makes the 6H group located between them more susceptible to oxidation. When the 6F group is located between ether linkages, thermal stability is increased, indicating that the C–F bonds are resistant to oxidation or attack by free radicals or that the 6F group is not affected by the electron-donating ability of the ether moieties. It has been reported[19] that free-radical substitution rates in toluenes are increased by electron-donating groups and decreased by electron-withdrawing moieties. Location of the 6H group between ketone functions, as in 6H6F-PEK, leads to an increase in thermal stability. Here the electron-withdrawing effects of the ketone moieties appear to decrease the oxidizability of the 6H group. All of the polymers displayed char yields of approximately 55% in nitrogen at 800 °C, except the 12H-PEK, which had a char yield of 35%. Fluorine anywhere on the backbone increased the char yield significantly.

The mechanical properties for the polymer series are shown in Table III. Tensile strengths ranged from 7600 to 10 600 psi and are comparable to those of similar polymer systems. Samples of 12H-PEK and 12F-PEK showed good toughness, with percent elongation values approaching 100. 6F6H and 6H6F-PEK samples showed signs of elongation, but these samples failed at the point of initial necking. Failure was attributed to the nonuniform thickness of the thin-film samples.

All of the polymers are soluble in common organic solvents such as chloroform, benzene, and tetrahydrofuran as well as polar aprotic solvents such as DMF, DMAc, and NMP. Surprisingly, the polymers were only swelled in the presence of DMSO. The enhanced solubility afforded by 6F groups can be observed in ethyl acetate. 12F-PEK was rapidly dissolved by ethyl acetate while the two combination polymers, 6H6F and 6F6H-PEK, were only swelled by this solvent. The 12H-PEK sample may have been slightly swelled but appeared to be largely unaffected by ethyl acetate.

Elemental analyses for the polymer series are given in Table IV. Values for all samples are within acceptable limits.

Permeation and selectivity data were obtained for various gases using 12F-PEK membranes.[20] Permeation rates (Table V) are similar to those of many polymer systems such as aromatic polycarbonates and polyethers.

Table VI
Ultraviolet Irradiation Results

| | | UV transmission, % | | | | | |
|---|---|---|---|---|---|---|---|
| | | Kapton H (0.5 mil)[b] | | PEEK (2.0 mil)[c] | | 12F-PEK (1.0 mil) | |
| exposure, h | UV intensity,[a] solar constants | 400 nm | 500 nm | 400 nm | 500 nm | 400 nm | 500 nm |
| 0 | 0 | 0 | 65 | 60 | 78 | 82 | 89 |
| 100 | 1.5 | 0 | 52 | 25 | 65 | 16 | 64 |
| 200 | 1.5 | 0 | 52 | 18 | 60 | 3 | 45 |

[a] Films irradiated against a silver reflecting surface with a 1-kW xenon lamp. [b] Commercial Kapton H film. [c] Commercial Victrex PEEK extruded film.

Table VII
Electron Irradiation Results

| | | UV transmission, % | | | | | |
|---|---|---|---|---|---|---|---|
| | | Kapton H (0.5 mil)[b] | | PEEK (2.0 mil)[c] | | 12F-PEK (1.0 mil) | |
| exposure, h | exposure rate,[a] rad/h | 400 nm | 500 nm | 400 nm | 500 nm | 400 nm | 500 nm |
| 0 | 0 | 0 | 65 | 60 | 78 | 82 | 89 |
| 20 | $5 \times 10^7$ | 0 | 51 | 52 | 77 | 71 | 88 |
| 100 | $5 \times 10^7$ | 0 | 51 | 28 | 74 | 35 | 81 |

[a] Films irradiated with 1-MeV electrons. [b] Commercial Kapton H film. [c] Commercial Victrex PEEK extruded film.

Many fluorine containing polymers are currently being evaluated for possible use as permselective membranes. When incorporated into polymers, fluorine has been shown to increase permeation rates without a decrease in the selectivity of the membrane. The 12F-PEK membrane showed moderate permeation rates with good selectivity ratios for $H_2/CH_4$ and $CO_2/CH_4$ gas combinations.

Thin-film samples of 12F-PEK, Victrex PEEK, and Kapton H film were characterized by IR and UV–visible spectroscopy before and after exposure to simulated solar radiation (in vacuum) in an effort to determine the possible use of 12F-PEK as a coating for thermal-control systems. In order for a thermally stable polymer to be useful for such space applications as thermal-control coatings or multilayer insulation blankets, the polymer must be able to maintain a high optical transparency in the 300–600-nm range of the electromagnetic spectrum.[16] Results of the UV irradiation tests are shown in Table VI. While the 12F-PEK starts out very transparent to UV radiation, exposure for 100 and 200 h to 1.5 solar constants of radiation causes a marked decrease, particularly at 400 nm, in the ability of the film to transmit ultraviolet light. Similar results were observed for the Victrex PEEK sample. The Kapton H film showed low UV light transmission before irradiation but experienced only a slight loss of transmission at 500 nm after irradiation. After irradiation, there was no observable change in the IR spectra for any of the polymers tested. Previous researchers have reported that polymers containing 6F and ether linkages in the backbone retain a high degree of transparency after exposure to UV irradiation.[21]

Thin-film samples of 12F-PEK, Victrex PEEK, and Kapton H film were exposed to 1-MeV electron radiation in vacuum for 20 and 100 h at $5 \times 10^7$ rad/h. The samples were characterized by IR and UV–visible spectroscopy before and after irradiation, with results shown in Table VII. The 12F-PEK sample retained most of its UV transmission properties at 500 nm after irradiation. UV transmission at 400 nm dropped significantly to 35% after 100 h of exposure. The Victrex PEEK sample behaved similarly, with good UV transmission maintained at 500 nm and a significant drop in transmission at 400 nm. Samples of Kapton H film started with low initial UV transmission at 500 nm but did not experience any loss in transmission between 20 and 100 h of exposure. There was no observable change in the IR spectra of any polymer samples after irradiation.

Table VIII
Properties of 12F-PEK/S2-Glass Fiber Composite Laminates

| layup | resin, % | flex str, ksi | flex modulus, ksi | SBS str, ksi | dielectric constant 8–12 GHz |
|---|---|---|---|---|---|
| 8 ply, uni | 34.2 | 137 | 5640 | | |
| 16 ply, uni | 31.9 | | | 4.4 | 3.85 |

Table IX
Property Comparison of 12F-PEK and PEEK

| property | 12F-PEK | PEEK |
|---|---|---|
| glass transition temp ($T_g$), °C | 180 | 150 |
| melt temp ($T_m$), °C | *a* | 343 |
| dielectric constant at 10 GHz | 2.40 | 2.85 |
| dynamic TGA, 10% wt loss in air,[b] °C | 491 | 540 |
| isothermal TGA, % wt loss after: | | |
| 100 h at 350 °C | 14 | 34 |
| 200 h at 350 °C | 20 | 96 |
| elongation at break,[c] % | 96 | >100 |
| tensile strength,[c] psi | 10 600 | 14 500 |
| soluble common organic solvents | yes | no |
| film former (from cast solution) | yes | no |

[a] Semicrystalline by X-ray diffraction but with no observable $T_m$. [b] Determined at a heating rate of 2.5 °C/min. [c] Values are for unfilled samples.

The mechanical and dielectric properties of 12F-PEK/S2-glass fiber composites are given in Table VIII. The dielectric constant of the S2-glass fibers used in the composites was 5.00 at 8–12 GHz while the raw 12F-PEK had a dielectric constant of 2.40. The resulting 16-ply unidirectional composite displayed an intermediate dielectric constant of 3.85 from 8 to 12 GHz. Flexural strength and flexural modulus measurements were determined using 8-ply unidirectional laminates. The results obtained are similar to those of composites made from polyimide resins. Short-beam shear strength data were obtained using 16-ply unidirectional panels. The shear strength was low compared to that of polyimide composites, but the amount of 12F-PEK available allowed only limited testing.

Selected properties of 12F-PEK are compared with those of Victrex PEEK in Table IX. The glass transition temperature of 12F-PEK is 30 °C higher than that of PEEK due to the inhibition of free rotation caused by the bulky $CF_3$ groups located in the 12F-PEK backbone. X-ray diffraction patterns indicated a semicrystalline structure for the 12F-PEK; however, there was no observable crystalline melt by DSC. The dielectric constant of 12F-PEK (at 10 GHz) was measurably lower than that of PEEK, indicating that the 6F groups improve the insulating ability of the polymer. PEEK exhibited a higher dynamic thermal stability in air by TGA; however, 12F-PEK was considerably more stable to isothermal aging in air at 350 °C for extended periods of time. The tensile strength of unfilled, extruded PEEK is higher than that of 12F-PEK solution-cast films, which might be attributed to the induced crystallinity in PEEK. Both polymers displayed similar percent elongation values. Weight-average and number-average molecular weights were obtained for 12F-PEK using gel permeation chromatography based on polystyrene standards. Values for $M_w$ and $M_n$ were found to be 193 000 and 73 500, respectively, giving a dispersity of 2.62.

## Conclusion

The 6F and 6H groups can be readily incorporated into a poly(ether ketone) backbone. Two new bis(fluorophenyl)-terminated monomers were prepared and reacted with bisphenols to produce soluble film formers. Incorporation of the 6F group into the backbone of PEK's results in soluble, film-forming polymers with desirable electrical properties, optical transparency, and isothermal stability.

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