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SOLUBLE POLY(ETHER KETONE)S AND POLY(ETHER SULFONE)S FROM PHENYL-SUBSTITUTED HYDROQUINONES

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ABSTRACT

Hydroquinones substituted with methyl and phenyl substituents were synthesized and new poly(ether ketone)s and poly(ether sulfone)s have been prepared by solution condensation polymerization in *N*-methylpyrrolidinone with 4,4'-difluorodiphenylsulfone or 4,4'-difluorobenzophenone in the presence of potassium carbonate. Polymers prepared from unsymmetrically substituted hydroquinones are amorphous and soluble in organic solvents such as methylene chloride, *N*-methylpyrrolidinone, and *N,N*-dimethylacetamide. Their glass transition temperatures increase with additional pendant phenyl groups on the arylene ring. Polymers synthesized from hydroquinones that are symmetrically substituted are semicrystalline and insoluble.

INTRODUCTION

Aromatic poly(ether ketone)s and poly(ether sulfone)s are known for their thermal stability and excellent mechanical properties as engineering plastics. Commercially available poly(ether ketone)s are highly crystalline and consequently have very limited solubility in organic solvents. As a result, they can be synthesized by nucleophilic substitution reactions only at high temperatures close to their melting temperature (T_m) to maintain the polymer in solution during the polymerization reaction [1]. However, most poly(ether sulfone)s are amorphous and are readily

soluble in aprotic dipolar solvents so that the polymerization reactions can be carried out at much lower temperatures.

Several systems have been described in which a soluble molecular weight poly(aryl ether) is initially formed which can subsequently be converted to the semicrystalline poly(ether ketone). Kelsey [2] utilized the ketals of 4,4'-dihydroxybenzophenone to form poly(aryl ether)s which could then be hydrolyzed to the poly(ether ketone). The cyclic acetal derived from ethylene glycol was the preferred monomer. McGrath [3] utilized the ketimine of the benzophenone to form soluble amorphous polymers which could then be hydrolyzed, and Sogah [4] utilized monomers that contained bulky *t*-butyl groups which could be subsequently removed.

An amorphous poly(ether ketone) has been synthesized containing a phenyl substituent on the arylene ring which has good solubility in organic solvents. Although the solubility was improved, the glass transition temperature was only slightly increased ($T_g = 154^\circ\text{C}$) compared to poly(ether ether ketone) (PEEK) [5] ($T_g = 146^\circ\text{C}$). Hergenrother [6] utilized the very bulky 9,9-bis(4-hydroxyphenyl)fluorene containing methyl substituents in the 3- and 5- positions to synthesize amorphous poly(ether ketone)s with high T_g 's, and Wang [7] made the corresponding phenyl-substituted polymers. The polymers are amorphous with T_g 's as high as 262°C . We [8] recently used highly hindered biphenols such as 2,2',3,3',5,5'-hexaphenyl-4,4'-biphenol to form amorphous and soluble poly(ether ketone)s and poly(ether sulfone)s with very high T_g 's.

In this paper we describe the synthesis of several different hydroquinones containing phenyl and methyl substituents. The poly(ether ketone)s and poly(ether sulfone)s prepared from asymmetrically substituted monomers, 2,3,5-trisubstituted-hydroquinones (**VIb**, **VIc**), and the symmetrically substituted monomer, 2,6-diphenylhydroquinone (**VIa**) are all amorphous polymers and are readily soluble in organic solvents at room temperature. However, the polymers prepared from the symmetrically substituted 2,3,5,6-tetraphenylhydroquinone (**VIId**) are semicrystalline and have limited solubility.

EXPERIMENTAL

General Methods

$^1\text{H-NMR}$ spectra were recorded as a CDCl_3 solution on a Varian XL-200 instrument, and chemical shifts are given in parts per million downfield from tetramethylsilane as internal standard. High resolution EI mass spectra were recorded on a ZAB 2F HS spectrometer fitted with a direct insertion probe and an electron impact ion source operating at 240°C with an impact energy of 70 eV. Melting points were determined on a Fischer-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories Inc. UV spectra were recorded on a SP 800 Unicam ultraviolet spectrophotometer with a deuterium lamp. In experiments requiring dry solvent, DMF was dried by shaking with 3 Å molecular sieves, and NMP was dried over calcium hydride and distilled under vacuum. Pure 2,6-diphenylphenol was supplied by the General Electric Company. 1,3-Diphenylacetone and chalcone were used as purchased from Aldrich Chemical Co. Common reagents, e.g., sodium methoxide, hydrazine monohydrate (98%), and bromine, were used without further purification.

Synthesis of Monomers

2,6-Diphenylhydroquinone (VIa)

To a 250-mL three-necked flask equipped with a condenser and magnetic stirrer were charged 2,6-diphenylphenol (20 g, 82.20 mmol) and DMF (150 mL). The mixture was gradually heated to 45°C, and *N,N'*-bis(salicylidene)-1,2-phenylenediaminocobalt(II) monohydrate (2.0 g, 6.15 mmol) was then added as a catalyst. Oxygen was passed into the solution for 4 h. After cooling, the mixture was poured into 250 mL of crushed ice containing 4 *N* hydrochloric acid (15 mL). The orange-red precipitate was filtered, washed with water (3 × 100 mL), and dried *in vacuo*. The crude 2,6-diphenyl-*p*-benzoquinone (Va) was recrystallized from *n*-butanol (89% yield), mp 135–137°C.

λ_{\max} (CHCl₃) 246 nm, 296 nm, 340 nm. MS (EI) *m/z*: 260 (M⁺). Elemental analysis (%). Calculated for C₁₈H₁₂O₂: C, 83.06; H, 4.65. Found: C, 82.94; H, 4.58.

Into a 250-mL round-bottomed flask fitted with a condenser were charged 2,6-diphenyl-*p*-benzoquinone (Va) (15 g, 57.6 mmol) and chloroform (150 mL). A small portion of hydrazine was added in order to reduce the quinone. The mixture was heated at reflux temperature for 3 h. The solvent was evaporated and the residue was recrystallized from toluene to give the title compound (95% yield), mp 180–181°C.

¹H NMR (200 MHz, CDCl₃) δ : 4.65 (s, 1H, —OH unhindered phenol), δ : 4.83 (s, 1H, —OH hindered phenol), 6.93–7.42 (m, 12 H, aromatic H). MS (EI) *m/z*: 262 (M⁺). Elemental analysis (%). Calculated for C₁₈H₁₄O₂: C, 82.42; H, 5.38. Found: C, 82.76; H, 5.42.

2,6-Diphenyl-3-methylhydroquinone (VIb)

The reaction was carried out using a procedure similar to that for VIa using *N,N'*-bis(salicylidene)-1,2-phenylenediaminocobalt(II) monohydrate (2.5 g, 7.69 mmol) as a catalyst at a temperature of 55°C for 6 h. The crude product (Vb) was recrystallized from acetone and methanol (85% yield), mp 94–96°C.

λ_{\max} (CHCl₃) 246 nm, 294 nm, 336 nm. MS (EI) *m/z*: 274 (M⁺). Elemental analysis (%). Calculated for C₁₉H₁₄O₂: C, 83.19; H, 5.14. Found: C, 83.15; H, 5.04.

The reduction of 2,6-diphenyl-3-methyl-*p*-benzoquinone (Vb) was accomplished with a small portion of hydrazine in hot chloroform. The resulting product was recrystallized from benzene (92% yield), mp 149–151°C.

¹H NMR (200 MHz, CDCl₃) δ : 2.00 (s, 3 H, —CH₃), 4.67 (s, 1 H, —OH, unhindered), 4.84 (s, 1 H, —OH, hindered), δ : 6.83–7.68 (m, 14 H, aromatic H). MS (EI) *m/z*: 276 (M⁺) Elemental analysis (%). Calculated for C₁₉H₁₆O₂, C, 82.58; H, 5.84. Found: C, 82.05; H, 5.80.

2,3,6-Triphenyl-*p*-hydroquinone (VIc)

A procedure similar to that for VIa using DMF (200 mL), *N,N'*-bis(salicylidene)-1,2-phenylenediaminocobalt(II) monohydrate (3.5 g, 10.76 mmol) as a catalyst and a reaction temperature 55°C for 10 h. After the usual work-up procedure, the crude product (Vc) was recrystallized from acetone (83% yield), mp 156–157°C.

λ_{\max} (CHCl₃) 246 nm, 352 nm. MS (EI) m/z : 336 (M⁺). Elemental analysis (%). Calculated for C₂₄H₁₆O₂: C, 85.69; H, 4.79. Found: C, 85.57; H, 4.73.

Reduction of 2,3,6-triphenylhydroquinone (**Vc**) with hydrazine produced 2,3,6-triphenylhydroquinone which was recrystallized in methanol and chloroform (94% yield), mp 153–154°C.

¹H NMR (200 MHz, CDCl₃) δ : 4.68 (s, 1 H, –OH unhindered), 4.84 (s, 1 H, –OH hindered), 7.03–7.67 (m, 16 H, aromatic H). MS (EI) m/z : 338 (M⁺). Elemental analysis (%): Calculated for C₂₄H₁₈O₂: C, 85.18; H, 5.36. Found: C, 85.32; H, 5.29.

2,3,5,6-Tetraphenyl-2-cyclohexenone (**III**)

A previous procedure [9] was modified as follows. 1,3-Dibenzylketone (20.0 g, 95.11 mmol), chalcone (benzalacetophenone) (20 g, 96.03 mmol), and methanol (220 mL) were charged into a 500-mL round-bottomed flask equipped with a condenser. After dissolution, sodium methoxide (5.2 g, 96.26 mmol) was added slowly. The mixture was stirred at room temperature for 1 h under a nitrogen atmosphere. The suspension was treated with additional sodium methoxide (5.2 g, 96.26 mmol) and methanol (100 mL) to give the ring-closed product. The mixture was heated at reflux for 3 h under nitrogen. During the reaction a white solid precipitated out of solution. The reaction mixture was cooled down to room temperature and the resulting product was collected on a filter funnel and recrystallized from benzene-petroleum ether (91% yield), mp 158–159°C (lit. 159–160°C).

2,3,5,6-Tetraphenylphenol (**IV**)

A procedure similar to that used previously was followed [9]. In a 1-L three-necked round-bottomed flask equipped with mechanical stirrer were charged 2,3,5,6-tetraphenyl-2-cyclohexenone (20 g, 49.94 mmol), acetic acid (400 mL), and bromine (7.9 g, 49.94 mmol). The mixture was heated to 70°C and maintained at this temperature for 7 h until the reaction mixture became colorless. A solid separated on cooling. The product was filtered and recrystallized from benzene-petroleum ether (80% yield), mp 270–273°C (lit. 272–273°C).

¹H NMR (200 MHz, CDCl₃) δ : 5.30 (s, 1 H, –OH), 7.17–7.38 (m, 21 H, aromatic H). MS (EI) m/z : 398 (M⁺).

2,3,5,6-Tetraphenylhydroquinone (**VId**)

The procedure was essentially the same as used previously. In a 1-L three-necked round-bottomed flask equipped with mechanical stirrer and thermometer were charged 2,3,5,6-tetraphenylphenol (16 g, 40.15 mmol), *N,N'*-bis(salicylidene)-1,2-phenylenediaminocobalt(II) monohydrate (4.5 g, 13.83 mmol), and DMF (500 mL). The reaction was then heated to 90°C and oxygen was bubbled through the solution for 30 h. The mixture was added slowly to 1 L of crushed ice in water containing 4 *N* HCl (50 mL) with stirring. The resulting crude product (**Vd**) was recrystallized from chloroform-methanol, mp 317–318°C.

λ_{\max} (CHCl₃) 250 nm, 370 nm. MS (EI) m/z : 412 (M⁺). Elemental analysis (%). Calculated for C₃₀H₂₀O₂: C, 87.36; H, 4.89. Found: C, 87.36; H, 4.87.

Reduction of 2,3,5,6-tetraphenyl-*p*-benzoquinone (**V**) with hydrazine in a mixture of chloroform and methylene chloride for 7 h gave 2,3,5,6-tetraphenyl-

hydroquinone which was recrystallized from chloroform, mp 323–325°C; $^1\text{H NMR}$ (200 MHz, CDCl_3) δ : 4.77 (s, 2 H, $-\text{OH}$), 7.07–7.13 (m, 20 H, aromatic H). MS (EI) m/z : 414 (M^+). Elemental analysis (%). Calculated for $\text{C}_{30}\text{H}_{22}\text{O}_2$: C, 86.93; H, 5.35. Found: C, 86.71; H, 5.20.

General Procedure for Polymerization (Villa)

Into a 50-mL three-necked round-bottomed flask fitted with a Dean-Stark trap, condenser, and thermometer were placed 2,6-diphenylhydroquinone (1 g, 3.81 mmol), 4,4'-difluorodiphenylsulfone (0.97 g, 3.81 mmol), NMP (10 mL), and toluene (7 mL). After the solids were dissolved, anhydrous potassium carbonate (0.69 g, 4.77 mmol) was added. The dark green mixture was vigorously stirred at 150°C until no further water formed by azeotropic distillation was collected, and the toluene was then removed slowly while the reaction mixture was heated to 165°C. The reaction temperature was maintained at 180–185°C for 20 h. After cooling to 100°C, the solution was diluted with additional NMP (7 mL). The mixture was precipitated in methanol–water (200/50 mL) containing a few drops of hydrochloric acid, filtered, and dried in vacuum. The resulting polymer was dissolved in chloroform (15 mL), filtered through Celite, and reprecipitated in methanol (250 mL). The polymer was dried at 140°C under vacuum for 24 h (89% yield).

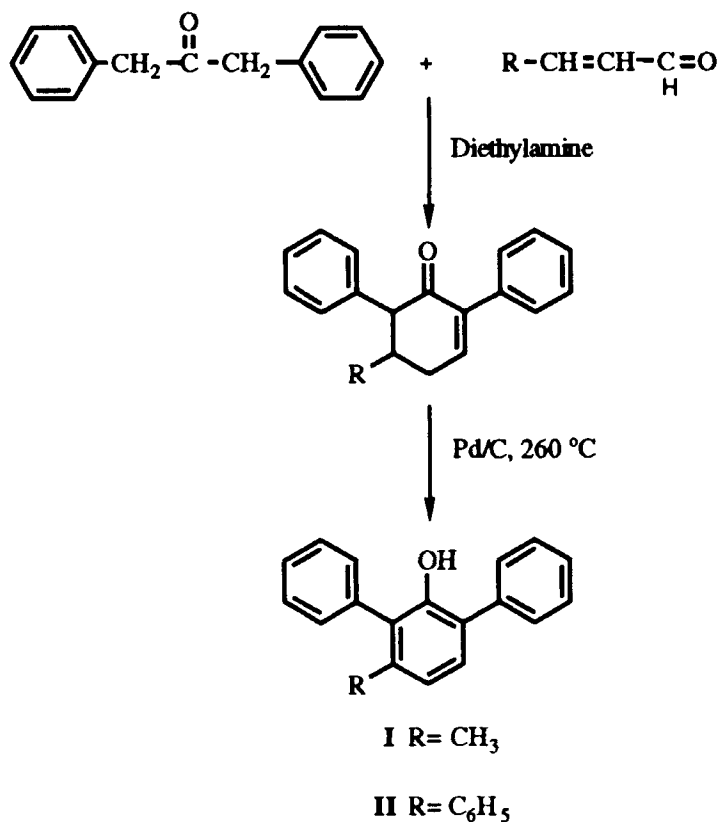
Polymer Characterization

Inherent viscosities were measured in a calibrated Ubbelohde viscometer at a concentration of 0.2 wt% polymer in CHCl_3 at 25°C. Molecular weights of polymers were determined relative to polystyrene by gel permeation chromatography (GPC) using CHCl_3 as solvent on a Waters 510 HPLC with a set of four μ -Styragel columns (500, 10^4 , 10^5 , and 100 \AA) in series and a UV detector. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with Seiko 220 DSC and Seiko 220 TG/DTA instruments, respectively, at a heating rate of 10°C/min under nitrogen and air. Mechanical properties were measured on a Seiko TMA/SS 120 instrument at 25°C with a heating rate of 3°C/min in static air. The polymer films for the mechanical analyzer were cast from chloroform solution on a glass plate (3 cm diameter) by evaporation of solvent at room temperature for 48 h and dried at 100°C for 24 h.

RESULTS AND DISCUSSION

Preparation of Monomers and Polymers

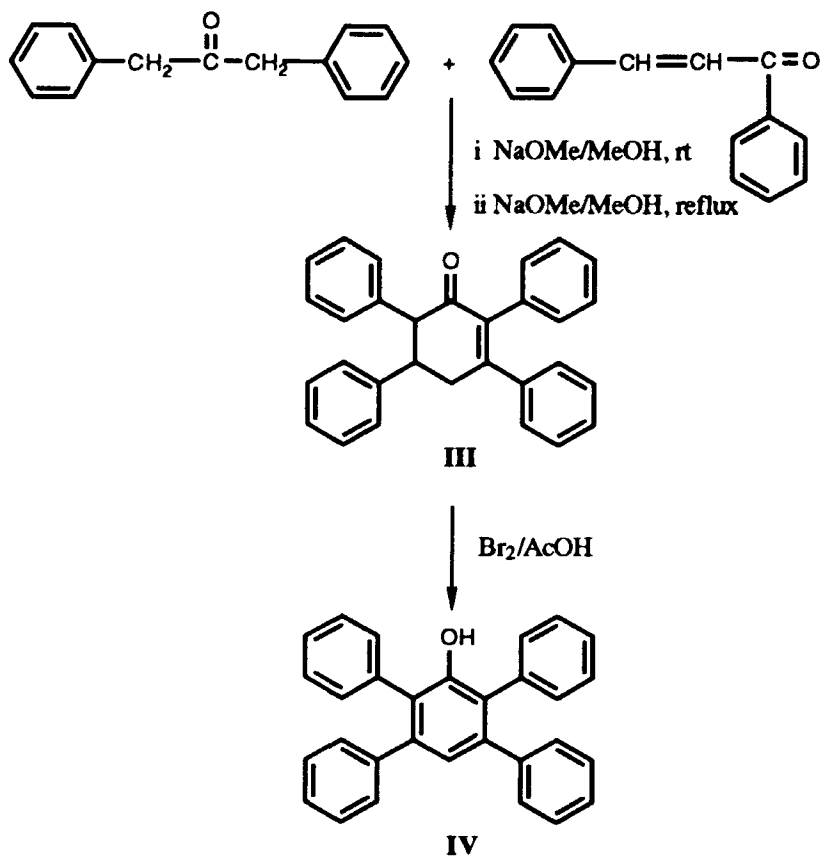
2,3,6-Triphenylphenol (**II**) [10] was prepared by condensation of cinnamaldehyde with 1,3-diphenylacetone and then followed by dehydrogenation of the intermediate cyclohexenone (Scheme 1). 2,6-Diphenyl-3-methylphenol (**I**) was synthesized by an analogous route. 2,3,5,6-Tetraphenylphenol (**IV**) was prepared as in the literature [9] with modifications which increased the yield and minimized the number of steps (Scheme 2). 2,3,5,6-Tetraphenyl-2-cyclohexenone (**III**) was synthesized by the Michael addition of 1,3-diphenylacetone and chalcone in methanol in the presence of excess sodium methoxide at room temperature to give 1,3,4,6-



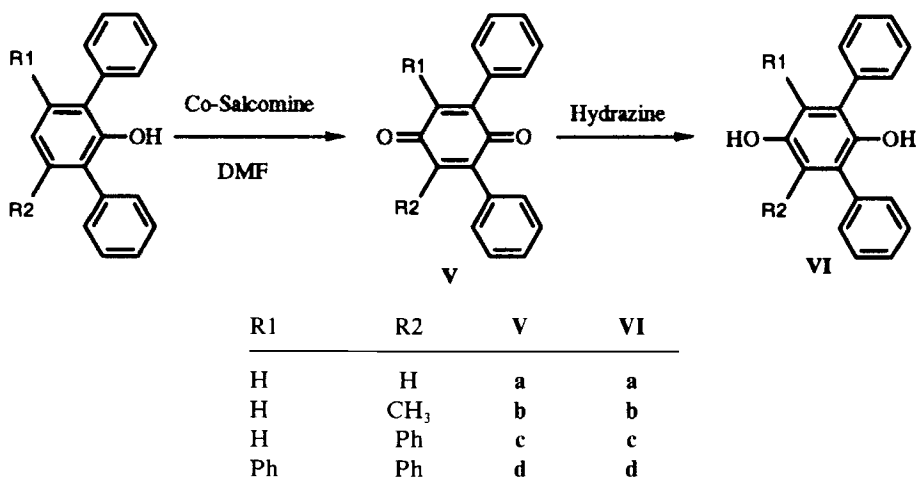
SCHEME 1.

tetraphenyl-1,5-hexanedione followed by heating with additional excess sodium methoxide which readily converted it to 2,3,5,6-tetraphenyl-2-cyclohexenone via aldolization and dehydration. 2,3,5,6-Tetraphenylphenol (**IV**) was prepared by aromatization of **III** with one molar equivalent of bromine.

Oxidation of phenols to benzoquinones has been achieved with a variety of oxidants [11, 12]. Recently, a new method of oxidation of 2,6-disubstituted phenols by hydrogen peroxide in the presence of bromine or hydrogen bromide as a catalyst has been reported [13]. However, in the case of highly hindered phenols, such as 2,3,6-trisubstituted or 2,3,5,6-tetraphenylphenol, we were not able to utilize this method. It is known that 2,6-diphenylphenol can be oxidized to 2,6-diphenylbenzoquinone in high yield with oxygen in the presence of *N,N'*-bis(salicylidene)-1,2-phenylenediaminocobalt(II) monohydrate as a catalyst [14]. This method was applied to the highly hindered phenols **I**, **II**, and **IV** (Scheme 3). *N,N'*-Bis(salicylidene)-1,2-phenylenediaminocobalt(II) monohydrate was prepared using the known procedure [15]. Oxidation of 2,3,6-trisubstituted phenols was carried out with a catalytic amount of *N,N'*-bis(salicylidene)-1,2-phenylenediaminocobalt(II) monohydrate, and a large excess of oxygen was bubbled into the solution at about 55°C. The quinones were obtained in 85–90% yields after recrystallization. Oxidation of



SCHEME 2.



SCHEME 3.

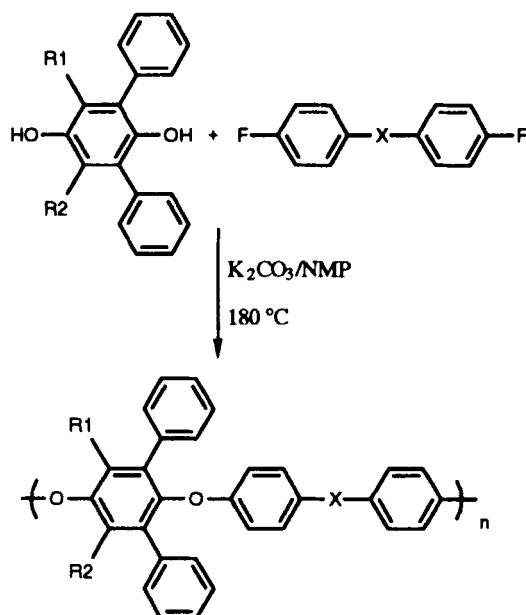
2,3,5,6-tetraphenylphenol (**IV**) also gives the quinone; however, it was necessary to use a longer reaction time and higher temperature (about 90°C) compared to the di- or tri-substituted phenols. All of the quinones prepared (**Va**, **Vb**, **Vc**, **Vd**) were reduced to hydroquinones (**VIa**, **VIb**, **VIc**, **VIId**) in quantitative yields by treatment with hydrazine in hot chloroform or in a mixture of chloroform and methylene chloride. The quinones obtained have colors ranging between orange and red. The ultraviolet spectrum of benzoquinone shows three bands at 250, 282, and 410 nm. The first two bands, 250 and 282 nm, have been assigned to π - π^* transition, while the broad and weak band at about 410 nm has been assigned to a n - π^* transition [16]. The substituted quinones prepared have similar spectra. The 2,6-diphenylquinone (**Va**) and 2,6-diphenyl-3-methylquinone (**Vb**) in chloroform solution show three absorption bands at about 245 nm (strong and sharp), 295 nm (shoulder), and 340 nm (weak and broad band). The corresponding 2,3,6-triphenylbenzoquinone (**Vc**) and 2,3,5,6-tetraphenylbenzoquinone (**Vd**) show changes in the position of the two main bands with maxima at about 250 nm (strong and sharp) and 360 nm (weak and broad).

The polymers were prepared in Scheme 4 by reaction with 4,4'-difluorodiphenylsulfone or 4,4'-difluorobenzophenone in the presence of potassium carbonate in NMP and toluene (1:1 ratio) as solvent [17]. The reactions were slowly heated at reflux until no further water was evolved at the azeotrope temperature, and the toluene was then removed and the temperature maintained at 180°C for 10 to 40 h. With these highly hindered monomers the polymerizations were carried out for very long reaction times to achieve reasonable molecular weight polymers and to obtain high yields (85–90%). Polymers prepared from 2,6- or 2,3,6-substituted hydroquinones are completely amorphous. The polymerization reactions with 2,6-diphenyl-3-methylhydroquinone (**VIb**) proceed much faster and this effect can be explained in part by the lower acidity influencing the rate. Substitution of methyl groups would decrease the acidity of the hydroquinone and hence increase the nucleophilicity of the anion relative to a phenyl substituent which would increase the rate of displacement. The poly(ether ketone)s and poly(ether sulfone)s from 2,3,5,6-tetraphenylhydroquinone (**VIId**) are crystalline and precipitate out of solution during the polymerization, even in sulfolane as a solvent at 220°C.

Polymer Properties

The polymers prepared were characterized by DSC, TGA/DTA, viscometry, TMA, and GPC. The results are summarized in Table 1 and described in the following text.

Poly(ether ketone)s (**VIIa**), (**VIIb**), (**VIIc**) and poly(ether sulfone)s (**VIIIa**), (**VIIIb**), (**VIIIc**) are soluble in polar organic solvents such as *N*-methyl-2-pyrrolidinone (NMP) and dimethylsulfoxide (DMSO), and are readily soluble in chloroform and methylene chloride at room temperature. However, polymers **VIIId** and **VIIIId** obtained from the symmetrically substituted hydroquinones **VIId** are not soluble in common organic solvents even at high temperature, but are soluble in hot benzophenone and diphenylsulfone. Polymers derived from the unsymmetrically substituted hindered hydroquinones have good solubility, while those derived from



| Polymers | R1 | R2 | X | r.t. (h) |
|---------------|----|-----------------|-----------------|----------|
| VIIa | H | H | CO | 20 |
| VIIb | H | CH ₃ | CO | 12 |
| VIIc | H | Ph | CO | 40 |
| VIIId | Ph | Ph | CO | 2 |
| VIIIa | H | H | SO ₂ | 20 |
| VIIIb | H | CH ₃ | SO ₂ | 7 |
| VIIIc | H | Ph | SO ₂ | 40 |
| VIIIId | Ph | Ph | SO ₂ | 2 |

SCHEME 4.

hindered and symmetrically substituted hydroquinones behave similarly to PEEK, which is soluble only at high temperatures.

Molecular weights of polymers were determined by gel permeation chromatography (GPC) using polystyrene standards. These polymers had molecular weights in the range 31,100 to 77,800 and a polydispersity (M_w/M_n) of 2.1–2.9 (see Table 1). The inherent viscosities and glass transition temperatures observed are presented in Table 1. The polymers have inherent viscosities ranging from 0.31 to 0.98 dL/g. The viscosity of polymers **VIIId** and **VIIIId** could not be measured because of the poor solubility. The poly(ether ketone)s have a significantly increased glass transition temperature compared to PEEK which has no substitution on the phenyl ring. Polymer **VIIa** containing 2,6-diphenyl substituents on the arylene ring has a T_g of 205°C, which is 60°C higher than PEEK ($T_g = 146^\circ\text{C}$) [5]. The glass transition temperatures increase gradually with the addition of substituents in the order H <

TABLE 1. Physical and Thermal Properties of Poly(Ether Ketone)s and Poly(Ether Sulfone)s

| Polymers | η_{inh}^a | $M_w^b (\times 10^3)$ | M_w/M_n | $T_g^c, ^\circ C$ | $T_c^c, ^\circ C$ | $T_m^d, ^\circ C$ | TGA, ^d N ₂ /air | Modulus, ^e GPa |
|----------|----------------|-----------------------|-----------|-------------------|-------------------|-------------------|---------------------------------------|---------------------------|
| VIIa | 0.62 | 77.8 | 2.9 | 205 | — | — | 504/504 | 1.46 |
| VIIb | 0.39 | 64.1 | 2.3 | 219 | — | — | 471/483 | 1.87 |
| VIIc | 0.50 | 54.6 | 2.4 | 225 | 279 | 383 | 529/504 | 2.15 |
| VIIId | — | — | — | 222 | — | — | 542/504 | — |
| VIIIa | 0.98 | 68.5 | 2.4 | 227 | — | — | 508/504 | 2.02 |
| VIIIb | 0.94 | 51.6 | 2.5 | 235 | — | — | 473/449 | 1.97 |
| VIIIc | 0.31 | 31.1 | 2.1 | 240 | — | — | 515/511 | 2.11 |
| VIIIId | — | — | — | 265 | 300 | 411 | 505/502 | — |

^aInherent viscosities (dL/g) were measured at a concentration of 0.5 g/dL in chloroform at 25°C.

^bDetermined by GPC measurements using polystyrene as the standard.

^cDetermined by DSC at a heating rate of 10°C/min in nitrogen (50 mL/min).

^dTemperature at which 5% weight loss was observed by TG/DTA at a heating rate of 10°C/min in nitrogen and air (200 mL/min).

^eDetermined by TMA at room temperature.

methyl < phenyl < diphenyls in the 5- or 5,6-positions as shown in Table 1 and Fig. 1. The highest T_g value of 265°C was obtained for polymer **VIII**d which contains four phenyl substituents on the phenyl ring. In the case of the tetraphenyl substituted polymers, the poly(ether ketone) is semicrystalline and DSC showed T_g (225°C), T_c (279°C), and T_m (383°C). The T_g 's did not increase as much as we expected, perhaps due to the low molecular weight of the polymers. Similar effects were also observed in poly(ether sulfone)s (**VIII**d) obtained from the 2,3,5,6-tetraphenylhydroquinone (**VI**d). Interestingly, the glass transition temperature of polymer **VIII**a only increased about 10°C compared to that of the unsubstituted polyethersulfone ($T_g = 210^\circ\text{C}$) [18]. The T_g 's of polymers **VIII**a, **VIII**b, **VIII**c, and **VIII**d increased gradually with increasing numbers of substituents.

The thermal properties of the polymers prepared are summarized in Table 1 and Fig. 2. All the modified polymers show excellent thermooxidative stability at high temperatures in both air and nitrogen atmospheres. The polymers containing methyl substituents on the arylene have a lower thermooxidative stability with 5% weight loss at about 450°C. The wholly phenyl-substituted poly(ether ketone)s and poly(ether sulfone)s have a higher thermooxidative stability with 5% weight loss temperatures in the range of 505 to 540°C.

Polymer films which were transparent and tough were cast from chloroform solution (120 mg/5 mL), and they maintained their excellent dimensional stability over a wide temperature range from ambient temperature to their glass transition temperatures as shown in TMA results (Fig. 3). The glass transition temperatures performed by thermomechanical analysis were in agreement with those obtained

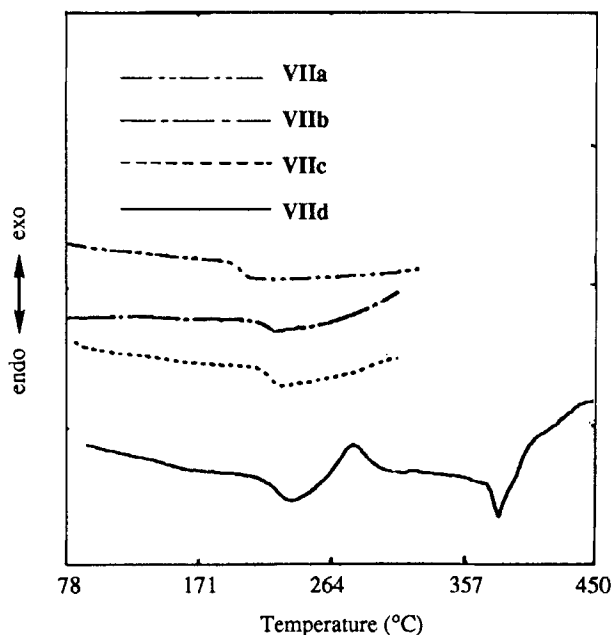


FIG. 1. DSC traces of poly(ether ketone)s **VII**a-**VII**d at a heating rate of 20°C/min in nitrogen.

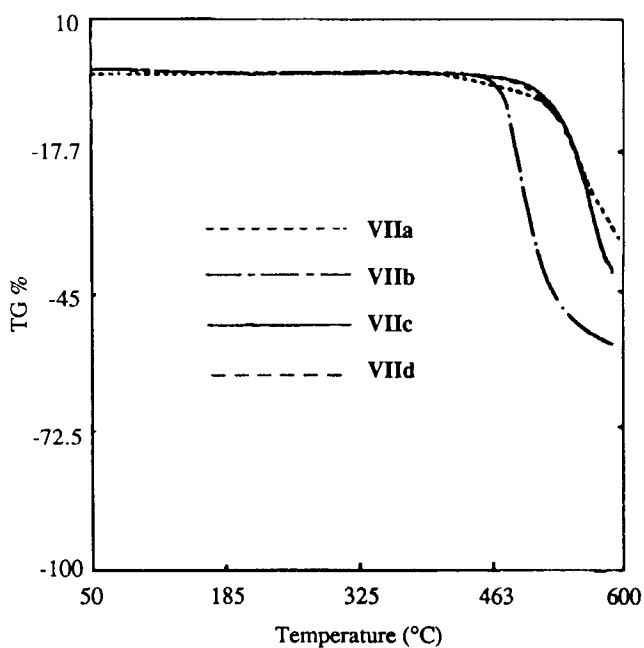


FIG. 2. TGA thermograms of poly(ether ketone)s **VIIa-VIIId** at a heating rate of 10°C/min in nitrogen.

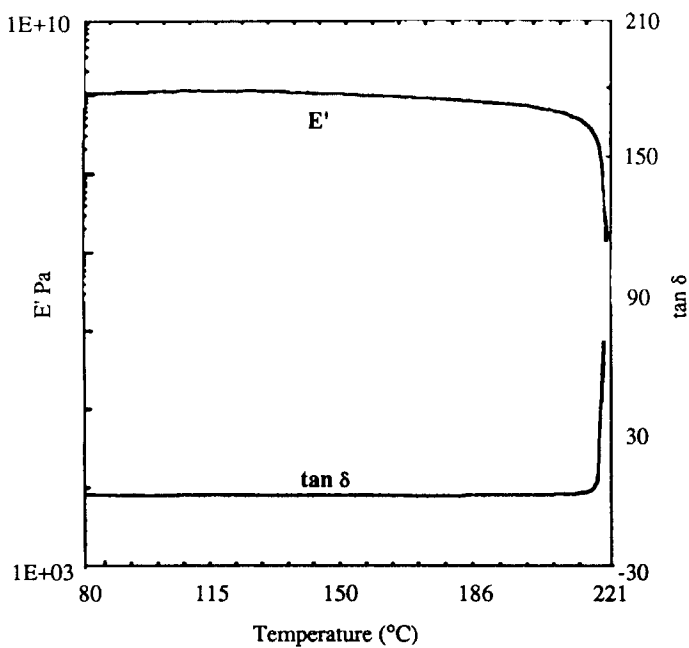


FIG. 3. Thermomechanical analysis for poly(ether ketone) **VIIb** at a heating rate of 3°C/min in static air.

from DSC. The moduli determined are in the range of 1.5 to 2.8 GPa at room temperature and 1.3 to 2.1 GPa at 200°C.

CONCLUSIONS

Hydroquinones having two to four methyl or phenyl groups on the arylene ring were successfully synthesized. Polymerization with 4,4'-difluorobenzophenone and 4,4'-difluorodiphenylsulfone in NMP in the presence of excess anhydrous potassium carbonate afforded high molecular weight polymers. The polymers derived from unsymmetrically substituted hydroquinones are amorphous and soluble in solvents such as chloroform and methylene chloride at room temperature, but polymers derived from symmetrically substituted hydroquinone are insoluble semicrystalline materials. The glass transition temperatures are higher than those of the corresponding polymers with no pendant groups on the hydroquinones, and the T_g 's gradually increased with increasing number of substituents. The methyl-substituted polymers exhibit lower thermooxidative stability than those of the corresponding polymers with aryl groups on the hydroquinone ring which show 5% weight losses above 510°C by thermogravimetric analysis.

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