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Poly(Aryl Ether)s from a Novel Biphenol Monomer Containing a Dicyanoarylene Group

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POLY(ARYL ETHER)S FROM A NOVEL BIPHENOL MONOMER CONTAINING A DICYANOARYLENE GROUP

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ABSTRACT

The preparation of a novel biphenol, 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene, from phenolphthalein is described. This biphenol was prepared in high yield in a four-step reaction sequence. The biphenol can be polymerized with activated dihalides such as 1,2-bis-(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene, bis(4-fluorophenyl) sulfone, and 4,4′-dichlorobenzophenone to give high molecular weight amorphous poly(aryl ether)s. The polymers have glass transition temperatures ranging from 284 to 319°C and are easily cast into flexible, colorless, and transparent films. The 5% weight loss temperatures of these polymers, by thermogravimetric analysis in air and nitrogen, are all above 500°C.

INTRODUCTION

One of our main interests is the synthesis of amorphous polymers with high glass transition temperatures and excellent thermooxidative stability. One of the advantages of these amorphous polymers is that they are soluble in common organic solvents, which allows for facile solution processing and chemical modification. For example, we have prepared amorphous poly(aryl ether ketone)s [1] which can also be converted into soluble poly(aryl ether phthalazine)s [2], poly(aryl ether isoquinoline)s [3], and ion-containing polymers [4]. The polymers can be cast into flexible and tough films. However, a drawback of these amorphous polymers is their poor solvent resistance. This problem could be solved if the amorphous polymers could be postcured. We are currently studying methods for postcuring these amorphous polymers [5].

We recently reported the synthesis of novel imidoaryl biphenols derived from phenolphthalein and the corresponding high molecular weight poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s prepared by polymerization of these biphenols with activated aromatic dihalides in dipolar aprotic solvents [6, 7]. In the synthesis of these monomers, if fumaronitrile is used for the Diels–Adler reaction instead of the *N*-substituted maleimides reported previously, a biphenol (**V**) containing the ortho-substituted dicyanonaphthalene moiety can be obtained. The pendant cyano groups present potential crosslinking sites as described previously for high temperature resins containing dicyano groups [8–10]. The poor solvent resistance of the amorphous polymers could then be overcome by postcuring.

Another interest in polymers containing dicyanonaphthalene moieties is the possibility of conversion into naphthalocyanine-containing polymers. Naphthalocyanine is an IR-absorbing dye and has potential applications in IR-laser printing [11, 12]. Naphthalocyanine-containing polymers would be interesting materials because they could combine the properties of high performance polymers, i.e., high glass transition temperature, high thermooxidative stability, and good mechanical properties, with the electro-optic properties of the IR-absorbing dye, naphthalocyanine.

This paper describes the synthesis of the novel biphenol monomer 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene (**V**) and poly(aryl ether)s (**VII**) obtained by condensation of this biphenol with several activated dihalide monomers. The thermal and mechanical properties of these polymers are discussed and compared to the previously reported poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s.

EXPERIMENTAL

Materials

Phenolphthalein, bis(4-fluorophenyl)sulfone, 4,4′-dichlorobenzophenone, 3,5-di-*tert*-butylphenol, and fumaronitrile were used as received from Aldrich Chemical Co. 4,4′-Isopropylidenediphenol (BPA) was from General Electric Co. 2,2′-Bis(4-hydroxyphenyl)hexafluoropropane was obtained from Kennedy & Klim Inc. All other dihalide monomers were prepared in this laboratory [1, 13]. All solvents (reagent grade) were from Aldrich and BDH.

Characterization

^{1}H-NMR spectra were recorded on a Gemini-200 and Varian Unity-500 spectrometer using dimethylsulfoxide-d_6 (DMSO-d_6) and methylene chloride-d_2 (CD_2Cl_2) as solvent. The NMR spectra for the measurement of number-average molecular weight were recorded using an acquisition time of 3 seconds and a delay time of 50 seconds. IR spectra were recorded on an Analect AQS-18 FT-IR spectrophotometer, using KBr pellets. Mass spectra were recorded on a ZAB 2F HS spectrometer, using FAB technique and molecular ion (*m/e*) for the assignment. Apparent molecular weights were determined by gel permeation chromatography on a

Waters 510 HPLC with a UV detector. Element analysis results were provided by Galbraith Laboratories, Inc., Knoxville, Tennessee, USA.

Inherent viscosities were measured using an Ubbelohde viscometer. Glass transition temperatures (T_gs) were determined by a Seiko 220 DSC instrument at a heating rate of 20°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) data were collected using a Seiko TG/DTA 220 instrument at a heating rate of 10°C/min in N_2 and air after samples were previously dried at a temperature 30°C above the corresponding T_g for 3 hours. Mechanical properties were measured on a Seiko TMA/SS 120 instrument, using films cast from chloroform.

Synthesis of 1,4-Bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene (V)

To a dry 500 mL round-bottom flask containing 200 mL hot toluene (60°C), fumaronitrile (4.85 g) and isobenzofuran (**III**) (18 g) freshly synthesized according to our previous procedure [6] were added. The solution was heated quickly to 90°C and maintained at this temperature for 2 hours. The Diels-Alder reaction was complete as indicated by a change in color from red to clear to light brown and finally to clear, and also by TLC. After concentration of the reaction mixture in a rotovap, a pale yellow precipitate deposited which was collected by filtration. The Diels-Alder adduct (**IV**) was then dissolved in 200 mL absolute ethanol containing 10 mL concentrated hydrochloric acid. The solution was maintained at 90°C for 2 hours to allow complete dehydration. The precipitate was recrystallized from toluene to give 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene (**V**) as a light gray powder, yield 48.2%; mp 402–403°C; IR absorption: 2242 cm^{-1}, CN stretch, strong; ^1H NMR (500 MHz, DMSO-d_6): δ 9.96 (s, 2H of —OH group); 7.78 (m, 4H, $H_{5,6,7,8}$ of naphthalene ring); 7.35 (d, 4H, $H_{3,5}$ of 4-hydroxyphenyl ring, J = 8.5 Hz); 7.00 (d, 4H, $H_{2,6}$ of 4-hydroxyphenyl ring, J = 8.5 Hz). High resolution mass spectroscopy: *m/e*: calculated for $C_{24}H_{15}O_2N_2$: 363.11335, found 363.11323.

Polymer Synthesis: Typical Procedure for VIIa

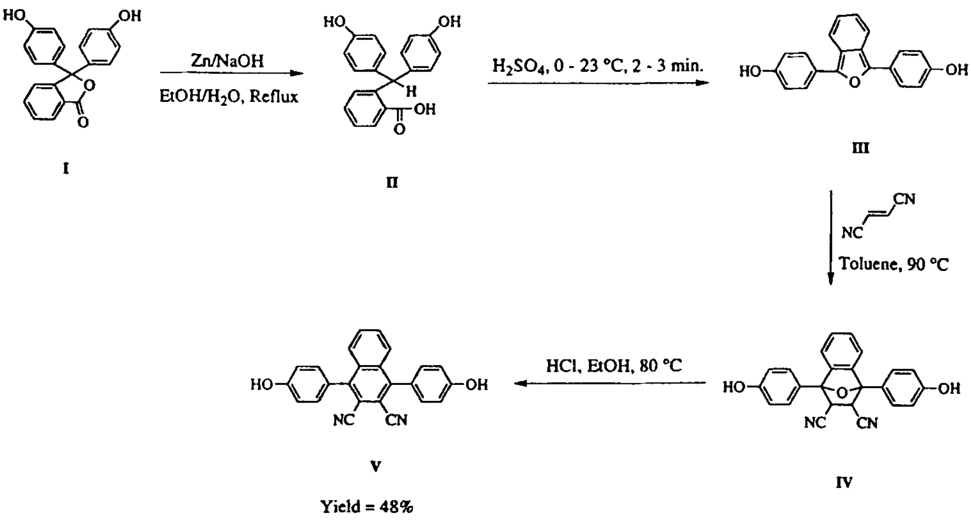
To a dry 100 mL three-neck flask equipped with a Dean-Stark trap, water condenser, thermometer, and argon gas inlet were added 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene (**V**) (1.0000 g, 2.76 mmol), bis(4-fluorophenyl)sulfone (**VIa**) (0.7016 g, 2.76 mmol), anhydrous potassium carbonate (0.39 g, 3.59 mmol), 10 mL toluene, and 16 mL *N,N*-dimethylacetamide (DMAc). Under an atmosphere of argon, the solution was heated and maintained at 140°C for 2 hours to remove all water by means of azeotropic distillation with toluene. The temperature was then increased to 165°C for 1 hour. The resulting pale brown reaction mixture was diluted with 15 mL chloroform and precipitated into 200 mL methanol. The white fibrous polymer was redissolved in 50 mL chloroform and filtered through a thin layer of Celite to remove inorganic salts. Acetic acid, which neutralized any remaining phenoxide end groups, was added dropwise to the chloroform solution until the pale yellow color disappeared. The chloroform solution was then concentrated to a volume of about 20 mL and precipitated into a mixture of 200 mL methanol and 100 mL water. White fibrous polymer was obtained in a yield of 85%. To remove oligomers, a reverse precipitation was employed. The final yield was then approximately 60%. The polymers were dried at 200°C for 10 hours and then at 330°C for 1 hour prior to characterization.

End-Capped Copolymer Synthesis: Typical Procedure for XIb

To a dry 100 mL three-neck flask equipped with a Dean-Stark trap, water condenser, thermometer, and argon gas inlet were added 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene (**V**) (0.2851 g, 0.79 mmol) BPA (**VIII**) (0.7183 g, 3.15 mmol), bis(4-fluorophenyl)sulfone (**VIa**) (1.0200 g, 4.02 mmol, 2% excess relative to the biphenol), 3,5-di-*tert*-butylphenol (**X**) (0.0325 g, 0.16 mmol), anhydrous potassium carbonate (0.6 g, 5.4 mmol), 10 mL toluene, and 20 mL DMAc. The mixture was heated to reflux at 140°C for 2 hours. The temperature was then increased to 165°C and maintained there for 2 hours. The resulting pale brown reaction mixture was diluted with 20 mL chloroform and precipitated into 300 mL methanol. The white fibrous polymer was redissolved in 80 mL chloroform and filtered through a thin layer of Celite to remove inorganic salts. Acetic acid was added dropwise to the chloroform solution until the pale yellow color was removed. The chloroform solution was then concentrated to a volume of about 25 mL and precipitated into a mixture of 300 mL methanol and 100 mL water. A white powder was obtained. The composition and number-average molecular weight were determined by solution ^{1}H-NMR spectroscopy. The polymers were dried at 230°C for 10 hours prior to characterization.

RESULTS AND DISCUSSION

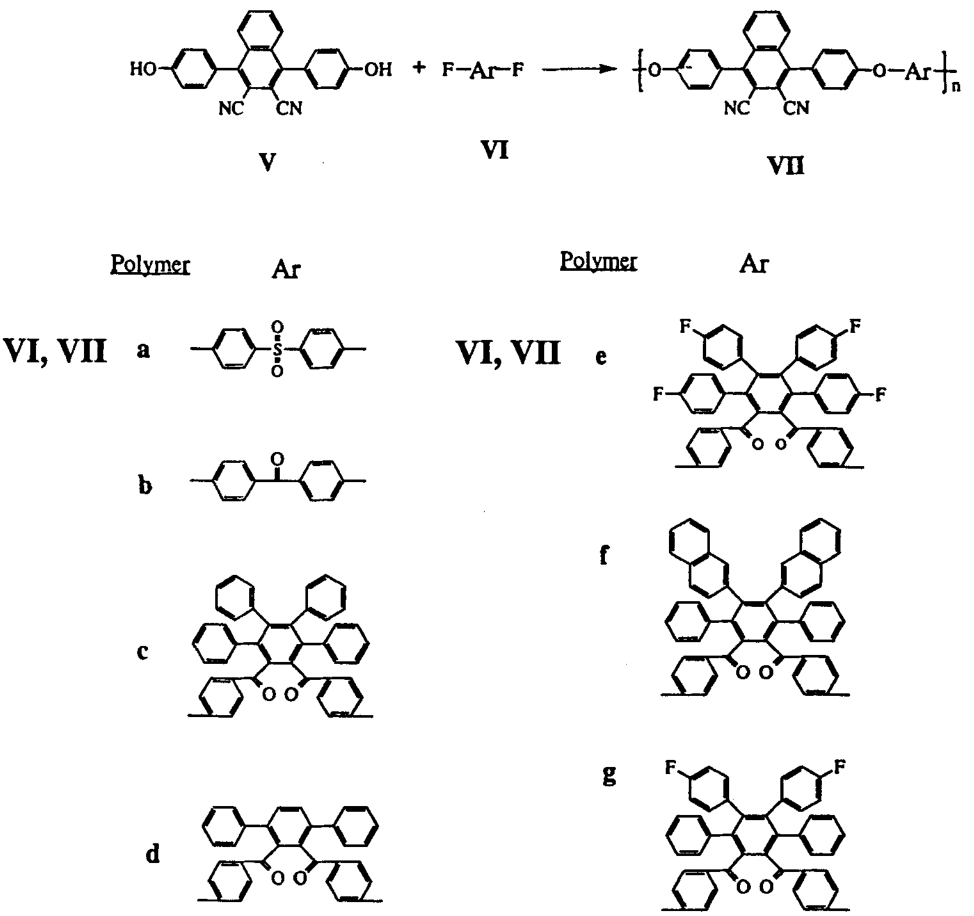
The synthesis of the biphenol monomer, 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene (**V**), as shown in Scheme 1, is a four-step reaction sequence. The overall yield is 48%. The intermediate isobenzofuran (**III**) is unstable; therefore



SCHEME 1.

it is important to react it with fumaronitrile within a very short time (e.g., 10 minutes) after isolation. The biphenol monomer **V** has a very high melting point (402–403°C). It is soluble in common organic solvents and is stable under the polymerization conditions.

The biphenol monomer **V** was polymerized with a series of activated dihalide monomers to give poly(aryl ether)s **VIIa–VIIg** (Scheme 2), employing standard conditions in DMAc as solvent [15]. Any water present or generated during the bisphenoxide formation was removed as an azeotrope with toluene. The reactions were maintained at the reflux temperature of 140°C for 2 hours, and upon complete bisphenoxide formation and dehydration, the polymerization reactions were heated to 165°C. After a period of 1 to 3 hours, depending on the individual dihalide monomer, a dramatic increase in the viscosity of the reaction mixture indicated the formation of high molecular weight poly(aryl ether). If the polymerization reactions were run for too long a time, the resulting polymers gelled and were no longer completely soluble. The polymers were characterized by ^{1}H-NMR spectroscopy.



SCHEME 2.

The 2D COSY and 1D ^{1}H-NMR spectrum in CD_2Cl_2 of polymer **VIIa** is shown as an example in Fig. 1 to confirm the assignment for polymer **VIIa**.

The polymerization reactions could also be run in DMSO below 135 °C. In this case it generally took 4 to 6 hours to give a high molecular weight polymer. The polymers obtained by carrying out the reaction under argon atmosphere, either in

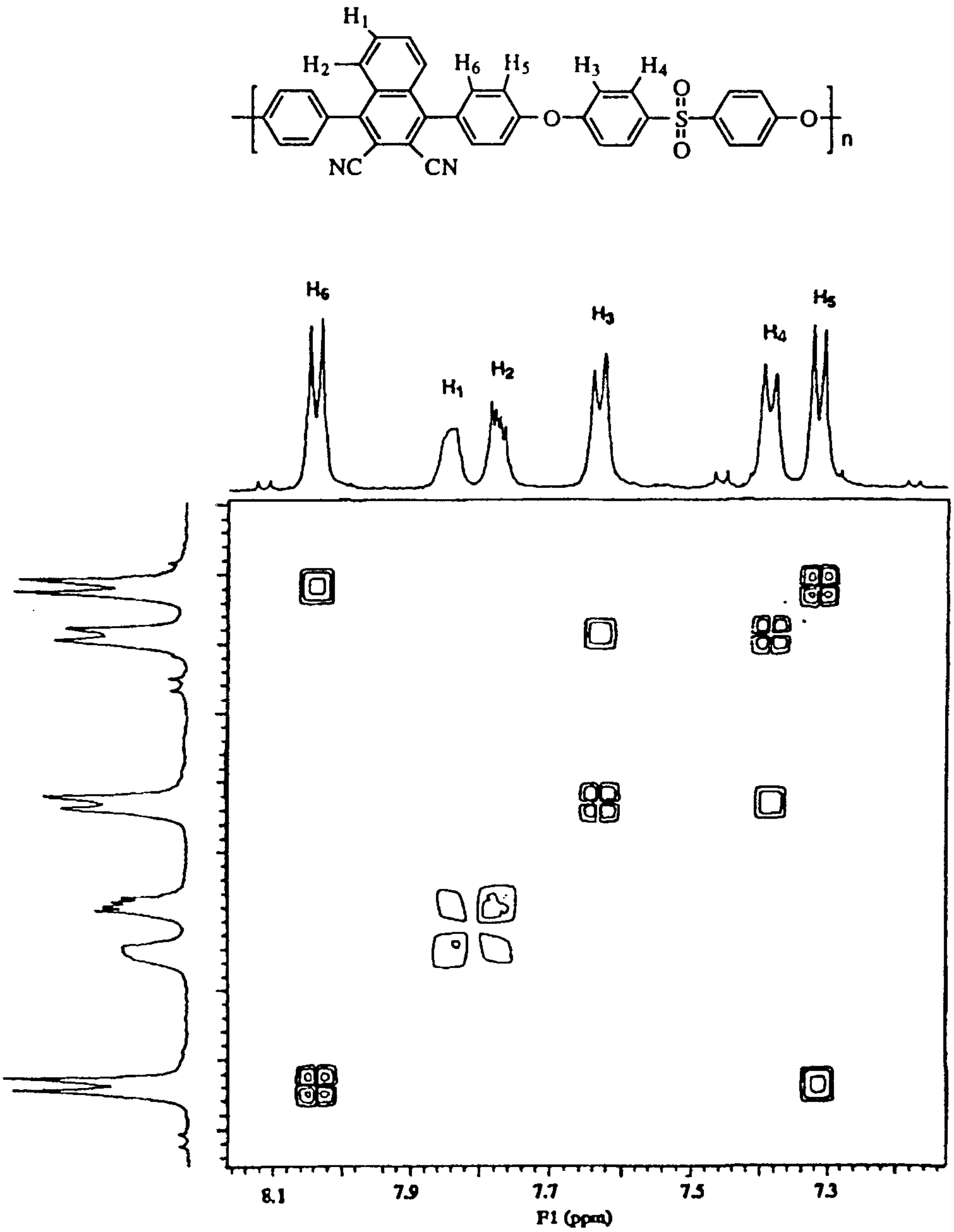


FIG. 1. 2D COSY ^{1}H-NMR spectrum of polymer **VIIa** with assignments.

DMAc or DMSO solvent, are obtained as white fibers and can be cast into colorless films. The polymers obtained under nitrogen atmosphere are pale yellow which is probably due to oxidation by a trace amount of oxygen in the nitrogen gas during the long polymerization reactions.

Table 1 summarizes properties of polymers **VIIa–VIIg**. All of the polymers are soluble in common organic solvents. They are high molecular weight and can be cast into tough, clear, and flexible films which block cross-polarized light, a characteristic of amorphous polymers. If the polymers were crystalline, they would allow the cross-polarized light to pass through. The inherent viscosities (η_{inh}) of the polymers were measured in chloroform at 25°C at a concentration of 0.5 g/dL. The viscosities range from 0.51 to 1.61 dL/g. Apparent molecular weights were determined by size exclusion chromatography, using polystyrene standards. The molecular weights ranged from 50,000 to 453,000.

The glass transition temperatures were determined by differential scanning calorimetry (DSC) at a heating rate of 20°C/min under an atmosphere of nitrogen. In all cases the midpoint of the change in the slope of the base line on the second heating scan was taken as the T_g. The glass transition temperature of polymers **VIIb** and **VIId** is the lowest (284°C). That of the polymer **VIIf** is the highest (319°C), higher than the highest T_g (310°C) of our previously reported poly(imidoaryl ether sulfone)s. The polymer **VIIf** consists of a rigid part (the biphenol monomer) and a very bulky part (the dihalide monomer). Therefore, it would be expected to have a very high glass transition temperature. The polymer **VIIa**, obtained from the condensation of the cyano-containing monomer (**V**) and bis(4-fluorophenyl)sulfone (**VIa**), has a higher T_g than the corresponding poly(imidoaryl ether)s [7].

All of the polymers have high thermooxidative stabilities. The temperature at which 5% weight loss occurs in air and nitrogen by TGA ranges from 501°C for polymer **VIIb** to 556°C for polymer **VIIe**. The results are comparable to the 10% weight loss temperatures for the poly(imidoaryl ether)s, indicating that the cyano-containing poly(aryl ether)s have somewhat higher thermooxidative stability. Isothermal aging by TGA was done under an atmosphere of nitrogen over a 10-hour period to assess the long-term thermooxidative stability of the polymers. From the aging experiments, the polymers show weight losses in the range of 0.18 to 0.47%. The high thermooxidative stability may be attributed to the presence of the cyano

TABLE 1. Properties of the Homopolymers[a]

Polymer	η_{inh}	M_w	T_g, °C	−5% wt (°C, N_2/air)	E'(GPa, 25/200°C)
VIIa	0.61	138,000	316	529/503	1.42/1.37
VIIb	0.72	85,700	284	524/501	1.29/1.15
VIIc	1.61	453,000	314	523/505	2.11/2.03
VIId	1.68	155,000	284	535/508	1.81/1.68
VIIe	0.63	55,000	314	556/535	1.55/1.10
VIIf	0.85	85,200	319	553/507	1.70/1.07
VIIg	0.51	50,000	315	554/537	

[a] Viscosities were measured in $CHCl_3$ at 25°C at a concentration of 0.5 g/dL.

groups which could act as crosslink sites upon heating to form a thermally stable resin [8–10]. All the polymers become less soluble and have higher glass transition temperatures after being cured above 360°C, indicating crosslinking had occurred.

Young's moduli for polymers **VIIa–VIIg** are all in the GPa range at both 25 and 200°C (Table 1). The polymers show ductile mechanical behavior with no failure at 40% elongation. The decrease in Young's moduli at 200°C is not significant, and the polymers maintain good mechanical properties above 200°C. Figure 2 shows the TGA and DSC thermograms of polymer **VIIa** as an example.

To control the molecular weight and the content of cyano-groups in the polymers, endcapping and copolymerization techniques were used. Scheme 3 shows the approach which uses a 2% excess of dihalide monomer, bis(4-fluorophenyl)sulfone

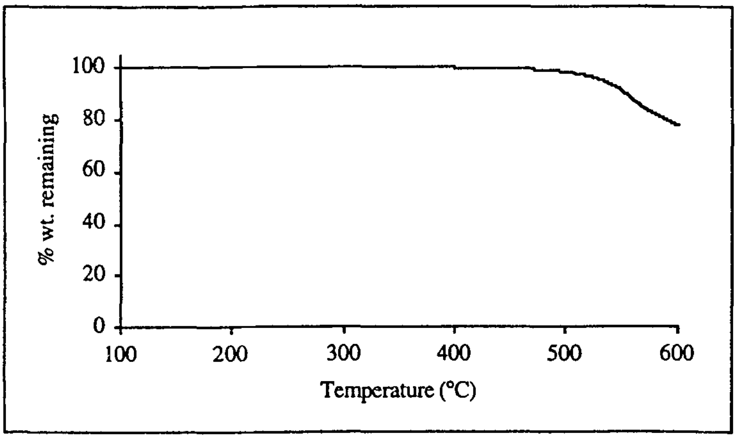


FIG. 2a

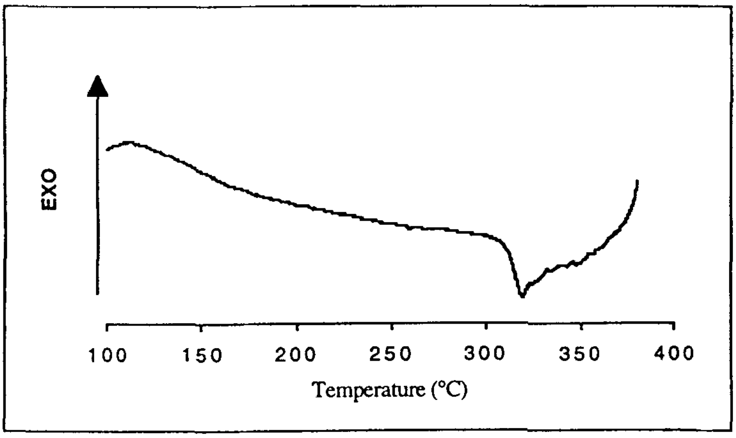
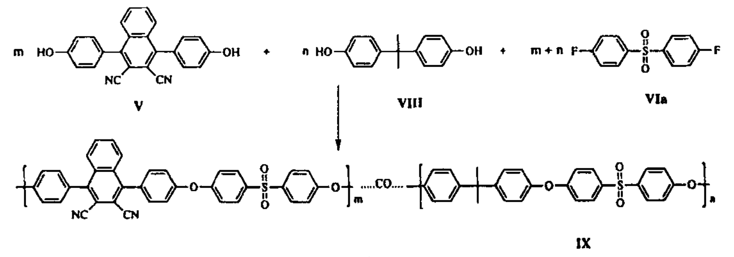
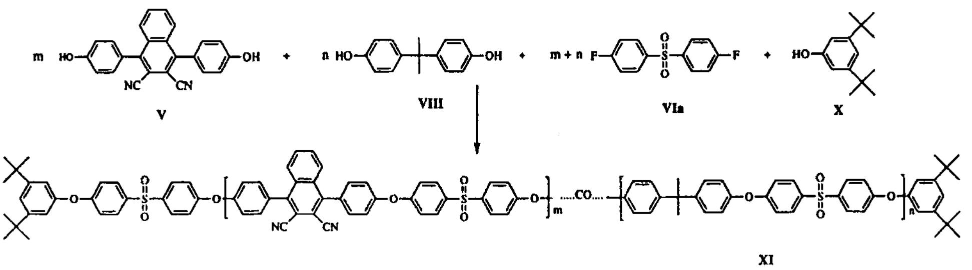


FIG. 2b

FIG. 2. (a) TGA thermogram of polymer **VIIa**; (b) DSC thermogram of polymer **VIIa**.



Uncapped Copolymer	m/n
IXa	10/90
IXb	20/80
IXc	50/50



Uncapped Copolymer	m/n
XIa	10/90
XIb	20/80

SCHEME 3.

(**VIa**), and enough 3,5-dibutylphenol (**X**) to react with the dihalide end groups. BPA (**VIII**) was used as a comonomer. The copolymer and endcapped copolymers were characterized, and their composition and number-average degree of polymerization determined by integration ratios of the aliphatic protons from BPA (δ 1.66) and 3,5-di-*tert*-butylphenol (δ 1.29) over four aromatic protons (δ 7.78, 7.84) on the naphthalene ring. A long delay time (50 seconds) was used to acquire ^{1}H-NMR spectra to ensure that the aromatic protons had sufficient time to fully relax and give the correct integration ratio of aromatic to aliphatic protons.

Properties of the copolymers **IXa**, **IXb**, and **IXc** and endcapped copolymers **XIa** and **XIb** are summarized in Table 2. The uncapped copolymers **IXa**, **IXb**, and **IXc** are high molecular weight. The glass transition temperatures of the copolymers fit the values calculated by the Fox equation [15]. The encapped copolymers **XIa** and **XIb** have a molecular weight corresponding to the stoichiometric amounts of reactants. The glass transition temperatures of the endcapped copolymers **XIa** and **XIb** are 201 and 210°C, respectively, a few degrees lower than those of the uncapped polymers **IXa** and **IXb**, which is probably because the molecular weights of polymers **XIa** and **XIb** are not high enough. The temperature at which 5% weight loss occurs in thermogravimetric analysis for the copolymers ranges from 475 to 512°C. The lower thermooxidative stability of copolymers **IXa**, **IXb**, **IXc**, **XIa**, and **XIb** than for the homopolymers is probably due to the aliphatic portions in the

TABLE 2. Properties of the Copolymers[a]

Polymer	η_{inh}	M_w	DP	T_g, °C	−5% wt (°C, N_2/air)	E'(GPa, 25/20°C)
IXa	0.76	114,944	244	205	495/482	1.12
IXb	0.46	57,998	124	218	508/491	1.05
IXc	0.62	105,230	151	249	512/497	1.31/1.02
XIa	0.33	24,536	49	201	510/475	2.80
XIb	0.36	25,347	54	210	507/469	2.41

[a] Viscosities were measured in $CHCl_3$ at 25°C at a concentration of 0.5 g/dL.

copolymers. All of the copolymers can be cast into tough and flexible films. Their Young's moduli range from 0.91 to 1.31 GPa at 25°C, slightly lower than those of the homopolymers.

CONCLUSIONS

A novel biphenol monomer, 1,4-bis(4-hydroxyphenyl)-2,3-dicyanonaphthalene (**V**), was prepared in a four-step reaction sequence in good yield. A series of poly(aryl ether)s (**VIIa–VIIg**) synthesized by condensation of this monomer with a series of activated dihalide monomers was obtained. The polymers are amorphous and high molecular weight. They are soluble in common organic solvents and can be cast into colorless, flexible films. The polymers have high thermooxidative stabilities. The 5% weight loss temperatures are all above 500°C. Glass transition temperatures of the polymers range from 284 to 319°C. The mechanical properties are typical of high performance engineering thermoplastics (Young's moduli = 1.42–2.11 GPa).

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