Synthesis and Properties of Poly(aryl ether sulfone)s Containing the Phthalazinone Moiety

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ABSTRACT: Three series of poly(aryl ether sulfone)s (PAESs) containing the phthalazinone moiety in the polymer backbone were synthesized by solution polycondensation of bis(4-chlorophenyl) sulfone with three commercial bisphenols and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one. Bisphenol-A, hydroquinone, and bis(4-hydroxyphenyl) sulfone, or bisphenol-S, were selected as the commercial bisphenols for copolymerization. The synthesized polymers exhibited very high glass transition temperatures and excellent thermooxidative properties. They also showed superior mechanical properties and fair rheological properties. The introduction of relatively flexible moieties, such as benzene rings, onto the poly(phthalazinone ether sulfone) (PPES) chain led to a decrease in glass transition temperature with respect to the phthalazinone homopolymer. However, the processability of PPES was improved dramatically by the addition of these commercial bisphenols. The properties of synthesized PAESs can be tailored by changing the molar ratios of bisphenols to phthalazinone monomer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 137–143, 1998

Key words: polysulfone; phthalazinone; poly(aryl ether sulfone); hydroquinone; bisphenol-A; bisphenol-S

INTRODUCTION

Poly(aryl ether sulfone)s (PAESs) exhibit a number of useful properties, such as thermal stability, excellent mechanical properties, radiation stability, and low flammability.[1–6] Because of the above outstanding properties, these high-performance polymers can be used as materials for composite matrices, high temperature films and adhesives, and electronic parts, as well as medical appliances. Therefore, a great deal of effort has been expended for developing newer PAESs with higher heat resistance during the past 30 years.

For example, the UDEL® polysulfone was initially commercialized in 1966 by Union Carbide. Owing to the excellent properties exhibited by UDEL polysulfone, work was accelerated and expanded to investigate the polymerization of other bisphenols and dihalides to explore this new class of high-performance polymer. In this respect, 3M corporation introduced another member of the polysulfone family, Astrel 360, which has a higher glass transition temperature (T_g) than UDEL polysulfone (PSF). Since then, various PAES products, such as VICTREX®–PES (Imperial Chemical Industries), RADEL® R, and RADEL® A polyethersulfone (Union Carbide) became commercially available. All of these polymers had higher T_gs than UDEL.

It is generally known that the chain rigidity

and polarity of a polymer affect both its T_g and melting point (T_m). The incorporation of phenylene rings in the polymer chain is an effective method to enhance the chain rigidity and usually leads to an increase in the glass transition temperature.[7] Astrel 360 and RADEL® polyethersulfones contain both phenylene and biphenylene rings.[8-12] Moreover, the introduction of rigid naphthalene rings into the polymer chain results in enhanced thermal stability compared to the phenylene rings.[13] Thus, PAESs derived from naphthalene have been studied extensively by some workers.[14-16]

In previous articles,[17,18] we have described the synthesis of poly(phthalazinone ether sulfone) (PPES) by the reaction of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ) with bis(4-chlorophenyl) sulfone. The PPES has a very high T_g of 305°C, owing to the incorporation of rigid phthalazinone rings in its backbone. The DHPZ monomer can readily undergo a nucleophilic substitution reaction to give PPES because the phthalazinone NH groups behave like phenolic OH groups. However, some difficulties were encountered during the melt processing of polymers containing only phthalazinone moieties because of their high T_gs. Therefore, we have attempted to improve the processability of these polymers containing the phthalazinone moiety by blending them with low-melt-viscosity polymers, such as PAES oligomers,[19] and liquid crystalline polymers (LCP) with completely aromatic structures.[20]

In this article, we describe the synthesis of PAESs containing the phthalazinone moieties in the main polymer chain by copolymerizing three commercial bisphenols with DHPZ. The main goals are to investigate the thermal and mechanical properties of these PAESs and to examine the effects of the introduction of three bisphenols with greater flexibility than DHPZ on the processabilities of synthesized PAESs.

EXPERIMENTAL

Materials

4-(4-hydroxyphenyl)–2,3-phthalazin–1-one (DHPZ) was synthesized according to the procedure described by Berard and Hay,[17] except that a mixture of chlorobenzene and sulfolane (3/1 v/v) was used as solvent instead of sulfolane. Bis(4-chlorophenyl) sulfone (BCS), bisphenol-A (BPA), hydroquinone (HQ), and bis(4-hydroxy-phenyl) sulfone or bisphenol-S (Bis-S) are commercial products. These monomers were used without further purification. Anhydrous potassium carbonate and reagent-grade solvents N,N'-dimethylacetamide (DMAc) and chlorobenzene (MCB) were also used without further purification.

Procedure for Synthesis of PAESs

The synthesis of the PAES copolymers was conducted in a 500-mL three-neck round-bottom flask equipped with a Dean-Stark trap, a condenser, a thermometer, and a nitrogen inlet. The reaction vessel was charged with DMAc solvent and dehydrating solvent, MCB (volume ratio is 1 : 1). The anhydrous potassium carbonate catalyst and monomers were then added to the reactor with stirring. The molar ratio of K_2CO_3 to BCS was 1 : 1.4. Three series of PAESs, with different molar ratios of DHPZ to commercial bisphenols, were synthesized. The mixture was mechanically stirred and heated to reflux under a nitrogen atmosphere for 20 min. The condenser was then removed, and the chlorobenzene was distilled out over a 1.5–2.0-h period. At this stage, the temperature in the reactor rose stepwise from 145 to 164°C as chlorobenzene was distilled out. Subsequently, the resulting solution was kept at 164–165°C for a further 7–30 h. At the end of the polycondensation, a small amount of phenol was added to the reactor to end-cap the PAES formed when the temperature decreased to 140°C. The reaction mixture was filtered and slowly poured into a vigorously stirring mixture of ethanol and water (3 : 1 volume ratio). The obtained PAES that precipitated was separated by filtrater again. The PAES produced was dissolved in chloroform (10 wt %), filtered, and precipitated in methanol. The above purification procedure was repeated twice. Finally, the purified PAES was dried at 130°C under vacuum. The yield was generally higher than 85%.

Instrumentation

The inherent viscosities (IVs) of PPES and PAESs were determined using an Ubbelohde viscometer at a concentration of 0.4 g/dL in chloroform at 25°C. The glass transition temperatures were examined using a differential scanning calorimeter (Perkin–Elmer DSC-7) at a heating rate of 10°C/min under nitrogen flow. The thermogravimetric analysis (TGA) was performed with a Perkin–
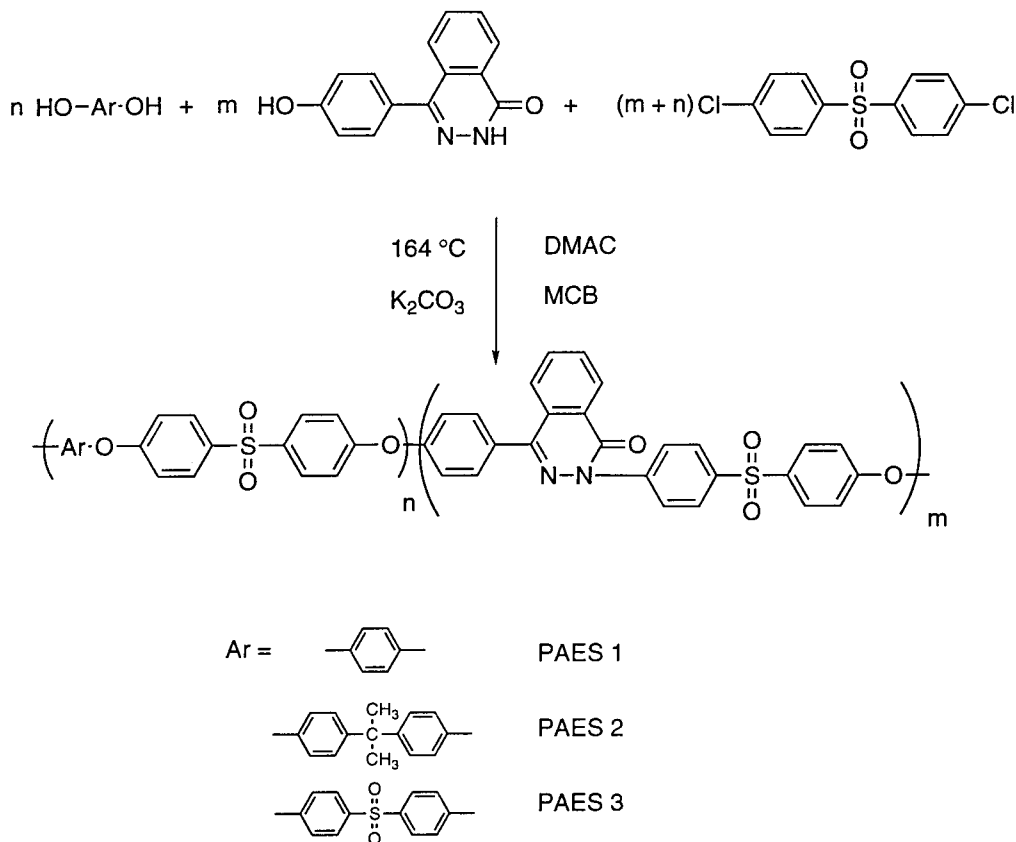
Figure 1 Synthetic scheme for PAESs.

Elmer TGA-7 at a heating rate of 10°C/min in nitrogen. The mechanical properties of synthesized PAESs were measured at 23°C using a Shimadzu AG-2000A tester at a cross head speed of 50 mm/min. The samples with dimensions of 0.2 $\times$ 6.0 $\times$ 50 mm^3 were prepared by the solution casting method. At least five samples for each composition were tested, and the average value was reported.

A Shimadzu AG-2000A capillary rheometer was used to perform the rheological characterization using a 5-mm-long, 1-mm-diameter capillary ($L/D = 5$) at a temperature of 320°C. Shear rate range studied was within 10–200 s^{-1}. The Rabinowitch correction and entrance effect were taken into consideration because of the short capillary employed. The samples were charged into the capillary as fast as possible and kept in the molten state for 5 min prior to testing.

RESULTS AND DISCUSSION

Three series of PAESs were prepared via nucleophilic polycondensation according to the procedure depicted in Figure 1. The synthesized PAESs

are designated as PAES 1, PAES 2, and PAES 3, respectively. Each kind of PAES with different composition is expressed as the PAES (DHPZ/related bisphenol). For example, the PAES 1 containing 25 mol % phthalazinone is written as PAES 1 (25/75).

Table I lists the polycondensation times for the three PAESs. It is apparent that the polycondensation time for producing truly high-molecular-weight PAES 1 is shortest, while that of PAES 3 is longest. Generally, the bisphenols with electron-withdrawing groups between the phenylene rings, such as sulfone or carbonyl, are much less reactive than those with alkyl groups, such as bisphenol-A. Therefore, a correspondingly longer polycondensation time or higher temperature is thus required to achieve useful molecular weight. It has

Table I Polycondensation Times for the PAESs

PAES	PAES 1	PAES 2	PAES 3
Polycondensation time (h)	7	17	30

Table II Thermal and Mechanical Properties for the PAES 1 with Varying Compositions

DHPZ/HQ (Molar Ratio)	25/75	35/65	50/50	100/0
IVs (dL/g)	0.33	0.33	0.41	0.45
T_g (°C)	214	231	242	305
5% Weight loss temperature (N$_2$)	547	552	553	520
Tensile strength at break (MPa)	63.9	90.8	103	109
Strain at break (%)	9.80	10.1	10.9	9.90

been reported by Seymour and Kirshenbaum[21] that the reactivity ratio of bisphenol-A to bisphenol-S is 1.4 : 0.3; thus, the more acidic bisphenol-S is not reactive enough to polymerize with dichlorodiphenyl sulfone (BCS) to produce the polymer with high molecular weight in dimethysulfoxide (DMSO) or in DMAc. However, it is interesting to note that high-molecular-weight polymer can be obtained when bisphenol-S is copolymerized with BCS dihalide in DMAc in the presence of DHPZ bisphenol, indicating that the DHPZ bisphenol is more reactive than Bis-S. Hydroquinone has the greatest reactivity, owing to the electron donating effect of its two OH groups. Thus, the reactivity order for the three bisphenols is as follows: HQ > BPA > Bis-S.

The thermal, tensile, and rheological properties for the synthesized PAESs are presented and discussed next.

Thermal Properties

The T_gs and 5% weight loss temperatures of the synthesized PAESs 1–3 are listed in Tables II–IV, respectively. It is evident that the T_gs for the three series of PAESs increase linearly with increasing molar phthalazinone content. When the molar phthalazinone content in the PAESs equals 100 mol %, the copolymer PAES corresponds to homopolymer PPES. The incorporation of the rigid phthalazinone moiety in the main chain leads to an increase of molecular rigidity in PAES.

In addition, the variation of T_g values with molar phthalazinone content fits the rule of random copolymers. Therefore, the T_gs of the PAESs investigated can be tailored by varying the molar phthalazinone content in PAESs. As shown in Table III, the PAES 2(25/75) provides a grade with T_g = 238°C, which is 43°C higher than UDEL polysulfone and 13°C higher than commercial PES. This result demonstrates that the introduction of the rigid phthalazinone moiety is an alternative to improve the heat resistance of UDEL polysulfone and commercial PES; that is, it provides an effective way of raising T_g. In the three series of PAESs, all the T_gs of PAESs 1–3 containing 30 mol % phthalazinone moiety are higher than that of the commercial PES (T_g = 225°C). Furthermore, the thermogravimetric data as shown in Tables II–IV reveals that the synthesized PAESs 1–3 are thermooxidatively stable, and all 5% weight loss temperatures are higher than 450°C. From these data, PAES 1 is the most thermooxidatively stable, and its 5% weight loss temperature is about 550°C. PAES 2 has the lowest 5% weight loss temperature among the synthesized PAESs since the methyl groups in PAES 2 are less stable than the phenylene ring in PAES 1 and the sulfonyl group in PAES 3. However, they still retain high 5% loss temperature in spite of this difference.

Based on the results as presented in Tables II–IV, it can be concluded that all these synthesized PAESs exhibit high T_g, are thermooxidatively sta-

Table III Thermal and Mechanical Properties for the PAES 2 with Varying Compositions

DHPZ/BPA (Molar Ratio)	0/100	25/75	50/50	75/25	80/20	100/0
IVs (dL/g)	0.60	0.33	0.36	0.32	0.32	0.45
T_g (°C)	195	238	245	—	258	305
5% Weight loss temperature (°C) (N$_2$)	470	474	451	—	461	520
Tensile strength at break (MPa)	70.5	72.5	81.4	84.5	—	109
Strain at break (%)	21.0	9.73	9.85	10.1	—	9.90

Table IV Thermal and Mechanical Properties for the PAES 3 with Varying Compositions

DHPZ/Bis-S (Molar Ratio)	25/75	35/65	50/50	65/35	100/0
IVs (dL/g)	0.73	1.10	1.40	1.30	0.45
T_g (°C)	234	240	260	271	305
5% Weight loss temperature (°C) (N_2)	503	490	492	488	520
Tensile strength at break (MPa)	80.6	83.1	85.9	89.9	109
Strain at break (%)	9.76	8.99	9.90	9.89	9.90

ble, and the T_g order of these PAESs is expressed as follows: PAES 3 > PAES 2 > PAES 1. This is similar to the rigidity order of Bis-S, BPA, and HQ bisphenols.

Mechanical Properties

The tensile strengths and strains at break for PAESs 1–3 with various compositions are also tabulated in Tables II–IV. From these tables, it can be seen that all three series of PAESs have high tensile strength, which is a typical characteristic of high-performance polymers. The values vary between 70 and 109 MPa. It is noted that the variation in tensile strength at break is subject to the rule of random copolymers; that is, the tensile strength of a copolymer lies between those of the parent homopolymers. The tensile strength increases with increasing molar phthalazinone content within PAESs 1–3, owing to the incorporation of phthalazinone moiety into the copolymers. Generally, the naphthalene ring within the polymer backbone contributes more to the mechanical strength than the phenylene ring or biphenylene ring. The reason for the lower tensile strength of PAES 2 than that of PAES 1 and PAES 3 is attributed to the existence of the aliphatic carbons in the main chain of PAES 2. It is well known that the sp^3-hybridized carbon in a main molecular chain usually results in poorer mechanical properties compared with sp^2-hybridized carbon. From these tables, the strain-at-break remains unchanged for the three series of PAESs synthesized with various copolymerization compositions, which is generally true for wholly aromatic amorphous polymers that usually have very low strain-at-break value. The PAES 2(0/100) exhibits the largest strain-at-break because of the greater flexibility of the —$C(CH_3)_2$— group in the main chain.

Processability

The rheological properties of three series of PAESs synthesized with various copolymeriza-

tion compositions were determined. In previous work,[22] we have reported that the homopolymer PPES, poly(phthalazinone ether sulfone), has extremely poor processability due to its very high T_g (305°C) and because of poor melt flow, even under very high temperature (380°C) and pressure. Thus, the rheological behavior of the blends of PPESK, poly(phthalazinone ether sulfone ketone), with two kinds of oligomers[19] and liquid crystalline copolyester[20] was investigated in order to improve its processability. The results demonstrated that the LCP acts as a processing aid as well as reinforcing agent in the blends of PPESK and LCP. On the other hand, it appears that copolymerization process can be used to improve the processability of PPES. The rigidity of the bisphenols (HQ, BPA, and Bis-S) containing phenylene ring is smaller than that of DHPZ containing phthalazinone ring. In this regard, the copolymerization of DHPZ with these flexible bisphenols should improve the processability of PPES. Figure 2 shows the melt viscosity versus shear rate for the PAES 1 with various DHPZ/HQ ratios. Apparently, PAES 1(80/20) exhibits very high melt viscosity (10^5–10^6 Pa s), while the PAES 1 (25/
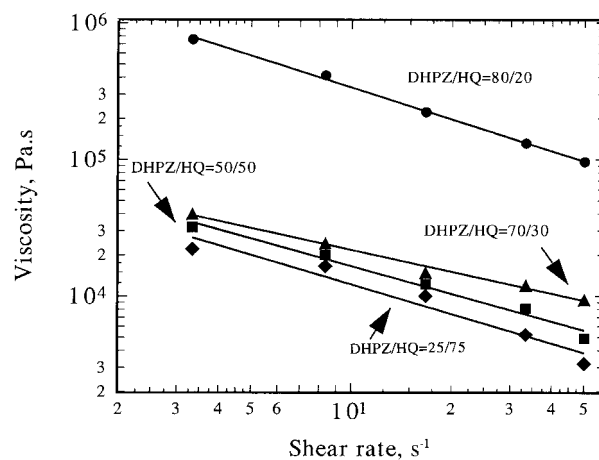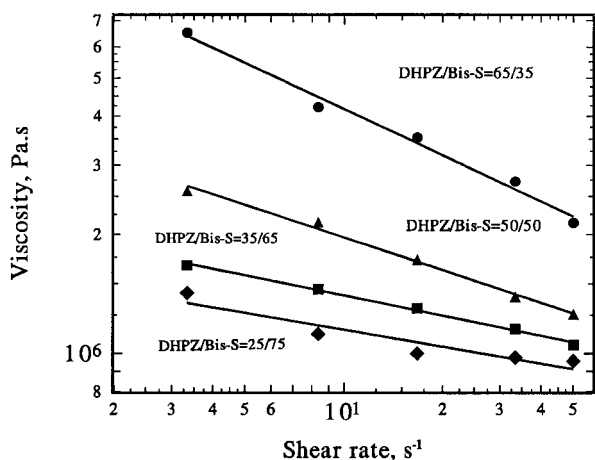

Figure 2 Melt viscosity versus shear rate for the PAES 1 with varying compositions.
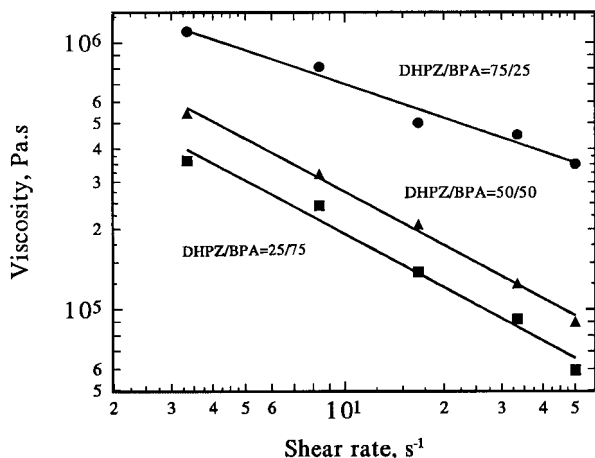
Figure 3 Melt viscosity versus shear rate for the PAES 2 with varying compositions.

75) has the lowest melt viscosity ($\sim 10^4$ Pa s), which is 10 times lower in melt viscosity compared with the PAES 1(80/20). It is noted that the tendency to decrease in melt viscosity tends to become smaller with a further increase in HQ content. The relationship between the melt viscosity and shear rate for PAES 2 is plotted in Figure 3. It is evident that the PAES 2(75/25) has the highest melt viscosity. Moreover, the melt viscosity appears to decrease with increasing BPA content, particularly when BPA content is higher than 50%. Finally, it can be seen from Figure 4 that the melt viscosity decreases sharply with increasing Bis-S content for PAES 3. In addition, the decrease in melt viscosity with increasing copolymerized bisphenol content for PAES 3 is similar to that for PAES 2 and PAES 1. It is worth

Figure 4 Melt viscosity versus shear rate for the PAES 3 with varying compositions.

Table V   Melt Viscosity Versus Shear Rate for the PAESs Containing 25% Phthalazinone Moiety

PAES	$\eta_a \times 10^{-5}$	Shear Rate (s^{-1})			
		3.34	8.35	16.7	33.4
PAES 1	(25/75)	2.21	1.90	1.35	0.62
PAES 2	(25/75)	3.60	2.47	1.60	0.92
PAES 3	(25/75)	14.7	9.99	9.88	9.75

noting that the melt viscosity of PAES 3 is much higher than those of PAES 1 and PAES 2 (over 10^6 Pa s), indicating that it would have poor processability. On the basis of these data, it appears that PAES 1 and PAES 2 exhibit low melt viscosities, particularly for those containing higher HQ and BPA contents. Hence, the processability of PPES can be improved via copolymerization with HQ or BPA bisphenols.

For the three series of PAESs containing 25% DHPZ, the melt viscosities at various shear rates are listed in Table V. From these results, we can conclude that the degree of improvement of the processability of synthesized PAESs containing three kinds of bisphenols is in following the order: HQ > BPA $\gg$ Bis-S.

CONCLUSIONS

Three series of poly(aryl ether sulfone)s (PAESs) containing the phthalazinone moiety in the polymer backbone were synthesized via solution polycondensation. The synthesized PAESs exhibited good mechanical properties, high T_gs, and excellent thermooxidative stability. The T_gs and mechanical properties of the PAESs tends to increase with increasing phthalazinone moiety content. Hence, the incorporation of the rigid phthalazinone moiety provided an effective way of raising the heat resistance of PAESs. The rheological measurements showed that the melt viscosities also tended to increase with increasing phthalazinone moiety content. The PAESs containing HQ and BPA bisphenols were observed to exhibit significantly lower viscosities. This implies that the processability of PPES with phthalazinone moiety can be improved by copolymerizing with HQ or BPA bisphenol. In conclusion, the heat resistance and the processability of the synthesized PAESs

can be tailored through changing the molar ratios of DHPZ to various bisphenols used in this work.

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