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## THERMALLY CROSSLINKABLE POLY(ARYL ETHER)S CONTAINING A CHALCONE MOIETY

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### ABSTRACT

High molecular weight poly(aryl ether)s containing internal chalcone groups have been synthesized from 4,4'-dihydroxychalcone and 1,3-bis(4-hydroxycinnamoyl)benzene by solution polycondensation with activated aromatic bishalides. Characterization of and crosslinking studies on these polymers were carried out utilizing DSC, TGA, GPC and NMR. The polymers can be thermally crosslinked when heated above 300°C, and the glass transition temperatures ( $T_g$ ) of the polymers increase after crosslinking. The resulting crosslinked networks are insoluble in all organic solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the crosslinking reaction. These polymers can be converted into polypyrazolines by reaction with hydrazine monohydrate.

### INTRODUCTION

Aromatic and heterocyclic polymers have been investigated for their thermal and chemical stabilities [1]. Polychalcones which contain the vinyl carbonyl function between two aromatic rings are an interesting group of these polymers. Polymeric materials that contain chalcone-type groups were first reported in 1959 [2]. Macromolecules have been synthesized with chalcone-type groups in the side chain, in the main chain, and in epoxy resins [3]. Oleinek et al. [4] and others [5] prepared polychalcones by polycondensation of aromatic diacetyl compounds with aromatic

dialdehydes. The polymers were semiconductors and thermally stable. The thermal properties were further improved by transforming the polychalcones to polypyrazolines. Teplyakov et al. [6] investigated the possibility of using the aromatic methyl ketone condensation yielding 1,3,5-substituted benzene rings to synthesize polychalcones. Substituted polychalcones were prepared by an acetylation of vanillin and *p*-hydroxybenzaldehyde followed by a Fries rearrangement of the acetates in nitrobenzene using  $\text{AlCl}_3$  as catalyst.

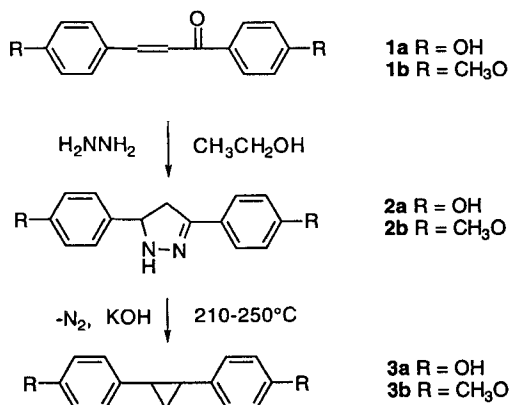
Due to solubility difficulties arising from the rigid-rod nature of main-chain-containing chalcone polymers, only low molecular weight polychalcones were obtained in some cases discussed above [7]. The condensation polymerization of aromatic dialdehydes with aromatic diacetyl compounds ( $\text{CH}_3\text{CO}-\text{Ar}-\text{X}-\text{Ar}-\text{COCH}_3$ ) gave high molecular weight polymers, some of which are soluble in *N,N'*-dimethylformamide when the aromatic diacetyl compounds have flexible ether linkages.

Besides the relatively good thermal stability of the polymers, chalcone compounds are light-sensitive. The chalcone group has been incorporated into photodegradable styrene copolymers [8]. Epoxides of hydroxychalcones produce light-sensitive materials for offset printing [9]. Glycidylethers of chalcones have also been investigated in "command-destruct" epoxy resins for easy removal of old epoxy coatings [10].

It is well known that pyrazolines are generally obtained by the reaction of  $\alpha,\beta$ -unsaturated ketones with hydrazines [11]. Polypyrazolines can be prepared by cyclocondensation of dichalcones and dihydrazines [12].

It was demonstrated that base-catalyzed thermal decomposition of substituted 3,5-diphenyl-2-pyrazolines **2b** (Scheme 1), which are the products of the reaction between hydroxychalcones **1b** and hydrazine monohydrate, results in elimination of molecular nitrogen and spontaneously affords substituted 1,2-diphenylcyclopropanes **3b** [13, 14]. We have found that this method can be used directly on the hydroxychalcones, thus 3,5-bis(4-hydroxyphenyl)-2-pyrazolines **2a** can be synthesized by reaction of 4,4'-dihydroxychalcone **1a** and hydrazine monohydrate [15].

We were interested in synthesizing high molecular weight amorphous chalcone or pyrazoline-containing polymers. The vinyl group in chalcone-containing poly-



SCHEME 1.

mers is a reactive group which may undergo thermal reaction to produce a cross-linked polymer matrix. The 2-pyrazoline group in pyrazoline-containing polymers should undergo thermal base-catalyzed decomposition to eliminate nitrogen, which might be useful for forming foamed products.

Herein we report the synthesis of poly(aryl ether)s containing the chalcone moiety and their conversion to 2-pyrazoline-containing polymers by reaction with hydrazine.

## EXPERIMENTAL

### 4,4'-Dihydroxychalcone (1a)

Synthesized by the method described previously [16, 17], mp 203–205°C (203.5–204.0°C<sup>3</sup>); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 6.75–6.95 (two d, 4 H), 7.60–7.75 (d, 2 H), 7.70 (s, 2 H), 7.98–8.06 (d, 2 H), 10.22 (s, 2 H).

### *trans*-3,5-Bis(4-hydroxyphenyl)-2-pyrazoline (2a)

To a solution of 30.7 g (128 mmol) **1a** in 300 mL ethanol was added 30 mL (618 mmol) of hydrazine monohydrate. The resulting solution was refluxed for 1.5 hours. Ice water was then added. The precipitate was collected, dried, and crystallized from ethanol, yield > 90%; mp 183–185°C; <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 2.90–3.45 (octet, 2 H), 4.70–4.80 (t, 1 H), 6.74–6.83 (two d, 4 H), 7.18–7.22 (d, 2 H), 7.51–7.56 (d, 2 H). MS *m/z* 254 (M<sup>+</sup>, 100), 161 (30), 134 (15), 120 (20). Calculated for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (254.29): C, 70.85; H, 5.55. Found: C, 70.10; H, 5.75.

### *trans*-1,2-Bis(*p*-hydroxyphenyl)cyclopropane (3a)

1.0 g (3.9 mmol) of **2a** was mixed with 1.0 g of powdered sodium hydroxide. The mixture was heated to 250°C under nitrogen and the decomposition proceeded for 30 minutes. The cooled reaction product was dissolved in water, neutralized with hydrochloric acid, and extracted with ether. The ether layer was washed with water to remove salts. Removal of the ether left the product which was crystallized from acetic acid; mp 190–191°C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 1.1.16–1.22 (t, 2 H), 1.80–1.98 (t, 2 H), 6.60–6.70 (d, 4 H), 6.90–6.96 (d, 4 H), 9.15 (s, 2 H). MS *m/z* 226 (M<sup>+</sup>, 100), 131 (15), 121 (45), 107 (20). Calculated for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> (226.27): C, 79.62; H, 6.24. Found: C, 79.40; H, 6.24.

### 1,3-Bis(4-hydroxycinnamoyl)benzene (6)

5.446 g (40 mmol) of 4-hydroxyacetophenone **4** and 2.68 g (20 mmol) of isophthalaldehyde **5** were dissolved in 80 mL of boiling alcohol. To this solution was added 26 mL of 60% potassium hydroxide solution at 55°C, and the clear solution was allowed to stand at room temperature for 1 week. The mixture set to a mass of solids; it was worked up by acidification in the cold and recrystallization of the product from alcohol; yield 80–85%. mp 165–167°C. <sup>1</sup>H NMR (200 MHz, DMSO) δ 8.10–8.06 (d, 4 H), 8.34–6.78 (m, 8 H), 6.91–6.86 (d, 4 H). MS (*m/e*, relative intensity %): 370 (M<sup>+</sup>, 100).

### Pyrazoline (7)

To a solution of 1.85 g (5 mmol) of **6** in 20 mL of ethanol, 2.2 mL (mmol) of hydrazine monohydrate was added. The resulting solution was refluxed for 1.5 hours. Ice water was then added. The precipitate was collected, dried, and crystallized from ethanol; yield > 90%; mp 145–147°C; <sup>1</sup>H NMR (200 MHz, DMSO) δ 9.64 (s, 2 H), 7.45–7.43 (d, 4 H), 6.78–6.75 (d, 4 H), 7.33–7.22 (m, 4 H), 4.75 (t, 2 H), 3.40–2.72 (octet, 4 H). MS (*m/e*, relative intensity %): 398 (M<sup>+</sup>, 100).

### Bis[4-(4-benzoylphenoxy)phenyl]-1,3-prop-2-en-1-one (9)

A mixture of **1a** (3.0 mmol, 0.7208 g), K<sub>2</sub>CO<sub>3</sub> (5.6 mmol, 0.774 g), and 4,4'-difluorobenzophenone **8** (6.0 mmol, 1.2013 g) in toluene (4 mL) and *N,N'*-dimethylacetamide (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 hours. Toluene was bled continuously from the Dean-Stark trap until the temperature rose to 155°C. The reaction mixture was lightly colored and was maintained at this temperature for 2 hours. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100°C and diluted with DMAc (5 mL) and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 hour to remove any trapped salts, filtered, and dried in a vacuum oven at 80°C; yield > 90%; mp 190–191°C. MS (*m/e*, relative intensity %): 599 (M<sup>+</sup>, 1), 301 (100). <sup>1</sup>H NMR (500 MHz, DMSO) δ 8.09–7.08 (m, 28 H). <sup>13</sup>C-NMR (500 MHz, ppm, CDCl<sub>3</sub>), 1195.39, 188.62, 160.37, 160.08, 159.79, 157.94, 143.71, 132.52, 130.87, 130.34, 129.84, 128.31, 121.02, 119.85, 118.87, 118.78, 118.06.

### Homopolymer 10a

A mixture of **1a** (3.0 mmol, 0.7208 g), K<sub>2</sub>CO<sub>3</sub> (5.6 mmol, 0.774 g), and bis(4-chlorophenyl)sulfone (3.0 mmol, 0.7628 g) in toluene (4 mL) and DMAc (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 hours. Toluene was bled continuously from the Dean-Stark trap until the temperature rose to 155°C. The reaction mixture was lightly colored and was maintained at this temperature for 2 hours. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100°C and diluted with DMAc (5 mL) and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 hour to remove any trapped salts, filtered, and dried in a vacuum oven at 80°C; yield > 90%. <sup>1</sup>H NMR (500 MHz, DMSO) δ 8.40–7.60 (m, 10 H), 7.50–6.8 (m, 8 H). <sup>13</sup>C-NMR (500 MHz, ppm, DMSO), 187.94 (carbonyl), 160.35, 159.16, 159.145, 156.76, 143.31, 135.83, 134.27, 131.84, 131.83, 131.81, 131.80, 131.56, 131.53, 131.50, 130.38, 130.33, 121.90, 120.66, 119.81, 119.47, 119.455, 118.75.

Polymers **13a** and **13b** were prepared as described above.

### Copolymers 10b–10e

A mixture of **1a** (3.0 mmol, 0.7208 g), the other bisphenol (2.4 mmol),  $K_2CO_3$  (0.774 g), and bis(4-chlorophenyl)sulfone (3.0 mmol, 0.7628 g) in toluene (4 mL) and DMAc (8 mL, freshly purified) was treated as described for the synthesis of the homopolymer.

### Homopolymer 11a

A mixture of 1,3-bis(4-hydroxycinnamoyl)benzene (**6a**; 3.0 mmol, 1.112 g),  $K_2CO_3$  (5.6 mmol, 0.774 g), and bis(4-chlorophenyl)sulfone (3.0 mmol, 0.7628 g) in toluene (4 mL) and DMAc (8 mL, freshly purified) was heated with stirring under nitrogen atmosphere with azeotropic removal of water for 3 hours. Some toluene was bled continuously from the Dean–Stark trap until the temperature rose to 155°C. The reaction mixture was lightly colored and was maintained at this temperature for 2 hours. At this time the reaction was assumed to be complete. The reaction mixture was cooled to 100°C and diluted with DMAc (5 mL) and filtered. The filtrate was neutralized with acetic acid and coagulated into methanol. The precipitate was filtered and washed with methanolic water and finally with water. It was then boiled in distilled water for 1 hour to remove any trapped salts, filtered, and dried in a vacuum oven at 80°C; yield > 90%.  $^1H$  NMR (500 MHz, DMSO)  $\delta$  8.29–7.26 (m, 24 H).  $^{13}C$ -NMR (500 MHz, ppm, DMSO), 188.05 (carbonyl), 160.43, 159.24, 144.50, 143.65, 136.40, 134.22, 131.64, 131.56, 131.46, 131.18, 130.99, 130.84, 130.77, 130.48, 130.44, 122.96, 119.86, 119.83, 119.78, 119.78, 119.50, 119.48, 117.23.

### Copolymers 11b–11e

A mixture of 1,3-bis(4-hydroxycinnamoyl)benzene (**6a**; 3.0 mmol, 1.112 g), the other bisphenol (2.4 mmol),  $K_2CO_3$  (0.774 g), and bis(4-chlorophenyl)sulfone (3.0 mmol, 0.7628 g) in toluene (4 mL) and DMAc (8 mL, freshly purified) was treated as described for the synthesis of the homopolymer.

### Characterization of Polymers

Glass transition temperatures of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 10°C/min in  $N_2$  (50 mL/min) and a Seiko 220 TMA instrument at a heating rate of 3°C/min. When recording  $T_g$  values, samples were never heated above 300°C to avoid crosslinking, and the values recorded are from the second scan. The  $T_g$  was taken from the midpoint of the change in slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10°C/min in nitrogen and air. Polymer samples were cured at 350°C under nitrogen in the TGA instrument. A DSC was then employed to determine the  $T_g$  increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were performed in  $CHCl_3$  at 25 or 50°C with a 1B(205) instrument. Molecular weights were obtained by gel permeation chromatography (GPC) relative to polystyrene standards in a chloroform solution

using a Waters 510 HPLC instrument equipped with  $\mu$ -Styragel columns (500,  $10^3$ ,  $10^4$ , and  $10^5$  Å) arranged in series and a UV detector.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded at 500 MHz using a Varian XL-200 spectrometer in  $\text{CDCl}_3$  with  $(\text{CH}_3)_4\text{Si}$  as the internal standard.

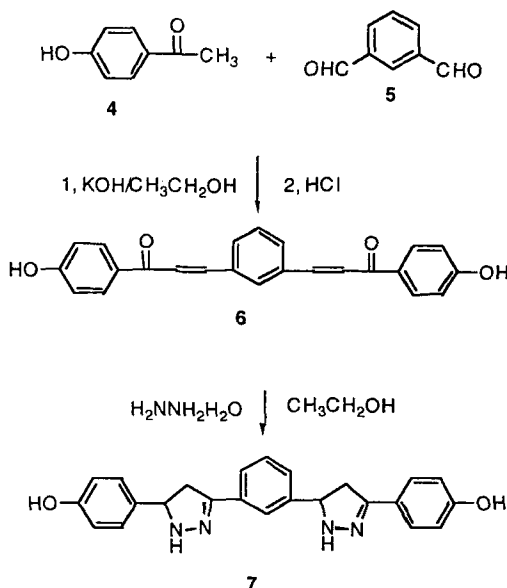
## RESULTS AND DISCUSSION

### Monomer Synthesis

4,4'-Dihydroxychalcone **1a** was prepared by reaction of 4-hydroxybenzaldehyde with 4'-hydroxyacetophenone by the hot condensation method [16, 17] (Scheme 1). 3,5-Bis(4-hydroxyphenol)-2-pyrazoline **2a** was synthesized by refluxing the ethanol solution of **1a** in the presence of a twofold excess of hydrazine monohydrate. 1,3-Bis(4-hydroxycinnamoyl)benzene **6** was prepared by the condensation of isophthalaldehyde **5** and 4-hydroxyacetophenone **4** under basic conditions (Scheme 2). 1,3-Bis(4-hydroxycinnamoyl)benzene **6** reacted with hydrazine in ethanol at reflux to afford the pyrazoline **7**.

### Preparation of Chalcone-Containing Polymers

Two major methods have been developed for the synthesis of poly(aryl ether sulfone)s. One method involves the base mediated nucleophilic displacement of aromatic bisphenols with activated aromatic bishalides. The second major method involves a Friedel-Crafts-type polysulfonylation of aromatic substrates with aromatic bis(sulfonyl chlorides). For the first method, dimethylsulfoxide (DMSO),



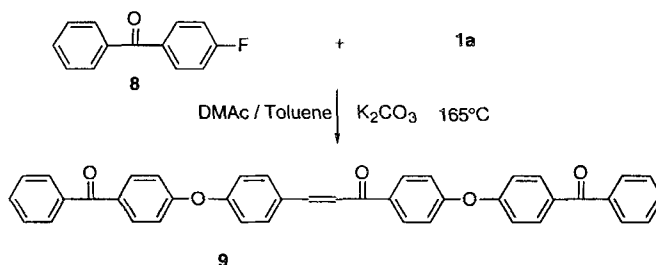
SCHEME 2.

*N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), and tetramethylene sulfone have been used as solvents. NMP or tetramethylene sulfone is used if the polymerization needs to be carried out at higher temperature. In the present case polymer hydrolysis via the attack of sodium hydroxide on the polymer chains and bisphenate insolubility posed a problem in the synthesis when DMSO was used as solvent. Therefore the potassium carbonate/DMAc route was chosen because, in this system, excess potassium carbonate does not interfere with the synthesis of high molecular weight macromolecules [18].

A model reaction for condensation polymerization was performed under the polymerization conditions used. The reaction of **1a** and 4-fluorobenzophenone **8** in DMAc at 165°C for 2 hours in the presence of potassium carbonate afforded bis[4-(4-benzoylphenoxy)phenyl]-1,3-prop-2-en-1-one **9** in quantitative yield (by HPLC) (Scheme 3). Compound **9** was isolated from the reaction mixture, purified, and characterized.

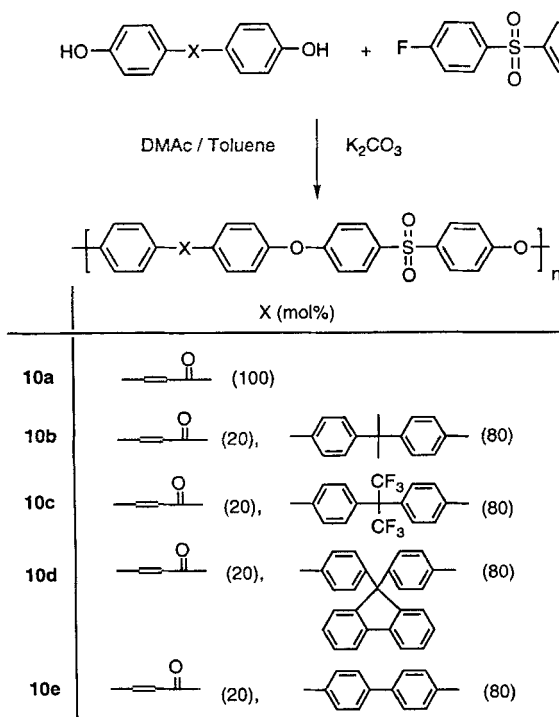
By comparing with the <sup>13</sup>C-NMR spectrum of **1a**, the peaks in the <sup>13</sup>C-NMR spectrum of compound **9** were assigned. A peak at 187.50 ppm for the carbonyl group, a peak at 143.29 ppm for the ethylene carbon bonded to benzene, and a peak at 122.23 ppm for the other ethylene carbon bonded to carbonyl group in the chalcone moiety appeared in the <sup>13</sup>C-NMR spectrum of **1a**. The <sup>13</sup>C-NMR spectrum of compound **9** shows a peak at 188.62 ppm which we have assigned to the carbonyl carbon, a peak at 143.71 ppm assigned to the ethylene carbon bonded to benzene, and a peak at 121.02 ppm assigned to the other ethylene carbon bonded to carbonyl group in the chalcone moiety. The <sup>13</sup>C-NMR studies indicated that no change occurs in the chalcone group when the model reaction was done in DMAc at 165°C in the presence of potassium carbonate, therefore it was concluded that **1a** can be polymerized by condensation polymerization under these conditions.

**1a** was polymerized with bis(4-fluorophenyl)sulfone to give a poly(aryl ether sulfone) **10a** in DMAc in the presence of excess (20%) anhydrous potassium carbonate (Scheme 4). A series of copolymers **10b–e** was also synthesized from **1a**, bisphenols, and bis(4-fluorophenyl)sulfone under the same conditions. The structure of all polymers were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR. The <sup>1</sup>H-NMR spectrum of homopolymer **10a** shows multiple peaks in the 7.19–8.22 ppm range and no peaks in the aliphatic region. The <sup>13</sup>C-NMR spectrum of homopolymer **10a** exhibits a peak at 187.94 ppm for the carbonyl group, a peak at 143.31 ppm for the ethylene carbon bonded to benzene ring, and the other peaks for the remaining carbons in the polymer backbone.



SCHEME 3.



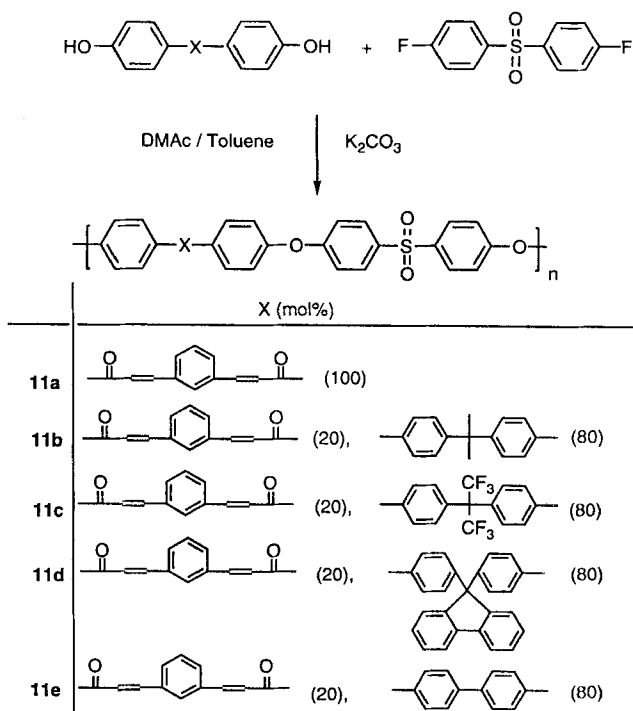


SCHEME 4.

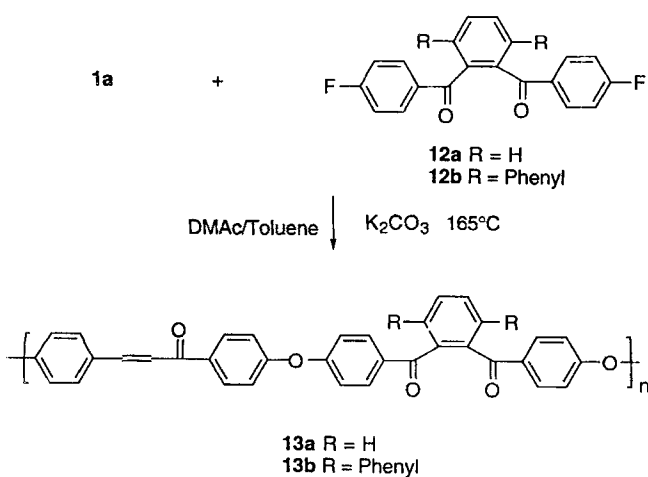
A homopolymer **11a** was obtained from the condensation polymerization of **6** and bis(4-fluorophenyl)sulfone using DMAC as solvent in the presence of excess (20%) anhydrous potassium carbonate (Scheme 5). Several copolymers **11b–e** were also prepared from **6**, bisphenols, and bis(4-chlorophenyl)sulfone under the same conditions. The structure of all polymers were determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The chalcone group in the polymer backbone was identified by comparing the  $^{13}\text{C}$ -NMR spectrum of monomer **6** to the polymers. In the  $^{13}\text{C}$ -NMR spectrum of monomer **6**, peaks at 187.00 and 143.20 ppm for the carbonyl group and the ethylene carbon, respectively, and other peaks between 160.00 and 110.00 ppm for the remaining carbons were observed. In the  $^{13}\text{C}$ -NMR spectrum of homopolymer **11a**, corresponding peaks at 188.05 and 143.65 ppm were assigned to the carbonyl carbon and the ethylene carbon, respectively, in the chalcone moiety and the remaining peaks at 160.00–110.00 ppm were assigned to the other carbons in the polymer backbone.

Poly(aryl ether ketone)s **13a–b** were synthesized from **1a** and 1,2-bis(4-fluorobenzoyl)benzene **12a** or 1,2-di(4-fluorobenzoyl)-3,6-diphenylbenzene **12b** utilizing DMAC as solvent and potassium carbonate as catalyst under the same conditions used to synthesize the poly(aryl ether sulfone)s (Scheme 6).

The  $^{13}\text{C}$ -NMR spectrum of homopolymer **13a** exhibits a peak at 195.22 ppm for the carbonyl group in the dibenzoylbenzene moiety, a peak at 188.56 ppm for the carbonyl group, a peak at 143.66 ppm in the chalcone moiety, and the other peaks at 160.86–115.45 ppm for the rest of carbons in the polymer backbone. A similar  $^{13}\text{C}$ -NMR spectrum was obtained for homopolymer **13b**.



SCHEME 5.



SCHEME 6.

### Properties of Chalcone-Containing Polymers

The properties of the chalcone-containing polymers are listed in Table 1. The homopolymer **10a** from **1a** is not soluble in  $\text{CHCl}_3$  but is soluble in hot DMAc, DMSO, and NMP. Flexible transparent films can be obtained by casting a DMAc solution of homopolymer **10a** at  $100^\circ\text{C}$ . The homopolymer **11a** from monomer **6** and bis(4-fluorophenyl)sulfone is soluble in both chloroform and DMAc, DMSO, and NMP. A flexible and transparent film was cast from a chloroform solution of homopolymer **11a** at room temperature. Poly(aryl ether ketone)s **13a–b** synthesized from **1a** and **12a** or **12b** are more soluble than poly(aryl ether sulfone)s **10a** from **1a** and bis(4-fluorophenyl)sulfone in  $\text{CHCl}_3$  and DMAc, DMSO, NMP, etc. Polymers **13a–b** are soluble in chloroform, and flexible and transparent films were cast from  $\text{CHCl}_3$  solution at room temperature. All poly(aryl ether sulfone) copolymers from **1a** as well as monomer **6** are soluble in  $\text{CHCl}_3$ , DMAc, DMSO and NMP at room temperature, except copolymers **10e** and **11e** containing the biphenyl moiety which are only soluble in hot DMAc, DMSO, or NMP. All of the copolymers are amorphous and give flexible and transparent films.

All polymers are high molecular weight. The inherent viscosities of the polymers are in the 0.30 to 0.62 dL/g range. The molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) based on polystyrene standards. GPC results are consistent with the respective inherent viscosities. Polydispersities of these polymers are less than 3,

TABLE 1. Properties of Chalcone-Containing Polymers from 4,4'-Dihydroxychalcone

Polymers	$\eta_{\text{inh}}^a$ , dL/g	$M_w/M_n^b \times 10^{-4}$	$T_g^c$ , $^\circ\text{C}$ (uncured)	$T_g^d$ , $^\circ\text{C}$ (cured)	TGA, $^\circ\text{C}$ , $\text{N}_2/\text{air}$
<b>10a</b>	0.54		190	ND	435/430
<b>10b</b>	0.43	7.01/2.96	188	208	446/435
<b>10c</b>	0.62	10.3/5.22	197	222	474/467
<b>10d</b>	0.38	6.81/2.74	266	296	450/447
<b>10e</b>	0.34	—	219	256	480/473
<b>11a</b>	0.32	6.35/2.42	190	ND	422/420
<b>11b</b>	0.55	8.35/2.78	188	222	428/424
<b>11c</b>	0.30	6.02/2.49	176	223	472/471
<b>11d</b>	0.46	8.01/3.15	255	295	448/432
<b>11e</b>	0.31	—	206	266	469/465
<b>13a</b>	0.36	6.62/2.32	150	ND	434/432
<b>13b</b>	0.52	8.21/2.44	207	ND	450/436

<sup>a</sup>0.5 g/dL in  $\text{CHCl}_3$  at  $25^\circ\text{C}$  or in DMAc at  $50^\circ\text{C}$ .

<sup>b</sup>Based on polystyrene standards.

<sup>c</sup>DSC, heating at  $10^\circ\text{C}/\text{min}$ .

<sup>d</sup>After curing for 2 hours at  $350^\circ\text{C}$  under nitrogen, DSC, heating at  $10^\circ\text{C}/\text{min}$ .

<sup>e</sup>TGA, heating at  $10^\circ\text{C}/\text{min}$ .

suggesting that the polymerization reaction proceeds without termination reactions that might be ascribed to the chalcone moiety.

The polymers are amorphous, with  $T_g$ s in the 150 to 266°C range, and they show no melting endotherm in their DSC scans. The homopolymers **10a** from **1a**, as well as the polymer **11a** from the monomer **6**, have a  $T_g$  at 190°C, which is close to the  $T_g$  of polysulfone from BPA. Thermogravimetric analysis of these chalcone-containing polymers in nitrogen and air shows no significant weight loss (–5%) before 420°C. Replacing some of the chalcone moiety in the copolymers by biphenyl, 1,1,1,3,3,3-hexafluoro-2,2-diphenylpropane, or fluorenonebiphenyl moiety increases the thermal stability in all cases. The copolymers containing the biphenyl moiety are the most stable among these polymers.

### Crosslinking Studies

The DSC scan of homopolymer **10a** is shown in Fig. 1. In addition to a  $T_g$  at 190°C, a large exotherm associated with the crosslinking reaction begins at 300°C and reaches a maximum at 413°C. The crosslinking reaction proceeds readily at 350°C. Similar results were observed in the DSC scans of homopolymers **11a**, **13a**, and **13b**. If polymers **10a**, **11a**, **13a**, or **13b** are cured at 350°C under nitrogen for longer than 30 minutes, no  $T_g$  is detected in the DSC scans of the cured polymers. The  $T_g$  of polymer **10a** increased to 243°C after being cured at 300°C for 30 minutes. No  $T_g$  was observed in the DSC scan of polymer **11a** after it was cured at 300°C for 30 minutes.

Thermal analysis is frequently used to characterize crosslinked polymers. It is well known that the  $T_g$  rises while the difference in specific heat capacity ( $\Delta C_p$ ) at  $T_g$  decreases with increasing numbers of crosslinks. The effect of curing time on the  $T_g$  (Fig. 2) of poly(aryl ether sulfone) copolymers containing 20 mol% of chalcone moieties, and the difference in  $\Delta C_p$  (Fig. 3) at  $T_g$  has been studied. After copolymers **10b–e** were cured at 350°C under nitrogen in the TGA instrument for different time periods, the cured polymers were examined in the DSC to determine the  $T_g$  increase and  $\Delta C_p$  decrease. It was found that  $\Delta C_p$  decreased rapidly and  $T_g$  increased as

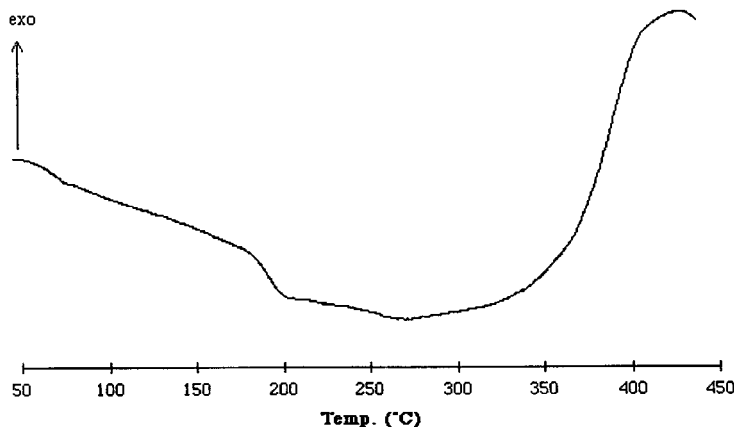


FIG. 1. DSC scan of homopolymer **10a**.

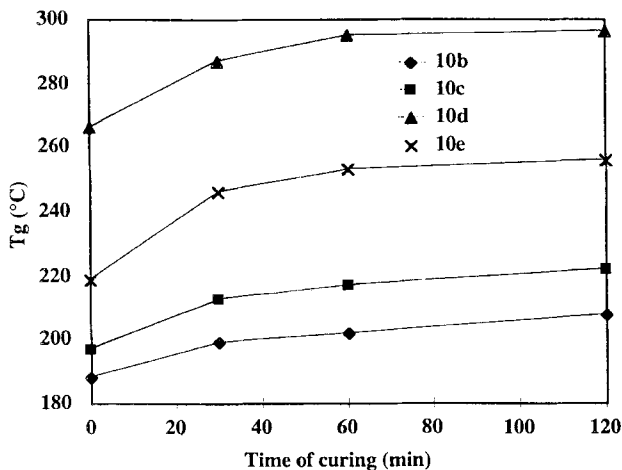


FIG. 2. DSC scans showing the effect of curing time on  $T_g$  ( $350^\circ\text{C}$  under nitrogen, heating rate of  $10^\circ\text{C}/\text{min}$ ).

curing time increased as a result of the crosslinking of the polymers. After 1 hour the changes in  $\Delta C_p$  and  $T_g$  slowed down significantly.

The  $T_g$ s of all polymers after curing at  $350^\circ\text{C}$  for 2 hours under nitrogen are listed in Table 1. A higher increase in  $T_g$  was found for the polymers from **6** than the other polymers from **1a**.

The solvent resistance of all cured polymers improved significantly. All cured polymers are insoluble in all solvents tried. The cured copolymers swelled in  $\text{CHCl}_3$ , while the cured homopolymers did not swell.

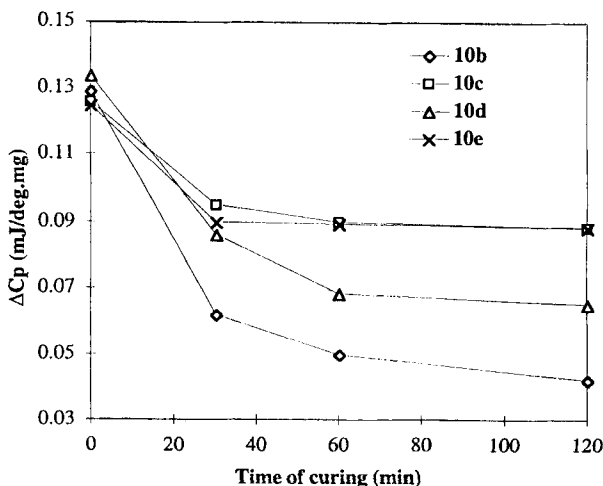
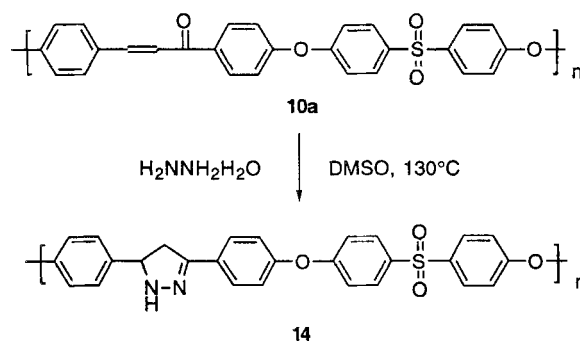


FIG. 3. Effect of curing time on  $\Delta C_p$  at  $T_g$  ( $350^\circ\text{C}$  under nitrogen,  $\Delta C_p$  at  $T_g$  was obtained in a DSC).

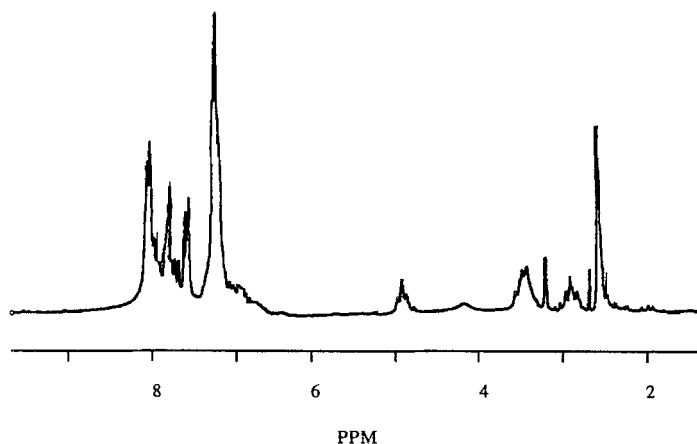


SCHEME 7.

### Conversion of Polychalcone to Polypyrazoline

The reaction of polychalcone **10a** and hydrazine monohydrate in DMSO at  $100^\circ\text{C}$  for 6 hours afforded polypyrazoline **14** (Scheme 7). The resulting polypyrazoline **14** is more soluble in DMSO than precursor polychalcone **10a**. No significant chain cleavage occurred since the inherent viscosity (0.52 dL/g) of polymer **14** is only slightly lower than that (0.54 dL/g) of precursor **10a**. The  $^1\text{H-NMR}$  spectrum of polypyrazoline **14** is shown in Fig. 4. A triplet at 4.90 ppm for the benzylic protons in the 2-pyrazoline moiety and two sets of multiplets at 3.60–2.80 ppm for the methylene protons were found in the  $^1\text{H-NMR}$  spectrum of polypyrazoline **14**.

The DSC scan of polypyrazoline **14** is shown in Fig. 5. A  $T_g$  at  $234^\circ\text{C}$  and an exotherm at  $430^\circ\text{C}$  was observed. Thermogravimetric analysis of polymer **14** under nitrogen shows a 5% weight loss at  $403^\circ\text{C}$ . Heating polymer **14** at  $300^\circ\text{C}$  for more than 30 minutes in the presence of a catalytic amount of sodium hydroxide under nitrogen afforded a crosslinked polymer. Initial elimination of nitrogen would be expected to give the cyclopropane-containing polymer which could then undergo a crosslinking reaction. A gas, presumably  $\text{N}_2$ , was generated during the heating.

FIG. 4.  $^1\text{H-NMR}$  spectrum of homopolymer **14**.

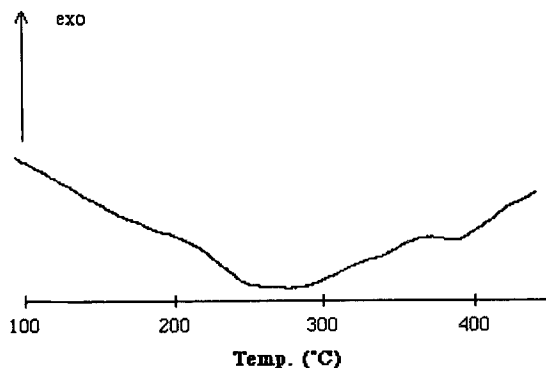


FIG. 5. DSC scan of homopolymer 14.

## CONCLUSIONS

High molecular weight poly(aryl ether)s containing internal chalcone groups have been synthesized from 4,4'-dihydroxychalcone and 1,3-bis(4-hydroxycinnamoyl)benzene by solution polycondensation with activated bishalides. The polymers can be thermally crosslinked when heated above 350°C, and the glass transition temperatures ( $T_g$ ) of the polymers increase after crosslinking. The resulting crosslinked networks are insoluble. Thermogravimetric analysis shows that no significant weight loss accompanies the crosslinking reaction. The chalcone-containing polymers can be converted into polypyrazolines by reacting with hydrazine monohydrate.

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