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Polyether ketones derived from bis[4-(4-fluorobenzoyl)phenyl]phenylphosphine oxide

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Abstract

A series of new poly(phosphine oxide ether ketone)s has been prepared from bis[4-(4-fluorobenzoyl)phenyl]phenylphosphine oxide (**1**) and various bisphenols by the aromatic nucleophilic substitution reaction in DMAc. Monomer **1** was readily prepared by Friedel–Crafts acylation from bis(4-chloroformylphenyl)phenylphosphineoxide and fluorobenzene. Film-forming polymers were produced which have inherent viscosities ranging from 0.76 to 1.32 dl/g. These polymers are thermally stable to more than 500°C in air and exhibit glass transitions at about 200°C. Water contact angles of these polymers ranged from 79 to 84°. © 1999 Elsevier Science Ltd. All rights reserved.

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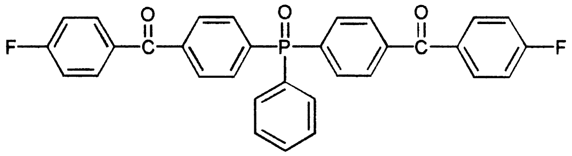
1. Introduction

Aromatic poly(ether ketone)s, PEK's, represent an important class of thermally stable materials for applications in the aerospace and electronics industries. Victrex PEEK, poly(ether ether ketone) for example, has achieved considerable commercial success because of its thermal stability, solvent resistance and ability to be fabricated by conventional molding and extrusion techniques [1,2]. However, much current work on PEK's is directed toward the synthesis of more easily processed materials, which retain the excellent thermal stability of PEEK. It has been found that certain backbone structures such as the hexafluoroisopropylidene group greatly improve the solubility of PEK's without reducing their stability [3]. Similarly PEEK and polyether backbone structures containing phenylphosphine oxide functions such as $[C_6H_4PO(C_6H_5)C_6H_4]$ also retain the excellent thermal stability of PEEK and yet have greatly increased solubility along with the added benefit of increased fire resistance [4–6]. In addition, polymers derived from triphenylphosphine oxide have been suggested for a number of uses such as coatings for low earth orbit application [7–9], heat shields [10], thermal blankets [10], oxygen plasma etch barriers [11] and in metal extraction, catalysis and as membranes for gas separation [12].

Recent work in our laboratory has led to the preparation of a series of new phenylphosphine oxide-derived polymers through reaction of bis[4-(4-fluorobenzoyl)phenyl]phenylphosphine oxide, **1** with bisphenols. Details of their preparation are reported at this time.



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2. Experimental

2.1. Materials

Reagent grade pyridine (Aldrich), *p*-bromotoluene (Aldrich), *N*,*N*-dimethylacetamide (DMAc) (Aldrich), aluminium chloride (Aldrich), thionyl chloride (Fluka), fluorobenzene (DuPont), dichlorophenylphosphine oxide (Jansen Chimica, 97%), toluene (Fisher) and anhydrous potassium carbonate (Fisher) were used as received. Hexane and tetrahydrofuran (Fisher) were dried over benzophenone/Na prior to use. The 2,2-bis(4-hydroxyphenyl)1,1,1,3,3,3-hexafluoropropane (Bis AF) (Central Glass Company), 2,2-bis(4-hydroxyphenyl)propane (Bis A) (Central Glass Company), hydroquinone (Aldrich), resorcinol (Spectrum),

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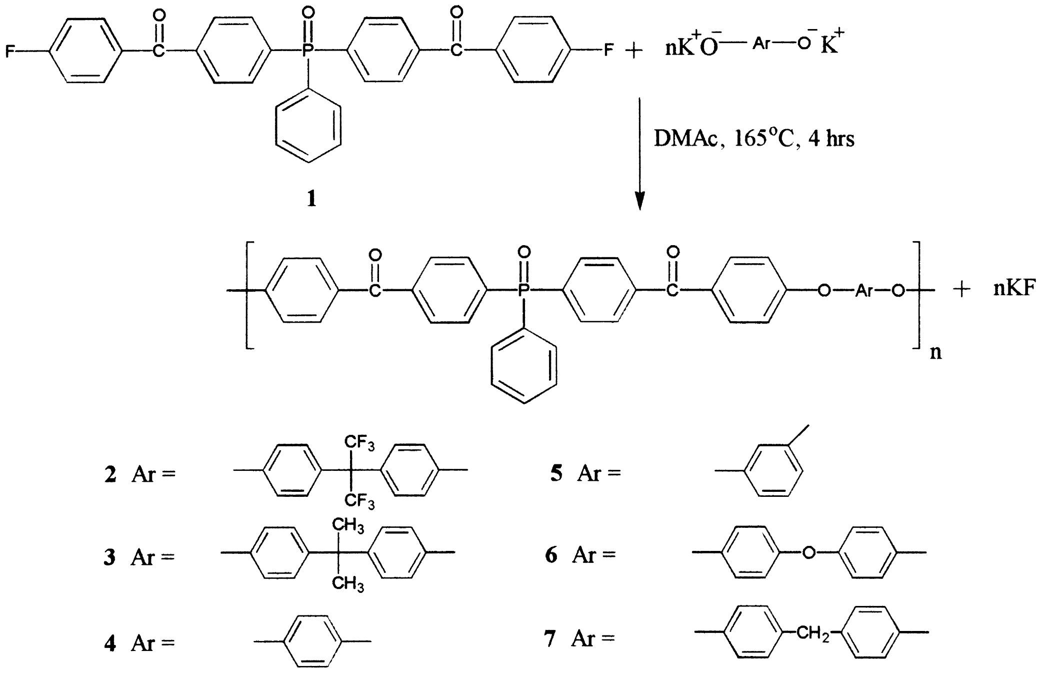

Scheme 1.

4,4-oxydiphenol (Aldrich) and bis(4-hydroxyphenyl)-methane were sublimed several times before use.

2.2. Characterization

Melting points were determined using a MEL-TEMP hot block melting point apparatus. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Inherent viscosities were determined at a concentration of 0.25 g/dl in chloroform at 25°C using a 50-bore Cannon-Fenske viscometer. Infrared spectra of polymer films were obtained on an IBM 80 MHz (NR-80) spectrometer. Thermogravimetric analyses were measured on a Rheometric PL-STA thermal analyzer in both nitrogen and air. Water contact angles were measured at 25°C on a Tantec model CAM-MICRO. Visible and ultraviolet spectra were obtained in chloroform solutions using a Beckman spectrophotometer model DU 7500.

2.3. Monomer synthesis

Bis(4-methylphenyl)phenylphosphine oxide and bis(4-carboxyphenyl)phenylphosphine oxide were both prepared according to the literature [13]. Bis(4-methylphenyl)phenylphosphine oxide was prepared by reaction of *p*-tolylmagnesium bromide (from 230 g, 1.47 mol, bromotoluene and 30 g, 1.23 mol, magnesium in 1.2 l ethyl ether) with dichlorophenylphosphine oxide (82 g, 0.42 mol, in 300 ml ethyl ether). The product, isolated as a viscous, fluorescent oil by Kugelrohr distillation (215–225°C, ≈ 0.1 Torr), was recrystallized (ethanol–water) to a white solid hydrate (90%; m.p. = 92°C, lit. m.p. = 91°C [13]). Bis(4-carboxyphenyl)phenylphosphine oxide was prepared from bis(4-methylphenyl)phenylphosphine oxide (15 g, 0.05 mol, in a boiling solution composed of 100 ml pyridine and 75 ml water) by oxidation with potassium permanganate (63 g added in portions over a 3-h period followed by an additional 2-h heating period). The acid was precipitated from the cooled, filtered reaction mixture by addition of HCl. The crude product was redissolved in $NaHCO_3$ solution (25 g $NaHCO_3$ in 500 ml water) and then reprecipitated with HCl to yield a white solid (96%; m.p. = 337–339°C; lit. m.p. = 335°C [13]).

2.4. Synthesis of bis[4-(4-fluorobenzoyl)phenyl]phenylphosphine oxide (**1**)

Bis(4-carboxyphenyl)phenylphosphine oxide (11 g, 0.03 mol) was heated at reflux in the presence of a trace of DMF (2 drops) with thionyl chloride (50 ml) for 2 h. Excess thionyl chloride was removed by distillation, and fluorobenzene (50 ml) was added to the remaining acid chloride. Aluminum chloride (15 g) was added, and the reaction mixture was boiled for 2 h as HCl was evolved. The reaction was the cooled and hydrolyzed in dilute HCl. The organic layer was collected, dried and evaporated to an oily residue which was crystallized by addition of absolute ethanol (100 ml). Recrystallization from 2-propanol yielded pure **1** (76%, m.p. = 197–198°C, anal. cal for $C_{32}H_{21}F_2O_3P$: C, 73.56; H, 4.02%. Found: C, 72.98; H, 3.93%).

2.5. Polymerization

Polymerizations were conducted in an argon atmosphere at 165°C for 4 h in a reactor fitted with a Dean–Stark water trap. In a typical reaction, a bisphenol (2.00 mmol),

Table 1
Properties of triphenylphosphine oxide-derived PEK's prepared from **1** and selected bisphenols

Polymer no./bisphenol precursor	η_{inh} (dl/g) ($CHCl_3$)	T_g DSC[a] (°C)	TGA[b] N_2 (°C)	TGA[b] air (°C)	Char yield at 700°C (%)	Water contact angle (±2°)
2/Bis AF	0.80	207	538	533	58	83
3/BisA	0.76	195	528	528	38	79
4/Hydroquinone	1.24	207	549	545	43	78
5/Resorcinol	1.32	201	532	513	50	84
6/Oxydiphenol	0.77	195	549	532	57	82
7/Methanediphenol	1.10	195	534	526	52	81

[a] Measured at 20°C/min.
[b] 10% weight loss measured at 20°C/min.

anhydrous K_2CO_3 (4.00 mmol), DMAc (10 ml) and toluene (10 ml) were allowed to react at reflux for 2 h. Compound **1** (1.04 g, 2.00 mmol) was then added; the reflux was continued for 2 h after which time the toluene was removed by distillation, and the polymerization was then completed at 165°C for additional 4 h. After cooling, the solution was added to water, and the precipitated polymer was collected by filtration. It was dried, dissolved in chloroform and reprecipitated into methanol. The polymer was then dried in vacuum at 100°C for 18 h (yield = 90%). Polymers derived from hydroquinone and resorcinol were decolorized using activated carbon in chloroform before precipitation into methanol.

3. Results and discussion

As depicted in Scheme 1, six new triphenylphosphine oxide-derived polymers (**2**–**7**) were synthesized by reaction of compound **1** with selected bisphenols. The polycondensation reaction between the preformed dipotassium phenolate and **1** was conducted as described earlier [3].

All of the off-white to tan, fibrous polymers are easily soluble in organic solvents such as chloroform, THF and acetone. Strong, transparent, creasable films are readily obtained from chloroform.

Polymers **2**–**7** have excellent thermal stability according to dynamic TGA results both in nitrogen and air (Table 1). Thermal stability as indicated by the temperature at which 10% weight loss was observed in nitrogen varies from 528°C for **3** to 549°C for **4** and **6**. Char yields at 700°C exceed 50% for polymers **2**, **5**, **6** and **7**. The resistance of the polymers to oxidation is suggested from their TGA behavior in air where the 10% weight loss temperature varies from 513°C for **5** to 545°C for **4**. Glass transition temperatures are rather high as expected for poly(ether ketone)s bearing bulky substituents [3], ranging from 195 to 207°C.

The polymers range in color from off-white to light tan and absorb strongly between 290 and 300 nm (Table 2). The

Table 2
UV Absorbance data for **12F-PEK** and polymer **2**–**7** (measured in chloroform solution)

Polymer	Wavelength of max. absorbance ($\lambda_{\max}$ nm)	Absorptivity at $\lambda_{\max}$ (a) ($l\ g^{-1}\ cm^{-1}$)	Absorptivity at $\lambda =$ 315 nm (a^1) ($l\ g^{-1}\ cm^{-1}$)
12F-PEK	290	56	14
2	294	45	17
3	299	58	40
4	299	66	40
5	297	54	25
6	298	58	35
7	299	52	32

tailing of this ultraviolet absorption band toward the visible spectrum is reflected in the absorption measurements at 315 nm and correlates with the observed color of the polymers. Thus compound **2** which is slightly off-white has an absorptivity of $17\ \mathrm{l\ g^{-1}\ cm^{-1}}$ at 315 mm, whereas **3** and **4** with absorptivities of $40\ \mathrm{l\ g^{-1}\ cm^{-1}}$ are tan.

Water contact angles, measured on polymer films by the sessile drop protocol, range from 79 to 84°. It is of interest to note that the water contact angle for **2**, containing the hexafluoroisopropylidene groups in the phenolic monomer is only 83 ± 2°, whereas, the value rises to 101 ± 2 in **12F-PEK** [3]. From the structure shown for **12F-PEK** it can be seen that the two polymers differ only in the substitution of the $C_6H_5P{=}O$ groups in **2** for one of the hexafluoroisopropylidine groups in **12F-PEK**.

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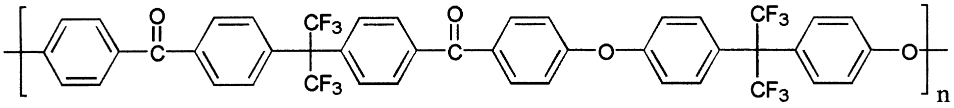

12 F-PEK

4. Conclusions

A series of poly(phosphine oxide ether ketone)s has been prepared and characterized. These polymers are soluble in a variety of solvents from which transparent, flexible films can be cast. The polymers have viscosities ranging from 0.76 to 1.32 dl/g. Thermal stabilities of the new polymers ranged from 513 to 545°C in air with char yields from about 40 to 60% and exhibit glass transition temperatures at about 200°C. All of the polymers exhibited UV absorption between 290 and 300 nm.

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