

Polyarylates Containing Sulfone Ether Linkages

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ABSTRACT: A series of polyarylates containing sulfone or both of ether and sulfone groups were synthesized from diacid chlorides such as 4,4'-sulfonyldibenzoyl chloride (SDBC), 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoyl chloride (SODBC), and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoyl chloride (4MeSODBC) with various bisphenols by the interfacial polycondensation technique. Moderate to high molecular weight polyarylates with inherent viscosity up to 1.22 dL g⁻¹ were obtained. Most of them were soluble in various organic solvents and afforded transparent, flexible, and tough films by solution casting. Two polyarylates based on SDBC exhibited a moderate level of crystallinity and poor solubility; however, the introduction of ether linkages into the polymer backbone caused a decreased crystallinity and an enhanced solubility. The incorporation of ether groups in the sulfonyl polyarylate main chain led to a decreased glass transition temperature (T_g) or softening temperature (T_s). The methyl-substituted poly(ether-sulfone-arylate)s from 4MeSODBC reveal higher T_g or T_s but lower decomposition temperatures than the corresponding non-substituted analogs from SODBC.

KEY WORDS Polyarylates / Ether-Sulfone-Diacid Chlorides / Interfacial Polycondensation /

Polyarylates are well accepted as high performance engineering thermoplastics which have found application in a variety of areas.^{1,2} However, the high melting or softening temperatures and limited solubility in organic solvents of most polyarylates make their processing into articles difficult unless flexible spacers are included in the backbone, thereby lowering the thermal stability. One of the successful approaches to increase solubility and processability without much sacrifice of thermal stability is the introduction of polar and kinked linkages such as sulfone and ether groups into the polymer backbone. In previous papers^{3–7} we have shown that multi-ring dianhydrides, diacids and diamines containing diaryloxy groups together with sulfonyl group are able to give rise to aromatic polyamides and polyimides with increased solubility as compared to rigid analogues, while retaining moderately high T_g and thermal stability. The present investigation deals with the synthesis and basic characterization of poly(ether-sulfone-arylate)s prepared from diacid chlorides SODBC and 4MeSODBC with various bisphenols, with the aim being to correlate their structural features with solubility, crystallinity, T_g and thermal stability. For comparison, related sulfonyl polyarylates without ether linkages were also prepared and characterized.

EXPERIMENTAL

Materials

The commercial available biphenols that included 4,4'-biphenol (**1a**) (TCI), 3,3',5,5'-tetramethyl-4,4'-biphenol (**1b**) (Mitsui Petrochemical Ind.), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A; **1c**) (Wako), 1,1-bis(4-hydroxyphenyl)-1-phenylethane (**1d**) (Mitsui Petrochemical Ind.), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (bisphenol AF; **1e**) (Kriskev), α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (**1f**) (Mitsui Petrochemical Ind.), α,α' -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (**1g**) (Mitsui Petrochemical Ind.),

4,4'-(octahydro-4,7-methano-5H-inden-5-ylidene) bisphenol (**1h**) (Acros) and 9,9-bis(4-hydroxyphenyl)fluorene (**1i**) (TCI) were used without further purification. The phase-transfer agent, triethylbenzylammonium chloride (TEBAC) (TCI), was used as received. As reported previously,³ 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoic acid (mp 291–292°C) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoic acid (mp 312–315°C) were synthesized in high purity and high yields *via* two main steps from commercially available reagents. The diacyl chloride monomers, 4,4'-sulfonyldibenzoyl chloride (SDBC) (mp 160–161°C; lit.⁸ 164°C), 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoyl chloride (SODBC) (mp 183–184°C; lit.^{9,10} 183–185°C) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoyl chloride (4MeSODBC) (mp 190–191°C), were prepared by chlorinating the precursor dicarboxylic acid with thionyl chloride in the presence of trace amount of *N,N*-dimethylformamide. Dichloromethane was purified by distillation. All other solvents were obtained commercially and used as received.

Polymer Synthesis and Film Preparation

The interfacial polycondensation technique was used to prepare the polyarylates in this research. A typical procedure for the synthesis of polyarylate **4b** is given below. A solution of 4MeSODBC (0.5834 g; 1 mmol) in dichloromethane (10 mL) was added all at once to a solution of 3,3',5,5'-tetramethyl-4,4'-biphenol (**1b**) (0.2423 g; 1 mmol) and 0.04 g TEBAC in 10 mL of 1 M aqueous sodium hydroxide. The reaction mixture was stirred vigorously at room temperature for 1 h. The mixture was poured into 350 mL of boiling water to remove dichloromethane. The precipitated polymer was collected by filtration, washed with water thoroughly, and dried. The yield of polymer **4b** was quantitative, and the inherent viscosity was 1.00 dL g⁻¹ as measured at a concentration of 0.5 g dL⁻¹ in 1,1,2,2-tetrachloroethane/phenol (40/60 by weight) at 30°C. The IR spectrum (film)

showed characteristic absorptions at 1733 (C=O str.), 1321, 1159 (S=O str.), 1267 cm^{-1} (C-O). *Anal.* Calcd for $(\text{C}_{46}\text{H}_{40}\text{SO}_8)_n$ (752.88) $_n$: C, 73.38%; H, 5.35%. Found: C, 72.88%; H, 5.40%.

The polymer thin film was cast from the solution of polyarylate **4b** in 1,1,2,2-tetrachloroethane (TCE) in a clean glass culture dish. The wet film was placed in a 90°C oven for 12 h to remove the solvent slowly. The semidried film was further dried under vacuum at 150°C for 6 h. The thickness of the film was about 60 μm . All the other polyarylates were prepared by a similar procedure described the above.

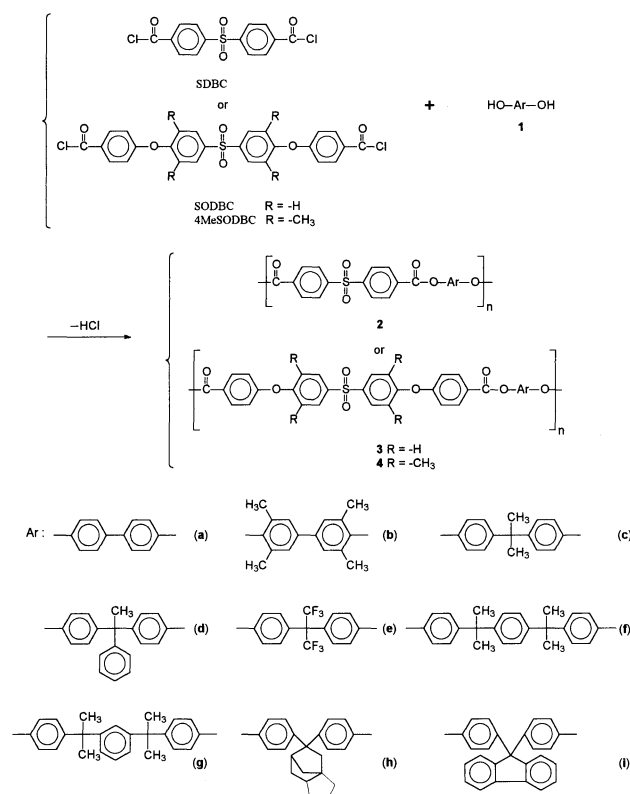
Measurements

Inherent viscosities (η_{inh}) of the polyarylates were measured with a Cannon-Fenske viscometer from a polymer solution at 0.5 g dL^{-1} concentration in 1,1,2,2-tetrachloroethane/phenol (40/60 by weight) at 30°C. Molecular weight data for some of the polyarylates were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) based on polystyrene standards on a Waters apparatus. The infrared spectra were recorded on a Horiba Fourier Transform Infrared Spectrometer FT-720. Wide-angle X-Ray diffraction measurements were performed at room temperature on a Siemens Kristalloflex D 5000 X-Ray diffractometer, operating in the 2θ range of 5–45° at the scan rate of 3° min^{-1} using Ni-filtered copper K_α radiation ($\lambda = 1.5418 \text{ \AA}$, operating at 40 kV and 20 mA). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 in flowing nitrogen with a heating rate of 20°C min^{-1} . Glass transition temperatures (T_g) were read at the middle of the baseline shift on the second DSC heating trace after quenching the sample from 400°C at a programmed rate of -200°C min^{-1} . Thermomechanical analysis (TMA) experiments were performed on a Perkin-Elmer TMA 7 at a heating rate 10°C min^{-1} with a loaded penetration probe under an applied constant load of 10 mN. The film samples were preheated at 250°C for 30 min prior to scan. The softening temperatures (T_s) were taken as the intersection of the extrapolation of the baseline with the extrapolation of inflection on the TMA traces. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050 Thermogravimetric Analyzer. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (100 $\text{cm}^3 \text{ min}^{-1}$) at a scan rate of 20°C min^{-1} . The measurements were taken after a 300°C/10 min drying step. An Instron universal tester model 1130 with a 5 kg load cell was used to measure the tensile properties of the solution cast films using a crosshead gauge of 2 cm and a crosshead speed of 5 mm min^{-1} . Measurements were performed at room temperature with film specimens (5 mm wide, 60 mm long, and approximately 60 μm thick). An average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Polymer Synthesis

Polyarylates have been prepared conveniently by the phase-transfer catalyzed polycondensation of aromatic diacid chlorides with bisphenols.^{11–13} The polycondensa-



Scheme 1. Synthesis of sulfonyl polyarylates.

tions of bisphenols **1a–1i** with diacid chlorides SDBC, SODBC, and 4MeSODBC leading to sulfone-containing or both ether and sulfone containing polyarylates were carried out in dichloromethane-aqueous sodium hydroxide system using TEBAC as a phase transfer catalyst, which is known to be a very effective catalyst for producing high molecular weight polyarylates.^{14–16} The molecular structures and codes of all the monomers and polymers are shown in Scheme 1, and the results of polycondensation are summarized in Table I. Polymer precipitation occurred during the polycondensation reactions of 4,4'-biphenol (**1a**) with any one of the three diacid chlorides due to insolubility of the resulting polyarylates. Unexpectedly, polymer **2f** also precipitated out from the reaction system during the reaction. Insolubility of polymer **2f** may be caused by its high level of crystallinity, as evidenced by X-Ray diffraction and DSC analysis discussed subsequently. All the polymers that precipitated during the polycondensation reaction could not be dissolved in suitable organic solvents for film casting. All other polyarylates were obtained with sufficient molecular weights for the casting of tough and flexible films. The cast films of the polyarylates (**2b**, **3b**, and **4b**) derived from 3,3',5,5'-tetramethyl-4,4'-biphenol (**1b**) appeared pale yellow in color, possibly due to bathochromic shifts caused by the methyl auxochromes. All the other films are transparent and colorless. The lower inherent viscosities of most polyarylates derived from SODBC, compared to those derived from SDBC and 4MeSODBC, may be attributed in part to their more flexible molecular structures. In interpreting the viscosity behavior, one must bear in mind that the inherent viscosity of a flexible polymer is much lower than that of

Table I. Synthesis and film quality of sulfonyl polyarylates

Diacyl Chloride	Bisphenol	Polymer				
		Code	η_{inh}^a dL g ⁻¹	M_p^b kg mol ⁻¹	Remarks ^c	Film Quality ^d
SDBC	1a	2a	— ^e		P	— ^e
	1b	2b	1.00		S	Flexible
	1c	2c	0.95		S	Flexible
	1d	2d	1.07	155	S	Flexible
	1e	2e	0.69		S	Flexible
	1f	2f	0.25		P	—
	1g	2g	0.79		S	Flexible
	1h	2h	0.70	112	E	Flexible
	1i	2i	0.60	95	E	Flexible
SODBC	1a	3a	0.21		P	—
	1b	3b	0.63		S	Flexible
	1c	3c	0.45		S	Flexible
	1d	3d	0.68	166	S	Flexible
	1e	3e	0.31		S	Flexible
	1f	3f	0.56		E	Flexible
	1g	3g	0.58	183	E	Flexible
	1h	3h	0.32	138	E	Flexible
	1i	3i	0.62	189	E	Flexible
4MeSODBC	1a	4a	0.22		P	—
	1b	4b	1.00	256	S	Flexible
	1c	4c	0.58	197	S	Flexible
	1d	4d	1.21	247	S	Flexible
	1e	4e	1.22	236	S	Flexible
	1f	4f	0.89	220	S	Flexible
	1g	4g	0.74	273	S	Flexible
	1h	4h	1.09	292	E	Flexible
	1i	4i	1.05	324	E	Flexible

^a Measured at a concentration of 0.5 g dL⁻¹ in 1,1,2,2-tetrachloroethane/phenol (40 : 60 by weight) at 30°C. ^b Molecular weights at the peaks of the chromatograms (GPC) relative to polystyrene standards. ^c Appearance of the polymerization: P, polymer precipitation occurred during the reaction; E: viscous emulsion; S, homogeneous organic solution (well-defined two phases). ^d Films were cast by slow evaporation of the polymer solutions in 1,1,2,2-tetrachloroethane. The films from polymers **2b**, **3b**, and **4b** are pale yellow in color, and the other films are colorless. ^e Insoluble.

a rigid one of the same molecular weight. This could be evidenced by GPC analysis. For example, polymer **3h** had a lower inherent viscosity of 0.32 dL g⁻¹ whereas showed a higher M_p value (138 kg mol⁻¹) than that (112 kg mol⁻¹) of **2h** which had a higher inherent viscosity of 0.70 dL g⁻¹. The structures of the polyarylates were confirmed by IR spectroscopy and elemental analysis. The sharp absorption peaks at around 1740 cm⁻¹ (C=O) and 1260 cm⁻¹ (C-O) are a clear indication of the ester-forming reaction. The characteristic absorptions due to the asymmetric and symmetric S(=O)₂ stretching of the sulfonyl groups appeared at around 1315 and 1160 cm⁻¹, respectively. Elemental analysis values were also in good agreement with those calculated.

Polymer Properties

The solubility of these polyarylates was determined qualitatively in various solvents, and the results are summarized in Table II. The polyarylates such as **2a**, **2f**, **3a**, and **4a** that precipitated in the polycondensation reaction reveal poor solubility; they are insoluble in most of the solvents tested. The other polyarylates show good solubility in various organic solvents, particularly in chlorinated hydrocarbons and phenols. In general, the ether-containing sulfonyl polyarylates have an improved solubility when compared to their analogs without ether linkages. However, it is worth noting that the methyl-substituted poly(ether-sulfone-arylate)s **4b**–**4i** are readily soluble in THF, but insoluble in DMSO.

The crystallinity of the polyarylates was evaluated by wide-angle X-Ray diffraction analysis. The X-Ray diffraction patterns of all polyarylates are shown in Figure 1. Polyarylates **2a**, **2f**, and **3a** showed stronger reflection peaks between $2\theta = 10$ to 20° , indicative of moderate to high degree of crystallinity. This corresponds to their poor solubility. The other polyarylates exhibited almost amorphous patterns. The amorphous nature of these polyarylates is generally consistent with their high solubility and outstanding film forming properties.

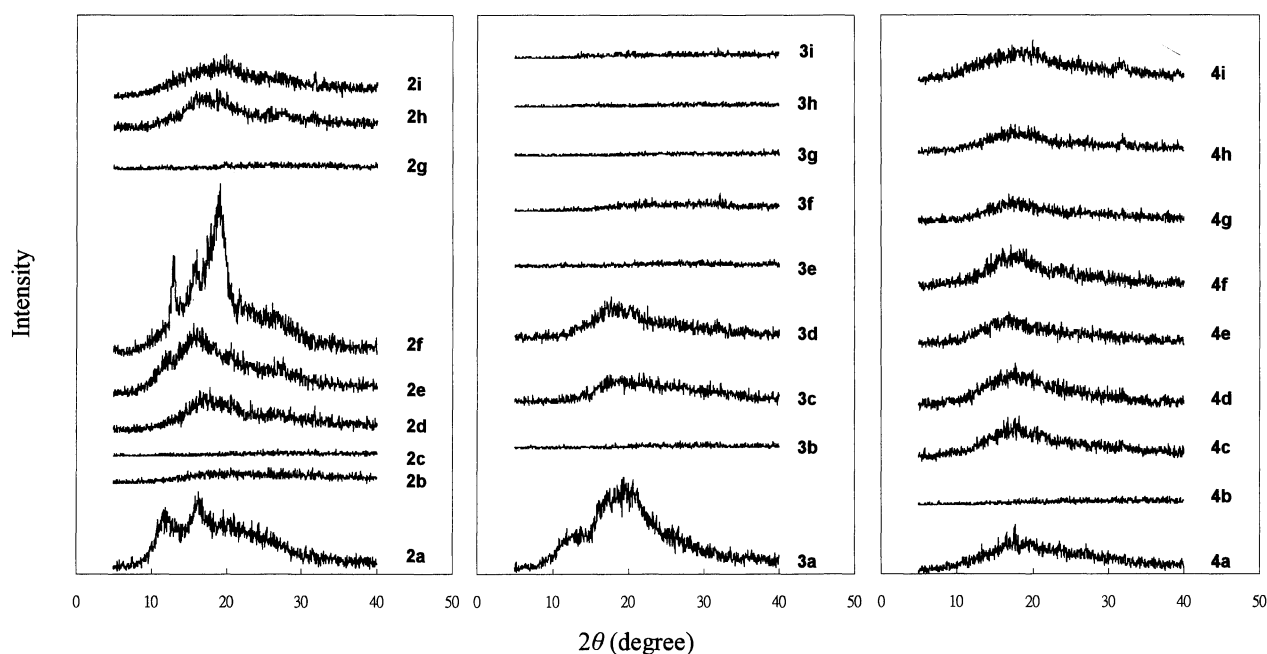
Transparent and flexible films of the soluble polyarylates could be obtained by casting from their TCE solutions. These films were subjected to tensile testing, and their tensile properties are summarized in Table III. They had tensile strengths of 49–76 MPa, elongations to break of 6–48%, and tensile moduli of 1.39–1.86 GPa. Most of them behaved as strong and rigid materials. Only the film of polyarylate **2b** behaved as a tough material. It necked during the tensile test and showed a relatively higher extension to break.

DSC, TMA, and TGA evaluated the thermal behavior of the polyarylates. The thermal data are summarized in Table IV. In the DSC experiments, the samples were first heated from 40 to 400°C with a heating rate of 20°C min⁻¹ and rapidly cooled to 40°C at $-200^\circ\text{C min}^{-1}$, followed by a second heating run from 40 to 400°C at 20°C min⁻¹. The glass transition temperature (T_g) was defined as the midpoint of baseline shift on the second DSC heating trace. DSC observed no discernible T_g s for

Table II. Solubility behavior of sulfonyl polyarylates^a

Polymer	Solvent ^b							
	NMP	THF	DMSO	Chloroform	TCE	<i>o</i> -CP	<i>o</i> -DCB	TCE/phenol (40/60)
2a	-	-	-	-	-	-	-	-
2b	+	-	-	+	+	+h	-	+
2c	+	-	+	+	+	+	-	+
2d	+	+	+h	+h	+h	+	+	+
2e	+	-	+	+	+	+	-	+
2f	-	-	-	-	-	+	-	+
2g	+	-	+	+	+	+	+	+
2h	+	+	-	+	+h	+	+	+
2i	+	+	+h	+	+h	+	-	+
3a	+	-	-	-	-	-	-	+
3b	+	-	+	+	+	+	+	+
3c	+	-	+	+	+	-	+	+
3d	+	+	+h	+	+	+	+	+
3e	+	-	+	+	+	+	-	+
3f	+	-	+	+	+	+	+	+
3g	+	+	+	+	+	+	+	+
3h	+	+	-	+	+	+	+	+
3i	+	+	+	+	+	+	+	+
4a	-	-	-	-	-	+	-	+
4b	+	+	-	+	+	+	+	+
4c	+	+	-	+	+	+	+	+
4d	+	+	-	+	+	+	+	+
4e	+	+	-	+	+	+	+	+
4f	+	+	-	+	+	+	+	+
4g	+	+	-	+	+h	+	+	+
4h	+	+	-	+	+	+	+	+
4i	+	+	-	+	+	+	+h	+

^a Qualitative solubility tested with 10 mg of sample in 1 mL of solvent. +: soluble at room temperature; +h: soluble on heating at 100°C; -: insoluble even on heating. ^b NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; TCE: 1,1,2,2-tetrachloroethane; *o*-CP: *o*-chlorophenol; *o*-DCB: *o*-dichlorobenzene.

**Figure 1.** Wide-angle X-Ray diffraction patterns of the polyarylates.

polyarylates **2a**, **2b**, and **2i**. The other polyarylates revealed distinct glass transition on their second DSC heating traces. The first heating run of the as-polymerized sample of **2f** (Figure 2) reveals a melting endotherm at 289°C ($\Delta H = 45 \text{ J g}^{-1}$). This result is consistent with that of X-Ray diffraction experiments and indicates that polymer **2f** is semicrystalline in origin.

The T_g s of polymers **3a**–**3i** occur between 130 and 208°C and are lower than those of the corresponding polymer **2a**–**2i**. This result is reasonable in light of the increased chain flexibility imparted by the two bisaryloxy groups present in the **3a**–**3i** polymers. As expected, the methyl-substituted poly(ether-sulfone-arylate)s (**4a**–**4i**) exhibited higher T_g s (194–283°C) as compared to the corre-

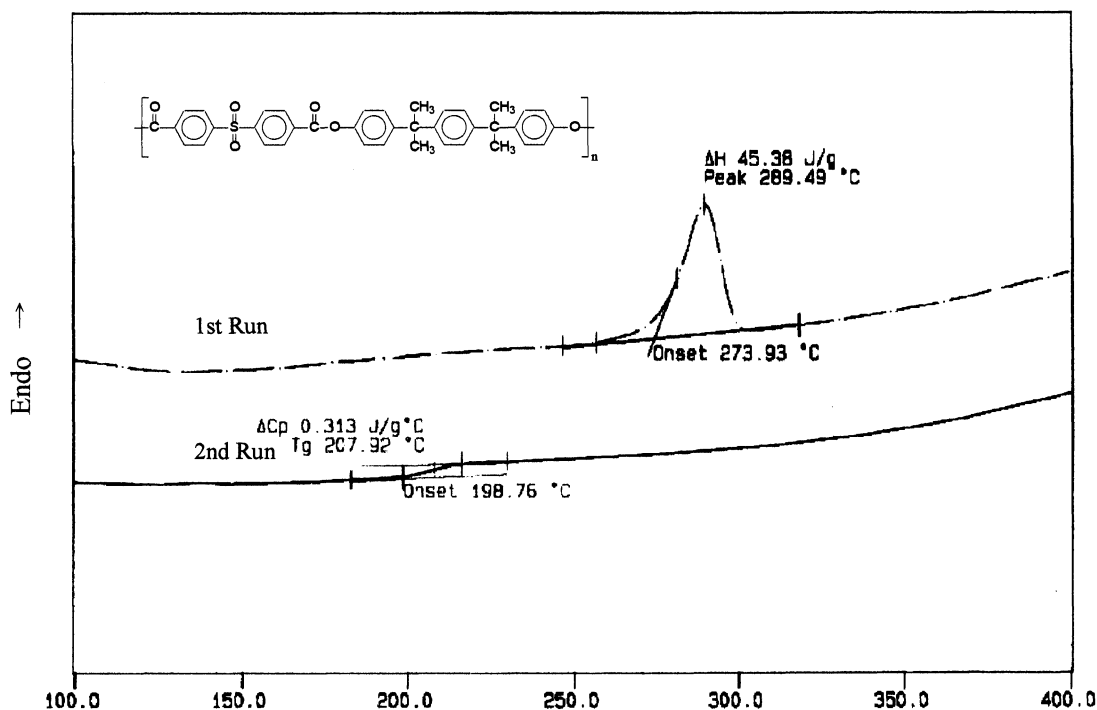


Figure 2. DSC curves of polyarylate **2f** at a heating rate of $20^{\circ}\text{C min}^{-1}$ in nitrogen.

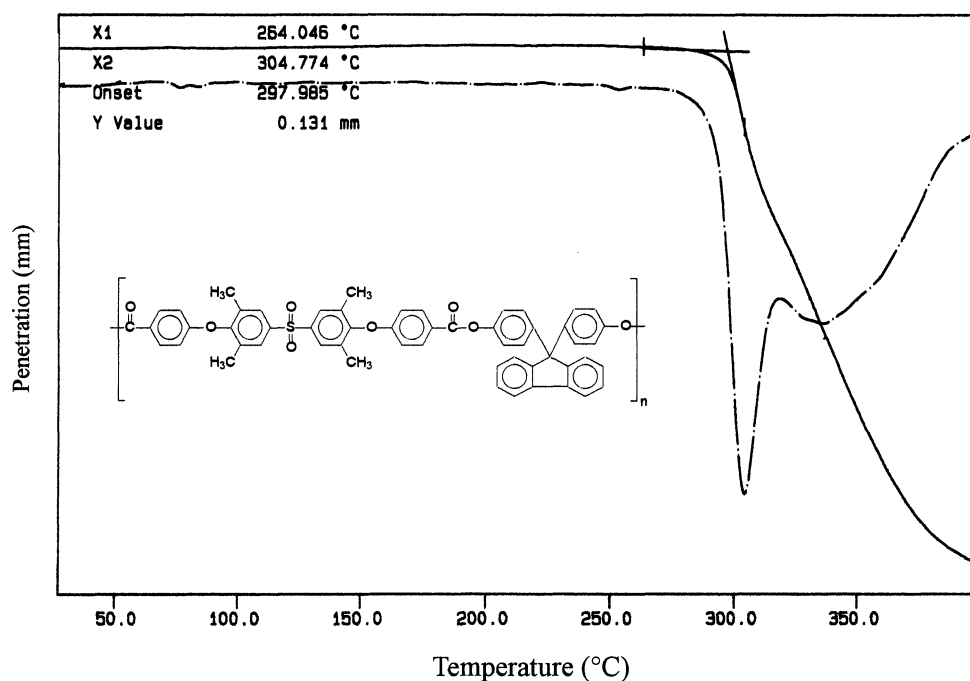


Figure 3. The TMA curves of polyarylate **4i**, conducted with a penetration probe of 1.0 mm diameter and using an applied constant load of 10 mN at a heating rate of $10^{\circ}\text{C min}^{-1}$.

sponding unsubstituted poly(ether-sulfone-arylate)s (**3a**—**3i**) due to the hindrance effect of the chain rotation in the methyl-substituted polymers.¹⁷ The T_g s of the polyarylates are also highly dependent on the bisphenol component structures. The bisphenols **1f** and **1g**-derived polyarylates containing flexible phenylenediisopropylidene structure generally revealed lower T_g s. On the other hand, the polyarylates obtained from bulky, rigid bisphenols such as **1h** and **1i** exhibited relatively higher

T_g s. In the case of polyarylates that give flexible films by solution casting, softening temperatures (T_s) were measured by TMA using a penetration method. A typical TMA curve for the representative polyarylate **4i** is illustrated in Figure 3. The T_s value was read as the intersection of the extrapolation of the baseline with the extrapolation of inflection on the TMA curve. In most cases, the T_s values measured by TMA are comparable to the T_g values determined by DSC.

Table III. Tensile properties of polyarylate films^a

Polymer	Yield strength	Strength to break	Elongation to break	Initial modulus
	MPa	MPa	%	GPa
2b	69	69	48	1.63
2c	64	61	11	1.42
2d	66	61	12	1.39
2f	49	49	6	1.62
2h	67	65	10	1.40
2i	69	68	12	1.39
3b	68	67	8	1.86
3c	73	73	6	1.84
3d	71	71	7	1.65
3f	70	69	7	1.66
3g	72	67	10	1.64
3h	71	71	7	1.51
3i	76	76	7	1.64
4b	76	76	6	1.82
4c	69	68	8	1.52
4d	67	63	11	1.51
4e	65	60	11	1.41
4f	72	64	10	1.47
4g	63	63	6	1.49
4h	66	60	13	1.48
4i	70	68	10	1.53

^a Films were cast from slow evaporation of polymer solutions in 1,1,2,2-tetrachloroethane. The cast films were dried under vacuum at 150°C for 6 h prior to the tensile test.

Table IV. Thermal behavior data of sulfonyl polyarylates

Polymer	$T_g^a/^\circ\text{C}$	$T_s^b/^\circ\text{C}$	$T_d^c/^\circ\text{C}$		Char yield ^d %
			In N ₂	In air	
2a	— ^e	—	469	456	36
2b	—	285	445	436	58
2c	253	245	478	462	32
2d	268	263	474	467	34
2e	253	250	491	479	51
2f	208 (289) ^f	—	487	464	29
2g	150	161	488	471	29
2h	287	287	456	437	35
2i	—	319	485	483	56
3a	186	—	478	432	42
3b	219	217	455	462	53
3c	169	178	489	473	36
3d	193	192	474	446	40
3e	184	187	499	486	54
3f	130	140	470	463	40
3g	135	152	490	464	31
3h	208	209	461	444	38
3i	197	201	470	480	56
4a	246	—	418	435	51
4b	234	237	411	435	54
4c	238	243	415	429	43
4d	245	245	419	432	50
4e	240	247	415	427	50
4f	229	220	421	427	39
4g	194	194	417	428	41
4h	283	268	433	426	38
4i	279	298	428	440	60

^a The samples were heated from 40°C to 400°C with a heating rate of 20°C min⁻¹ and rapidly cooled to 40°C at -200°C min⁻¹. The midpoint of baseline shift on the subsequent second DSC heating trace was defined as T_g . ^b Softening temperatures measured by TMA (penetration method) at a heating rate of 10°C min⁻¹. ^c Decomposition temperatures at which 10% weight loss was recorded by TGA at a heating rate of 20°C min⁻¹. ^d Residual weight (%) at 600°C in nitrogen. ^e No discernible transition was observed. ^f The endotherm peak temperature observed on the first heating DSC trace.

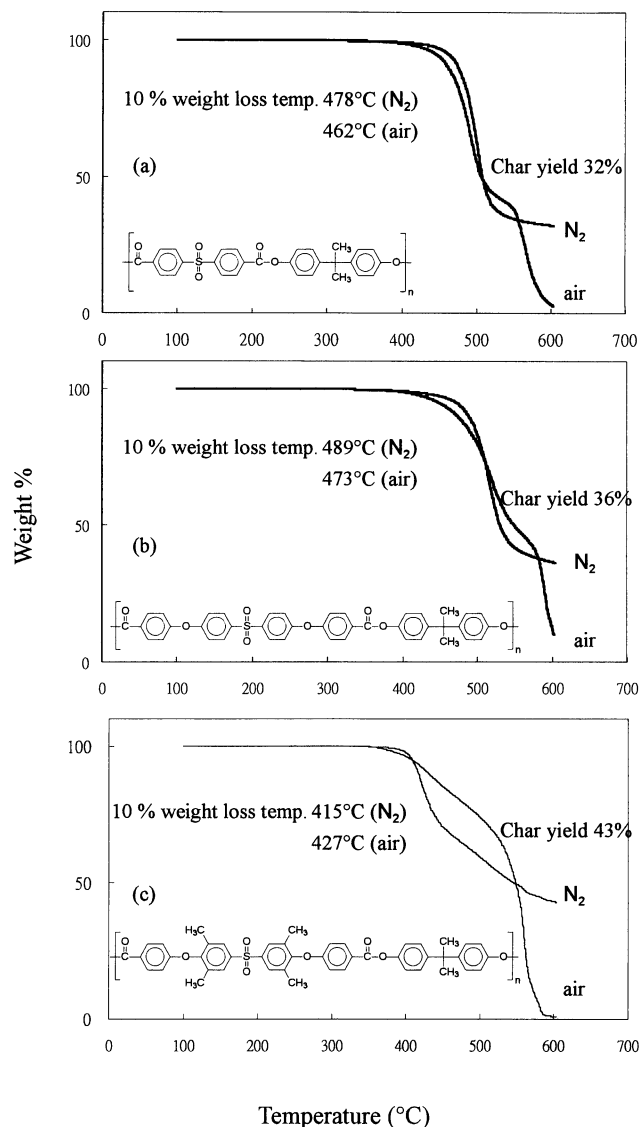


Figure 4. TGA curves of polyarylates (a) 2c, (b) 3c, and (c) 4c with a heating rate of 20°C min⁻¹.

Dynamic TGA indicates that all the polyarylates have good thermal and thermo-oxidative stability due to no significant weight losses were observed up to 400°C in air or nitrogen atmosphere. Typical TGA thermograms of polyarylates 2c, 3c, and 4c are shown in Figure 4. It is quite reasonable that the methyl-substituted polyarylate 4c began to decompose at lower temperatures compared with the unsubstituted polymers 2c and 3c. The TGA data of all polyarylates are also summarized in Table IV. Decomposition temperatures (T_d) corresponding to a 10% weight loss were recorded in the range of 426–486°C in air and 411–499°C in nitrogen, with 29–60% char residue remaining at 600°C in nitrogen.

CONCLUSIONS

A series of polyarylates having the sulfone group or both of the ether and sulfone groups were successfully synthesized by means of the interfacial polycondensation of the sulfonyl diacid chlorides SDBC, SODBC, and

4MeSODBC with various bisphenols. Most of the polyarylates have moderate to high molecular weights and form strong, transparent, and colorless films. Depending on the structures of the diacid chloride and bisphenol moieties, the T_g or T_s values of the polyarylates can be controlled in a wide range of 130–319°C. The introduction of ether groups in the polymer main chain led to a decreased T_g and T_s . Methyl substitution resulted in an enhanced T_g and T_s , but a lower initial decomposition temperature. Good solubility, moderate T_g and T_s values suitable for molding, and reasonable thermal stability make these sulfonyl polyarylates promising high performance engineering plastics or polymeric membranes.

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