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SYNTHESIS AND CHARACTERIZATION OF POLY(ARYL ETHER-BISSULFONE)S

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ABSTRACT

A series of poly(aryl ether-bissulfone)s were synthesized from bisphenols, 4,4′-bis(4-chlorophenylsulfonyl)biphenyl, and 4,4′-bis(4-fluorophenylsulfonyl)biphenyl. The bishalide monomers were synthesized by reaction of 4,4′-bis(chlorosulfonyl)biphenyl with a suitable aryl halide. Potassium carbonate mediated reaction in dimethylacetamide gave high molecular weight polymers in excellent yield. The polymers are soluble in dipolar aprotic solvents. Unlike the corresponding monosulfone analogues, the poly(aryl ether-bissulfone)s exhibited poor solubility in chlorinated hydrocarbons. The glass transition temperatures of the polymers are among the highest known for poly(aryl ether)s (241–271°C). In addition, the polymers exhibit excellent thermal stability and they produce clear, colorless tough films by solution casting or compression molding.

INTRODUCTION

Poly(aryl ether sulfone)s and poly(aryl ether-ketone)s belong to a class of materials known as engineering thermoplastics [1]. They exhibit many desirable characteristics including exceptional thermooxidative and dimensional stability, relatively high glass transition temperatures (T_g) ranging from 150 to 220°C, and excellent mechanical properties [2]. The presence of ether linkages in the polymer backbone renders hydrolytic stability to the polymer. Furthermore, it has long been recognized that aromatic ether functionalities provide improved solubility and processability as well as lower T_g [3]. Therefore, attempts have been made to raise the glass transition temperature of the polymers (while retaining the desirable attributes of the ether functionalities) by the introduction of rigid groups into the polymer backbone. For example, poly(ether-imide)s and poly(ether-phenylquinoxaline)s exhibit glass transitions ranging from 230 to 275°C [4, 5]. Comparable glass transition values have been reported for poly(aryl ether-bissulfone)s 1 [6, 7]. Detailed synthesis and characterization studies of this interesting class of material have not been discussed. In this paper we report model compound studies and synthesis of bissulfone functional monomers and polymers based upon isopropyliedenediphenol (Bisphenol-A), tetramethylbisphenol-A, hydroquinone, biphenol, and sulfonyldiphenol (Bisphenol-S). The polymers have been characterized by spectroscopic, thermal, and thermomechanical means. The physical properties of Bisphenol-A functional polymer have been compared with those of the corresponding monosulfone analogue, UDEL, prepared from Bisphenol-A and 4,4′-dichlorodiphenylsulfone [2].

EXPERIMENTAL

Materials

Dimethylacetamide (DMAC) (Aldrich) was dried over calcium hydride and then distilled at reduced pressure. Chlorobenzene (Fisher) and nitrobenzene (Aldrich) were purified following the same procedure. Diphenyl sulfone (DPS) (Aldrich) was recrystallized from acetone. 4,4′-Isopropyledenediphenol (Bisphenol-A), kindly supplied by Dow Chemical Co., was purified by recrystallization from toluene and dried at reduced pressure at 80°C for 24 h. Hydroquinone, biphenol, and 4,4′-dihydroxydiphenyl sulfone (Aldrich) were recrystallized from acetone. 2, 2′-bis(3,3′-Dimethyl-4-hydroxyphenyl)propane (tetramethylbisphenol-A) prepared in our laboratory according to a previously reported procedure, was recrystallized from methanol [8]. Thionyl chloride was stirred over triphenylphosphite and distilled at normal pressure prior to use. Anhydrous potassium carbonate (Fisher) was dried in an oven overnight at 100°C. 4,4′-Biphenylsulfonyl chloride was either purchased (Aldrich) or prepared from biphenyl by chlorosulfonation according to a procedure reported earlier [9]. All other reagents were used as received.

Monomer Synthesis

4,4′-bis(4-Chlorophenylsulfonyl)biphenyl (2). A 2000-mL, three-necked, round-bottomed flask fitted with a condenser, a nitrogen inlet, and a mechanical stirrer was charged with 102.64 g (0.29 mol) of 4,4′-biphenylsulfonyl chloride and 600 mL chlorobenzene (excess). The reaction vessel was cooled in an ice bath, and anhydrous aluminum chloride (81.76 g, 0.61 mol) was added in small increments to the reaction mixture. After the initial exotherm, the ice bath was removed and the mixture was refluxed for 48 h. The deep orange colored reaction mixture was then poured into strongly acidified cold water with vigorous stirring. The precipitated solid was collected by filtration and washed with copious quantities of water followed by saturated aqueous sodium bicarbonate solution. The crude product was crystallized ($CHCl_3$) to afford 2 as white needles: mp 277.2°C (DSC); ^{13}C NMR ($CDCl_3$); δ 128.5, 128.6, 129.4, 129.9, 140.2, 140.4, 141.6, 144.4; IR (KBr): 1323, 1153 cm^{-1}.

Analysis. Calculated for $C_{24}H_{16}O_4S_2Cl_2$: C, 56.27; H, 3.20; S, 13.74; Cl, 14.08. Found: C, 56.19; H, 3.19; S, 12.33; Cl, 14.12.

4,4′-bis(4-Fluorophenylsulfonyl)biphenyl (3). In a 1000-mL, three-necked, round-bottomed flask fitted with an overhead stirrer, a nitrogen inlet, and a condenser, 400 mL nitrobenzene (excess) was placed. To this, 29.5 mL (0.30 mol) fluorobenzene and 48.7 g (0.139 mol) of 4,4′-biphenylsulfonyl chloride were added followed by portions of anhydrous aluminum chloride (40.85 g, 0.30 mol). The reaction mixture was heated under reflux for a period of 22 h. The reaction vessel was cooled to room temperature, and the contents were poured into cold concentrated aqueous hydrochloric acid solution and stirred for 4 h. The residue was collected by filtration and dissolved in methylene chloride. The solution was dried over anhydrous magnesium sulfate, filtered, and the filtrate was decolorized using charcoal. Recrystallization from the same solvent afforded white flakes in 85% yield: mp 255.9°C (DSC); ^{13}C NMR ($CDCl_3$): δ 105.00, 116.75 (J_{C-F} = 23 Hz), 128.42, 130.63 (J_{C-F} = 10 Hz), 137.43 (J_{C-F} = 6 Hz), 141.52, 144.14, 165.63 (J_{C-F} = 257 Hz); IR (KBr): 1324, 1154 cm^{-1}.

Analysis. Calculated for $C_{24}H_{16}O_4S_2F_2$: C, 61.26; H, 3.42; S, 13.62; F, 8.07. Found: C, 61.19; H, 3.19; S, 12.43; F, 7.97.

Model Compound Synthesis

Model compounds 4a–c were synthesized according to the following general procedure [10]. Analytical data for the compounds are summarized in Table 1.

General Procedure for Model Compound Synthesis. A three-necked, 100-mL, round-bottomed flask fitted with a nitrogen inlet, a thermometer, and a Dean–Stark trap fitted with a condenser was charged with 1.6611 g (0.0033 mol) of 2 and 0.0066 mol of the desired phenol (Table 1), 0.6385 g (0.0033 mol + 40% excess) of anhydrous potassium carbonate, 35 mL DMAC, and 30 mL toluene. The reaction mixture was refluxed at 145°C, and water, the byproduct of the reaction, was removed by azeotropic distillation. The reaction mixture was heated to 160°C for 22 h and then cooled to room temperature. It was filtered, and the filtrate was distilled under reduced pressure to remove all solvents. The residue was dissolved in methylene chloride, and the solution was washed repeatedly with water, dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation at reduced pressure. The crude product was purified by crystallization from 1:1 methylene chloride/hexane.

General Procedure for Polymer Synthesis. A typical synthesis of poly(aryl ether-bissulfone) was conducted in a 250-mL, four-necked, round-bottomed flask equipped with a nitrogen inlet, a thermometer, an overhead stirrer, and a Dean–Stark trap. A detailed synthetic procedure used to prepare 1a is provided. The flask was charged with 5.7 g (0.025 mol) Bisphenol-A and 12.575 g (0.025 mol) of 2, and carefully washed with 60 mL DMAC. Anhydrous potassium carbonate, 10 g (excess), was added followed by 45 mL toluene. The reaction mixture was then heated until toluene began to reflux at 140°C. Water (by-product of the reaction) was continuously removed via the Dean–Stark trap. The reflux temperature was maintained for 4 to 6 h until the presence of water could not be detected further in the Dean–Stark trap. The reaction mixture turned light yellow at the initial stage due to the formation of the phenoxide, and it slowly deepened to brown with time. The reaction temperature was gradually raised to 160°C by removing toluene from the Dean–Stark

TABLE 1. Analytical Data for Model Compounds

					Elemental analysis					
					Calculated			Found		
Compound	X	% Yield	mp, °C	Observed ^{13}C-NMR ($CDCl_e$) shifts, δ	C	H	S	C	H	S
3 a	*t*-Butyl	97.5	191–192	117.7, 120.0, 127.2, 128.3, 128.3, 130.1, 135.0, 142.2, 148.0, 153.0, 162.8, 35.0, 31.5	72.70	5.27	8.82	72.07	5.48	8.65
b	H	95.9	273–274	117.9, 120.4, 125.2, 128.3, 128.3, 130.1, 130.3, 135.0, 142.2, 144.0, 155.0, 162.4	69.89	4.24	10.36	69.79	4.27	10.20
c	Ph	99.0	256–258	117.9, 120.6, 127.0, 127.5, 128.2, 128.2, 128.9, 128.9, 130.1, 135.0, 138.4, 140.2, 142.2, 143.9, 154.4, 162.3	74.48	4.46	8.32	74.52	4.37	8.49

trap. The reaction mixture was heated at that temperature for a period of 18 h. An additional amount (20 mL) of DMAC was added to reduce the high viscosity of the reaction mixture, and the heating at 165°C was continued for an additional 6 h. In reactions involving less reactive phenoxides or phenoxide of lower solubility, 45 g DPS was added in place of DMAC. These reactions were carried out at 230°C for a period of 3-4 h. The viscous reaction mixture was allowed to cool to room temperature, diluted with 100 mL of DMAC, and filtered to remove inorganic salts. The filtrate was acidified with several drops of glacial acetic acid to neutralize the phenoxide end groups, and the polymer was recipitated with a 10-fold volume of methanol. The polymer was then dried at reduced pressure at 50°C for 8 to 10 h. It was redissolved in the appropriate solvent, the solution was filtered, acidified with glacial acetic acid, and the polymer coagulated in methanol. The fibrous solid was dried as before.

CHARACTERIZATION

NMR spectra of the model compounds were recorded using a General Electric QE-300 instrument. IR spectra were obtained with a Nicolet 20 DXB FT-IR spectrophotometer. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured either with a DuPont DSC 2100 or a Perkin-Elmer DSC-7 at a heating rate of 10°/min. Thermal gravimetric analysis (TGA) of the polymer samples was conducted with a heating rate of 10°/min in nitrogen. Intrinsic viscosity measurements were determined by using a Cannon-Ubbelohde dilution viscometer in *N*-methyl pyrrolidone (NMP) (25°C). Mechanical property measurements on compression molded films were made on an Instron Tensile Tester at a strain rate of 10 mm/min. Dynamic mechanical behavior was assessed on a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in bending with a heating rate of 4°C/min (1 Hz).

RESULTS AND DISCUSSION

A wide variety of aromatic polymers containing a biphenyl linkage in the basic repeat unit of the polymer have been synthesized. For example, conventional biphenyl functional poly(aryl ether-sulfone), synthesized by the reaction of biphenol with 4,4′-dichlorodiphenyl sulfone, exhibits excellent thermooxidative stability and high toughness. These desirable properties have been attributed to the biphenyl linkage [11]. Thus, polymers derived from 2 with a variety of bisphenols are expected to exhibit superior characteristics with respect to those of the analogous poly(aryl ether-sulfone). It was to provide detailed synthetic studies and measurements of physical properties of these polymers that this investigation was undertaken.

The purity of 2 and 3, which is of critical importance, was ascertained by DSC. The crude monomers 2 and 3 were crystallized three times from chloroform and methylene chloride, respectively, to obtain sharp melting endotherms (Fig. 1). Other characterization data, such as IR and NMR of 2 and 3, were consistent with the structures. A good correlation was also observed between the calculated and the observed elemental analyses values.

Model compound studies were carried out by treating phenol or substituted phenols with 2 in a dipolar aprotic solvent in the presence of excess potassium carbonate (Scheme 1).

An analysis of the data in Table 1 indicates that model compounds derived from phenol, 4-phenylphenol, and *tert*-butylphenol could be synthesized in very high yield. This was not the case when 2,6-dimethylphenol was used. Repeated crystallization was necessary to purify the product. Elemental analysis of the purified product was also not very satisfactory. This was indicative of nonquantitative replacement of a chlorine atom by the sterically hindered phenoxide derived from 2,6-dimethylphenol. Indeed, the polymer derived from tetramethylbisphenol-A and 2 was of low molecular weight. Only brittle films of this material could be obtained by solution casting. Higher molecular weight polymer could not be obtained either by increasing the reaction time or temperature. This suggested that the more reactive fluoro monomer, 3, would be required for the synthesis of relatively high molecular weight polymer with tetramethylbisphenol-A. Similar observations had been made earlier for reactions involving tetramethylbisphenol-A, 4,4′-dichlorodiphenylsulfone, and 4,4′-difluorodiphenylsulfone [10]. Model compound reaction corresponding to the polymer derived from 4,4′-dihydroxydiphenylsulfone and 2 was not carried out due to the fact that the required phenol, 4-hydroxydiphenylsulfone, was not readily available.

Besides elemental analysis, the structures of the model compounds were verified by carbon-13 NMR analysis. The observed ^{13}C absorbances

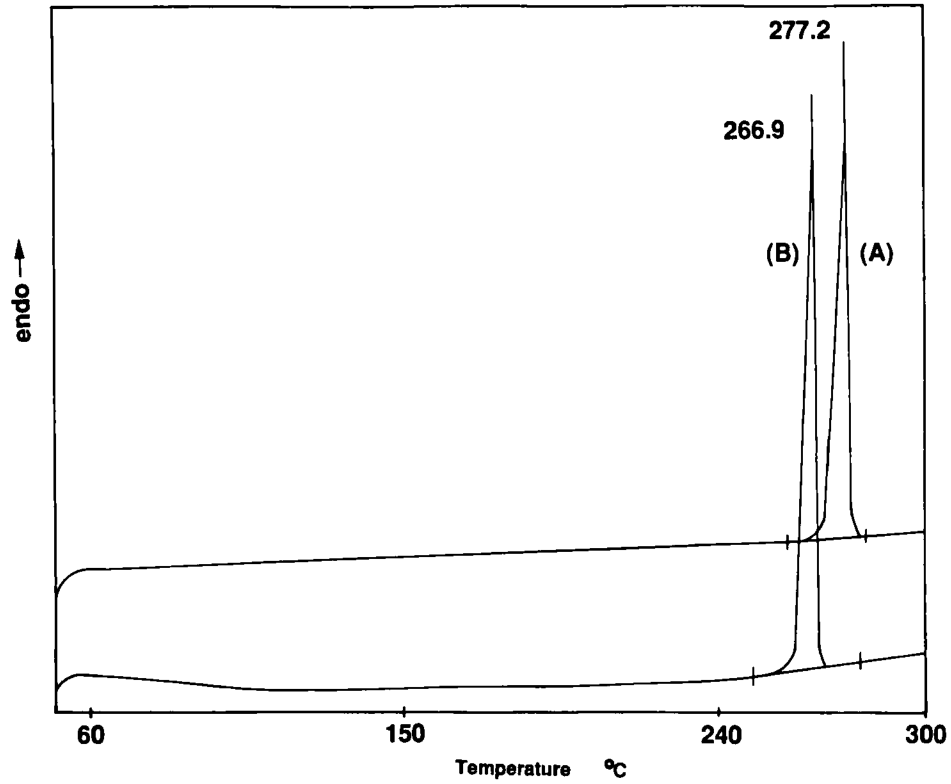
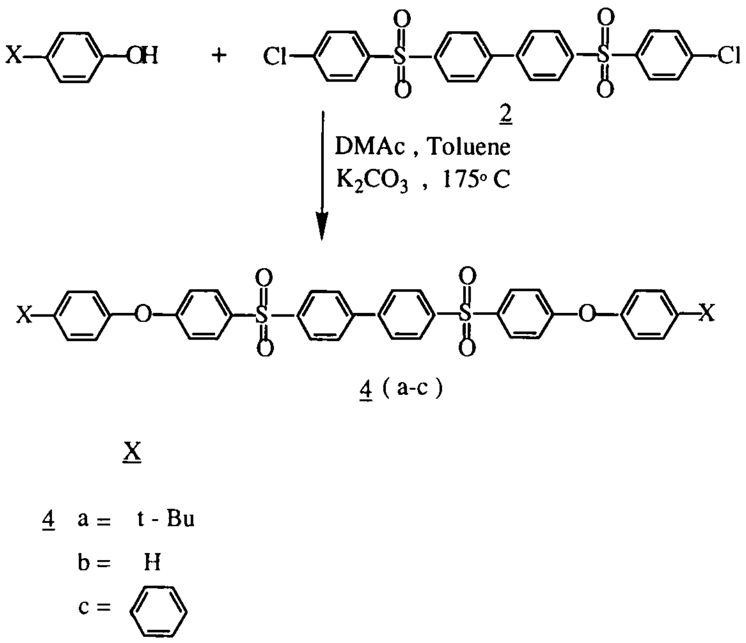


FIG. 1. DSC thermograms of (A) 4,4′-bis(4-chlorophenylsulfonyl)biphenyl and (B) 4,4′-bis(4-fluorophenylsulfonyl)biphenyl monomers.

for the model compounds (Table 1) are in close agreement with calculated values [12]. To characterize the polymer solubility, a 10% (w/v) solution was taken as a criterion. The model compounds were found to be soluble in either hot or cold DMAC, which was chosen as the solvent of choice for the polymerization reactions.

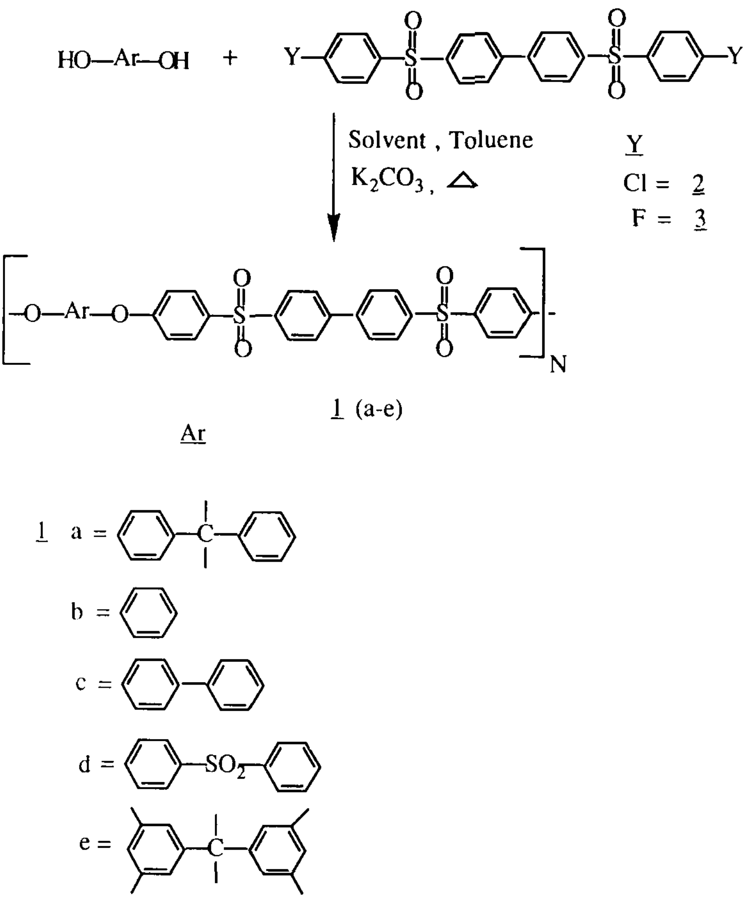
Polymerization of 2 with various bisphenols was carried out in the presence of potassium carbonate in a DMAC/toluene (2:1) solvent mixture (Scheme 2). The concentration of the reactants was maintained between 20 to 25 wt%. The polymerization temperature was initially maintained at 150°C, and water (formed during phenoxide formation) was removed as an azeotrope with toluene. After the removal of at least



SCHEME 1.

the stoichiometric amount of water, the reaction temperature was raised to 165 °C to effect the displacement reactions. Polymerization time varied between 18 and 24 h.

This general procedure was applied to synthesize hydroquinone and Bisphenol-A functional polymers. In the case of biphenol, during the course of the polymerization reaction the oligomeric products precipitated from the reaction mixture. Solubility did not improve even in boiling DMAC. During the synthesis of the corresponding model compound, this problem of product insolubility had not been encountered, although the synthesized compound was only soluble in hot DMAC. It therefore appears that oligomers with two phenoxide end-groups exhibit poor solubility in refluxing DMAC. In order to circumvent this problem and to achieve high molecular weight polymer, DPS was added to the reaction mixture. The reaction temperature was then gradually raised to 250 °C while removing DMAC via the Dean-Stark trap. High molecular weight polymer was obtained within 3 h as judged by the dramatic rise in viscos-



SCHEME 2.

ity. During the polymerization of Bisphenol-S with 2, a noticeable increase in viscosity of the reaction mixture was not observed even after 24 h at 175°C. Since the sulfone moiety is strongly electron withdrawing, the resulting bisphenoxide from Bisphenol-S can be regarded as a weak nucleophile in contrast to the bisphenoxide from Bisphenol-A. Similar observations were made earlier for reactions of the phenoxide from Bisphenol-S and a variety of activated halides [2, 5]. Moderately high molecular weight polymer could be synthesized by the reaction of Bisphenol-S with 3 at 175°C in 24 h. Also, the reaction of the more reactive bisfluoride, 3, with tetramethylbisphenol-A at 165°C resulted in a high molecular weight polymer within 3 h.

The molecular structure of the polymers was confirmed by both ^{13}C NMR and FT-IR. The ^{13}C-NMR spectrum of polymer 1a is shown in Fig. 2. The observed peak positions were in agreement with calculated chemical shifts. The FT-IR spectra of the polymers established the presence of ether and sulfone linkages in the polymer repeat units.

The solubility behavior of polymers 1b–e were in sharp contrast to those of the corresponding monosulfone analogues. These poly(aryl ether-bissulfone)s were only soluble in a dipolar aprotic solvent such as DMAC, insoluble in tetrahydrofuran, and only swellable in a chlorinated hydrocarbon such as chloroform. For example, polymer 1d was soluble in hot DMAC, whereas the correspondingly poly(aryl ether-sulfone) was soluble in cold DMAC, tetrahydrofuran, and a series of chlorinated hydrocarbons. The reason for the difference in solubility behavior may be attributed to the presence of the biphenyl and two sulfone moieties in the polymer repeat unit.

The glass transition temperatures and the intrinsic viscosity values for

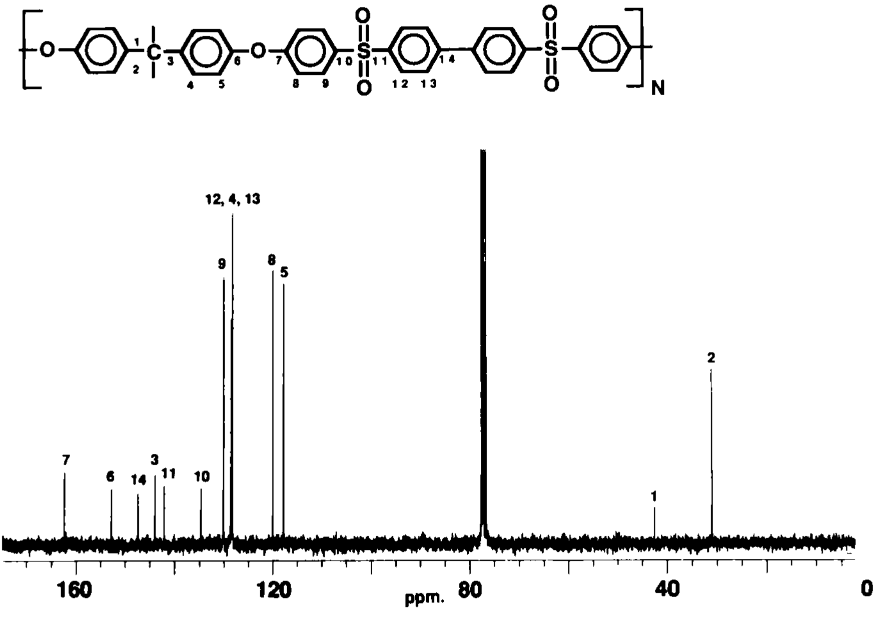


FIG. 2. ^{13}C-NMR spectrum of poly(aryl ether-bissulfone) in $CDCl_3$ based on 1a.

1a–e are displayed in Table 2. The intrinsic viscosity values suggest the moderate to very high molecular weight nature of the polymers. The glass transition temperatures ranged from 241 °C for 1a to 271 °C for 1e depending on the nature of the bisphenol used in the polymer synthesis. These values are among the highest reported for poly(aryl ether)s and are comparable to those recently reported for poly(aryl ether-phenylquinoxaline)s [5]. The T_g of polymer 1a derived from Bisphenol-A is approximately 50°C higher than that of the corresponding monosulfone analogue. A similar trend can be observed for the remainder of the poly(aryl ether-bissulfone)s. The dynamic mechanical thermal analysis of these polymers corroborated the T_g data obtained from DSC measurements. The dynamic mechanical behavior for the synthesized polymer along with that of Bisphenol-A functional poly(aryl ether-sulfone), UDEL, is shown in Fig. 3. These data clearly show the high T_g and good dimensional stability exhibited by the materials, and they also indicate a glassy or amorphous morphology for this polymeric system. In addition, a major low temperature secondary relaxation (β-transition) in the vicinity of -100°C can also be seen in all cases. Figure 4 illustrates one such typical transition for 1b. Such transitions have been investigated by dynamic mechanical [13–15] and NMR [16] techniques. The origins of β-relaxation are believed to be associated with polymers which can exhibit ductile deformation [13].

In spite of the high T_g of these materials, the poly(aryl ether-bissulfone)s can be thermoformed by compression molding in contrast to other conventional high performance rigid rod polymers. Samples were molded at approximately 70°C above the glass transition temperature. That this can be done is reflective of the excellent thermal stability

TABLE 2. Glass Transition Temperature, T_g, and Intrinsic Viscosity, $[\eta]^{\mathrm{NMP}}_{25°\mathrm{C}}$, Values of Poly(Aryl Ether-bissulfone)s, 1a–e

Polymer		$[\eta]^{\mathrm{NMP}}_{25°\mathrm{C}}$, dL/g	T_g, °C
1	a	0.62	241
	b	0.40	252
	c	0.35	262
	d	0.51	269
	e	1.06	271

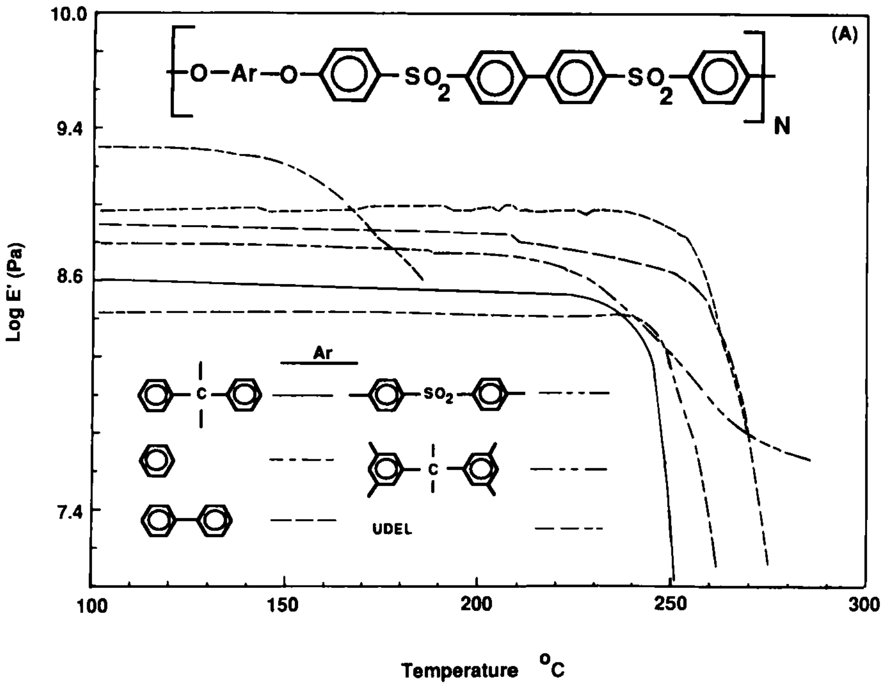


FIG. 3A. Storage modulus (bending) versus temperature.

of these materials. The thermal stability of these polymers was further affirmed by thermogravimetric analysis in both the isothermal and variable temperature modes. The variable temperature TGA thermograms of the polymers are shown in Fig. 5. From examination of the figure it is apparent that the poly(aryl ether-bissulfone)s demonstrate very good thermal stability with polymer decomposition temperatures in excess of 400°C, except for 1e which exhibits the onset of decomposition at a lower temperature, 381°C. This is presumably because of the presence of benzylic methyl groups. The thermal stability of 1a is comparable to that of the corresponding monosulfone analogue. As expected, polymers 1a and 1e with isopropyledene linkages are of lower stability than are the polymers from more rigid bisphenols. Isothermal TGA (400°C, under nitrogen atmosphere) was also used to assess the thermal stability of the polymers (Table 3). The data, consistent with the variable temperature TGA scans, demonstrate that the structures based on hydroquinone and

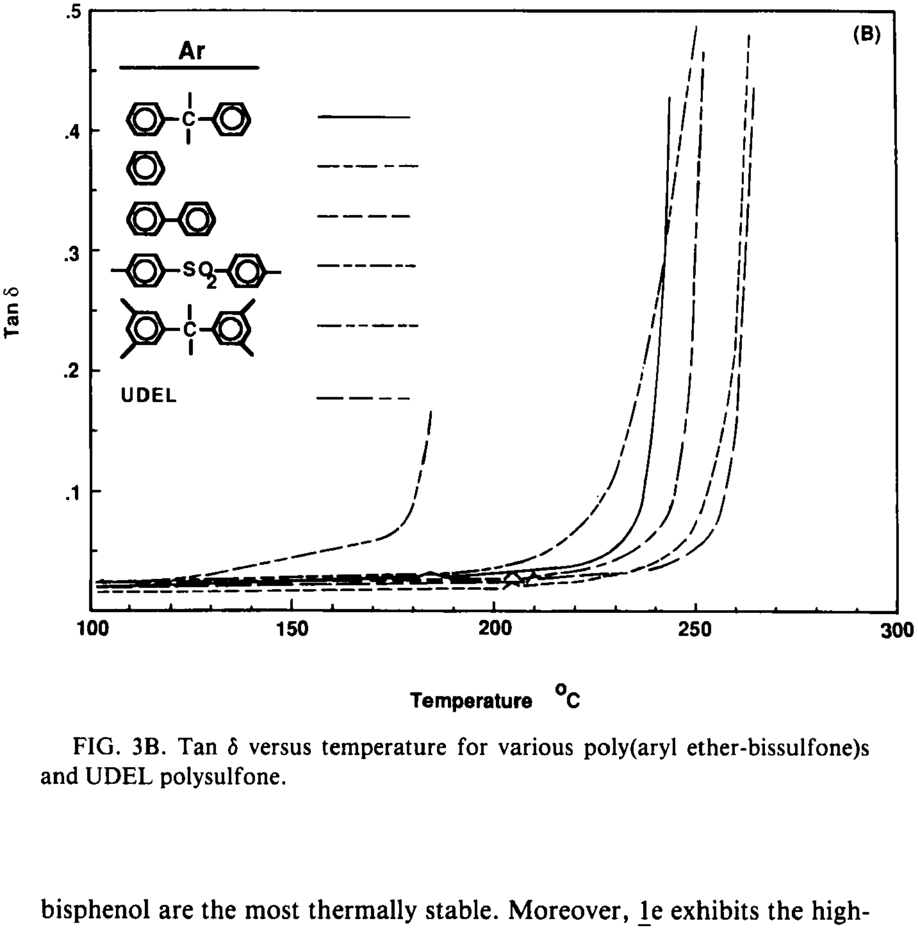


FIG. 3B. Tan δ versus temperature for various poly(aryl ether-bissulfone)s and UDEL polysulfone.

bisphenol are the most thermally stable. Moreover, 1e exhibits the highest percent weight loss (15.8%) in the isothermal run. The initial loss of approximately 10% occurs in the first 15 min and the remainder over a 45-min period. It is highly likely that the benzylic methyl groups which constitute 8.4% of the repeat unit molecular weight are thermally cleaved at a rapid rate and contribute to the overall initial weight loss.

The mechanical properties of poly(aryl ether-bissulfone)s were comparable to those of Bisphenol-A functional poly(aryl ether-sulfone). The polymers exhibit expected ductile mechanical behavior typical of engineering thermoplastics. These behaviors include yield points with necking and drawing. Further, they exhibit high moduli and tensile strength.

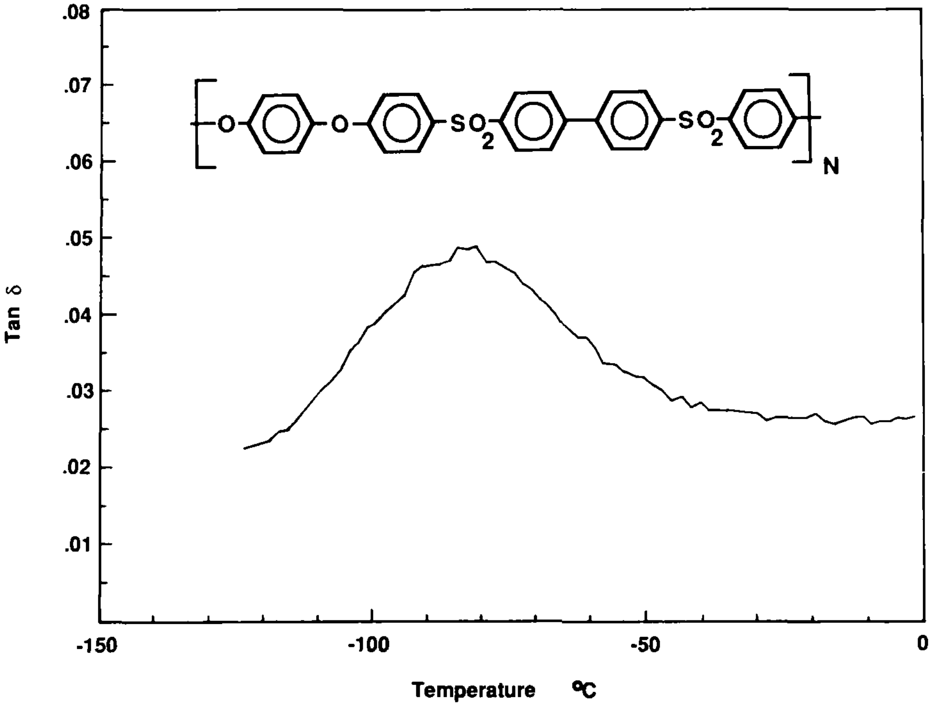


FIG. 4. Tan δ versus temperature for 1b.

CONCLUSIONS

A series of high molecular weight poly(aryl ether-bissulfone)s were synthesized by the reaction of 4,4′-bis(4-chlorophenylsulfonyl)biphenyl with suitable bisphenols. Like the monosulfone analogue, the bissulfone functional bischloride was not reactive enough to synthesize high molecular weight polymers with either Bisphenol-S or tetramethylbisphenol-A. High molecular weight polymers could be prepared, however, by using the more reactive bisfluoride monomer with Bisphenol-S and tetramethylbisphenol-A. The synthesized amorphous polymers exhibited high glass transition temperatures comparable to some of the highest T_gs known for poly(aryl ether)s. In addition, the polymers possess excellent thermal stability, which was judged from both dynamic and isothermal thermogravimetric analysis. Furthermore, the poly(aryl ether-bissulfone)s afford tough, transparent films upon solution casting or compres-

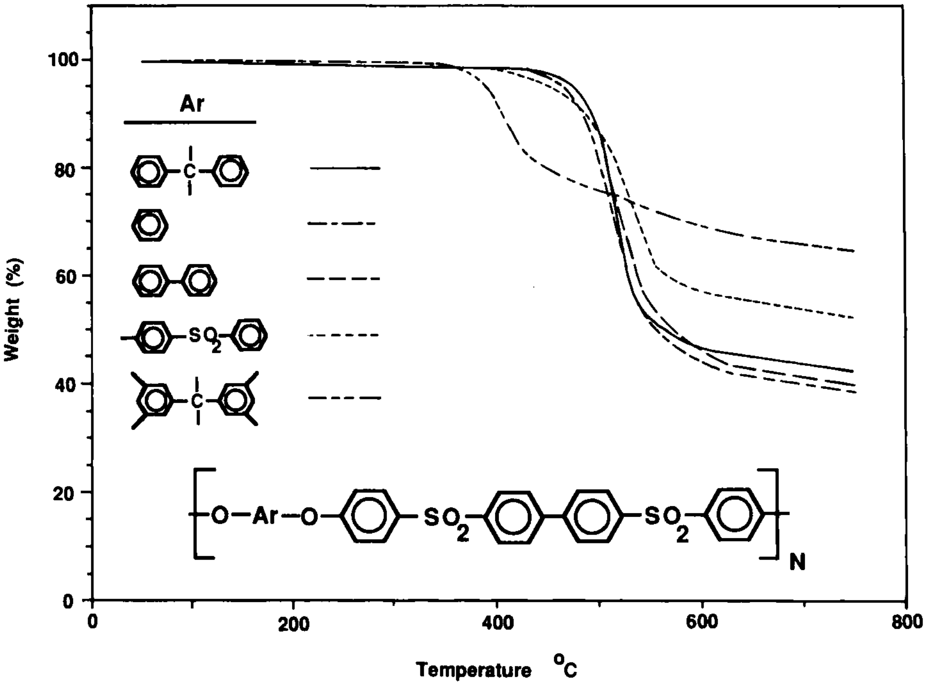


FIG. 5. TGA thermograms (weight loss versus temperature) for various poly(aryl ether-bissulfone)s.

TABLE 3. Thermogravimetric Analysis of Poly(Aryl Ether-bissulfone)s

Polymer		Weight loss on isothermal aging at 400°C, wt%/h	Polymer decomposition temperature, °C
1	a	3.3	492
	b	2.5	480
	c	3.2	485
	d	3.8	487
	e	15.8	381

sion molding. These structures show a major secondary relaxation like other ductile engineering thermoplastics.

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