

# Developing Toughened Aromatic Polybenzoxazines Using Thermoplastic Oligomers and Telechelics, Part 1: Preparation and Characterization of the Functionalized Oligomers

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**ABSTRACT:** The preparation and characterization of three families of thermoplastic oligomers ( $M_n = 2918\text{--}13263\text{ g mol}^{-1}$ ) based on polyarylsulfone (PSU) differing in both molecular weight and terminal functionality and one series of polyarylethersulfone (PES) of different molecular weights is reported. Infrared and nuclear magnetic resonance spectroscopy data support the formation of both the hydroxyl terminated oligomers and conversion (67–89% depending on molecular weight) to the telechelic PSU oligomer bearing reactive benzoxazine groups. Differential scanning calorimetry reveals that the onset of homopolymerization in the telechelic PSU oligomer occurs at around 100°C (peak maximum 125°C at 10 K/min) and rescans show values of the glass transition (for the homopolymers) ranging from 124 to 167°C depending on molecular weight. The influence on the oligomer backbone and terminal functionality is examined using thermal analysis. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40875.

**KEYWORDS:** crosslinking; differential scanning calorimetry; thermal properties; thermoplastics; thermosets

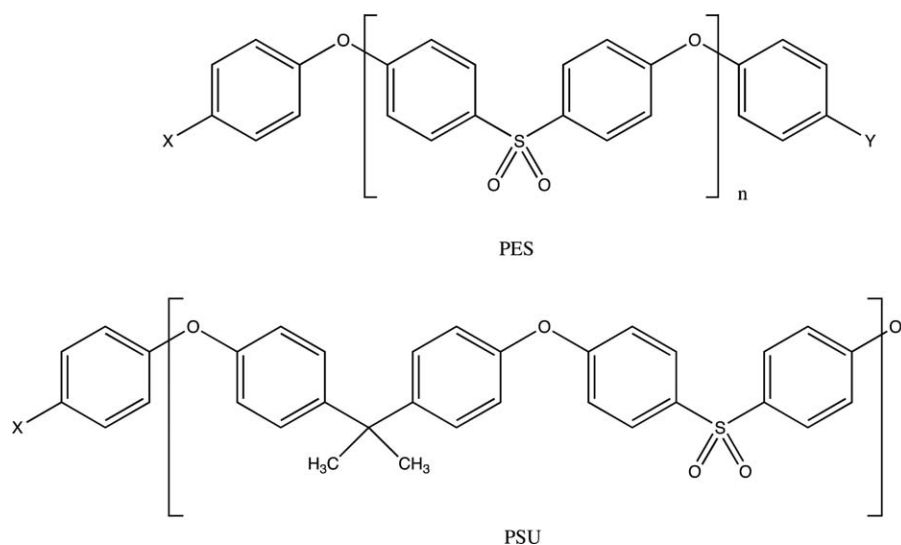
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## INTRODUCTION

The potential for the use of oligomers based on engineering thermoplastics has been examined for some years e.g. as modifiers in aerospace composite matrices,<sup>1,2</sup> due to their inherent toughness and the ability to blend them more easily than high molecular weight species without incurring the penalty of high melt viscosity.<sup>3</sup> Poly(arylene ether sulfone)s are amongst the most widely reported high performance thermoplastics and were originally developed during the 1960s following independent research work by the 3M Corporation,<sup>4</sup> Union Carbide,<sup>5</sup> and the Plastics Division of ICI<sup>6</sup> to develop thermally stable thermoplastics suitable for engineering applications; their chemistry has recently been reviewed.<sup>7</sup> The materials are highly aromatic polymers that comprise phenylene backbones bridged with heteroatoms (O, S) or groups (SO<sub>2</sub>, CH<sub>2</sub>, C(CH<sub>3</sub>)<sub>2</sub>, etc.), to offer thermal stability, good mechanical properties, creep resistance, and chemical resistance. These polymers have now reached a degree of maturity with many variants having been reported in both laboratory and

commercial publications, and have been reviewed extensively.<sup>8</sup> Commercial products (e.g., Udel®, Radel®, and Victrex®) are now available in a variety of grades to satisfy different high performance applications and widely used. Poly(arylene ether sulfone)s display a wide range of glass transition temperatures ( $T_g$ ) influenced to a large degree by the chemical structure.<sup>8</sup> Hence, polymers produced from dichlorodiphenylsulfone and simple bisphenols yield high  $T_g$  materials, typically in the range 180 to 230°C with the magnitude being influenced by the bulk of the substituents on the central carbon atom. The prediction of thermal and mechanical properties in as yet unsynthesized polymers is beginning to be realized and we have demonstrated this in a variety of thermosetting polymers such as epoxy resins,<sup>9</sup> cyanate esters,<sup>10</sup> and polybenzoxazines,<sup>11</sup> as well as engineering thermoplastics.<sup>12,13</sup> In a previous publication,<sup>14</sup> we reported the use of a quantitative structure property relationship (QSPR) to predict the  $T_g$  of a polymer of this type, but the model was severely limited by the size of the training set used to generate the QSPR equation.



**Figure 1.** Structures of the oligomers studied in this work, where X and Y may be Cl, OH, or Bz.

In the present work, the preparation of low molecular weight oligomers ( $M_n < 15,000$  g/mol) is the target as the materials will ultimately be examined as property modifiers in combination with high performance thermosetting polymers (polybenzoxazines). Shorter chains are more miscible with the unreacted thermoset monomers and consequently improve the processability of the blend significantly. The purpose of investigating different functionalities is to see whether any interaction or reaction between the polybenzoxazine and the thermoplastic can be observed and ultimately whether this influences the resin toughness (as has been found for epoxy blends containing similar polymers). It has been proposed that increased interaction between the thermoplastic and the benzoxazine matrix will prevent “pulling out” of the thermoplastic at the crack front, so increasing the force required to progress a crack or diverting the crack front and dissipating its energy that way.<sup>15,16</sup> The hydroxy-terminated thermoplastics have been observed<sup>17</sup> to be more reactive than the corresponding chloro-oligomers towards benzoxazine monomers. The acidic phenolic protons not only initiate the ring opening reaction, but also improve toughness through hydrogen bonding interaction with the benzoxazine polymer network.<sup>18</sup>

## EXPERIMENTAL

### Materials

The following chemicals were used in the synthetic steps and are listed with the purities and sources. 4,4'-Isopropylidenediphenol (BPA) (97%), 4,4'-dichlorodiphenyl sulfone (DCDPS) (98%), bis-(4-hydroxyphenyl)sulfone (BPS) (98%), 1-methyl-2-pyrrolidinone (A.C.S. reagent > 99%), paraformaldehyde (95%), sulfolane (99%), aniline (99%), and methanol were obtained from Sigma Aldrich. Anhydrous potassium carbonate, acetic acid (Laboratory Reagent Grade), toluene (LRG—low in sulfur), methanol, chloroform, and sodium hydroxide were all purchased from Fisher Scientific. *N,N*-Dimethylacetamide (DMAc) (99%) was obtained from ACROS Organic. Lithium bromide was obtained from Fluka Analytical.

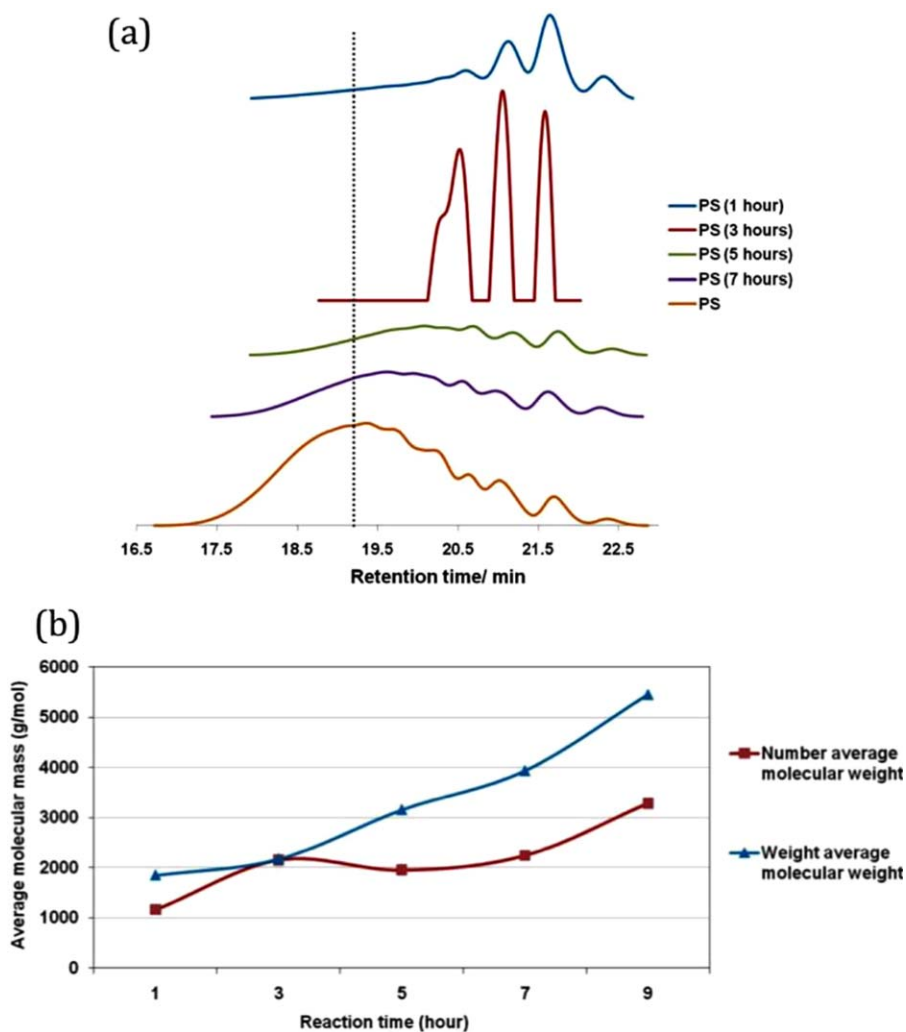
### Preparative Procedures

The polymers examined in this work (Figure 1) were originally prepared during a study of oligomeric engineering thermoplastics.<sup>19</sup> The synthetic procedures (e.g., on 20 g scale) used were all based on published methods,<sup>20–23</sup> albeit modified versions in order to achieve controlled lower molecular weight species.<sup>24</sup>

### Typical Preparation of a $\alpha,\omega$ -Dihydroxypolyarylsulfone (Exemplified by PES<sub>OH</sub>9000)

To a dry 250 cm<sup>3</sup> three necked round-bottom-flask were added DCPS (65 g) and BPS (59.69 g) followed by sulfolane (150 cm<sup>3</sup>), and the resulting mixture was stirred overnight using an overhead mechanical stirrer under nitrogen to ensure that all the solid was broken up and well distributed. Potassium carbonate (33.93 g, 3 mol % excess) was added in small aliquots over a 10 min period with stirring. Slow addition was necessary to reduce the foaming that was experienced and produce a beige colored solution. The flask was heated under nitrogen with overhead stirring in an oil bath using the following heating schedule: 180°C (30 min), 210°C (1 h) and 230°C (4 h). Water was driven off using nitrogen and outlet pipe during the first 60 min. After heating, the flask solution formed a black solution, which was removed from the heat and cooled on a cork ring overnight. During this time the solution became very viscous and required gentle warming before being poured into hot water (3.5 dm<sup>3</sup>) and broken up using a Silverson mixer with a large hole head and washed for 20 min.

The resulting mixture was allowed to settle and the majority of the supernatant water and the small quantity of fine particles of polymer (that did not settle) were decanted off. These were subsequently analyzed and found to contain higher molecular weight polymer (in excess of 30,000 g/mol), but were discarded as being not of use in the intended application. The beaker was then filled with cold water (3.5 dm<sup>3</sup>) and washed for a further 20 min using a medium head (*N.B.* The lower molecular weight material formed a gel-like consistency in the water and the solid did not settle out, so it had to be washed in aliquots). The solid



**Figure 2.** Comparison of (a) GPC data (obtained in THF) and (b) average molar masses of  $\text{PSU}_{\text{OH}}$  showing the development of the polymer chain as a function of reaction time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

was filtered using a grade 3 Whatman filter paper and then washed again in water ( $3.5 \text{ dm}^3$ ) with acetic acid ( $2M$ ,  $2 \text{ cm}^3$ ) for 20 min using a medium head. The crude product was then filtered and washed a further 4 times for 20 min with water ( $3.5 \text{ dm}^3$ ) each of the times using a fine Silverson head. After the final wash the solid was filtered and enough methanol to fill the funnel was added (solid was agitated) and filtered to dryness. The off-white solid (darkened with decreasing molecular weight) was then dried in a  $500 \text{ cm}^3$  glass jar at  $85^\circ\text{C}$  *in vacuo* for about 48 h. Molecular weight by NMR ( $M_n$ ):  $8,014 \text{ g mol}^{-1}$ , Molecular weight by GPC, ( $M_n$ ):  $8,047 \text{ g mol}^{-1}$ . Elemental analysis data: 60.02% C, 3.63% H, 0% N (calculated for  $\text{C}_{12}\text{H}_8\text{SO}_3$  62.06% C, 3.47% H, 0% N).

#### Typical Preparation of a $\alpha,\omega$ -Dihydroxypolyarylethersulfone (Exemplified by $\text{PSU}_{\text{OH}3000}$ )

A dry  $500 \text{ cm}^3$ , 3-neck round-bottom-flask under nitrogen was charged with DCDPS (25.16 g), BPA (40 g), and DMAc ( $400 \text{ cm}^3$ ) and stirred to dissolve, before adding 3 mol % excess potassium carbonate (24.94 g), rinsing weighing vessels with toluene ( $150 \text{ cm}^3$ ). The mixture was heated to  $155\text{--}160^\circ\text{C}$  under nitro-

gen, tapping off water and toluene using a Dean-Stark trap, from about  $140^\circ\text{C}$ . The temperature was maintained for 6 h and cooled to about  $100^\circ\text{C}$  before chlorobenzene ( $100 \text{ cm}^3$ ) was added and the reaction mixture allowed to cool to about  $50^\circ\text{C}$  then poured quickly into rapidly stirring ice water. The resulting solid foam was broken up using a blender and then washed with copious amounts of water and finally with methanol ( $300 \text{ cm}^3$ ), filtering on a grade 4 sintered funnel. The whitish solid was dried at  $65^\circ\text{C}$  *in vacuo* for 48 h. (*N.B.* the polymer did not always precipitate depending on the molecular weight prepared and in these cases the organic layer was allowed to settle, the water was decanted and the solvent removed using the rotary evaporator). Molecular weight by GPC (PS standard), ( $M_n$ ):  $2,918 \text{ g mol}^{-1}$ , ( $M_w$ )  $3,730 \text{ g mol}^{-1}$ . Elemental analysis data: 71.60% C, 5.04% H, 0% N (calculated for  $\text{C}_{27}\text{H}_{22}\text{SO}_4$  73.28% C, 5.01% H, 0% N).

#### Typical Conversion of $\alpha,\omega$ -Dihydroxypolyarylethersulfone to the Corresponding Benzoxazine Telechelic (Exemplified by $\text{PSU}_{\text{Bz}3000}$ )

A dry  $500 \text{ cm}^3$ , 3-neck round-bottom-flask under nitrogen was charged with DCDPS (25.16 g), BPA (40 g) A  $500 \text{ cm}^3$ , 2-neck

**Table I.** Molecular Weights ( $\text{g mol}^{-1}$ ) of Synthesized Thermoplastic Oligomers Obtained Using Different Analytical Techniques and the Ratios of Starting Materials Used

Polymer	GPC Data			$M_n$ ( $^1\text{H NMR}$ )	Ratio of BP : DCDPS or BPS : DCDPS	BZ conversion (%)
	$M_n$ (PMMA, UV)	$M_n$ (PS, RI)	$M_w$ (PS, UV)			
PSU <sub>OH</sub> 3000		2918	3730		2 : 1	
PSU <sub>OH</sub> 6000		6090	7601		1.07 : 1	
PSU <sub>OH</sub> 10000		11,706	20,778		1.04 : 1	
PSU <sub>Bz</sub> 3000		2842	3504			83
PSU <sub>Bz</sub> 6000		5882	7529			89
PSU <sub>Bz</sub> 12000		13,263	22,087			67
PSU <sub>Ci</sub> 3000		3826	7967		1 : 1.2	
PSU <sub>Ci</sub> 6000		6486	7900		1 : 1.08	
PSU <sub>Ci</sub> 9000		8050	12,072		1 : 1.11	
PES <sub>OH</sub> 3000				3293	1.16 : 1	
PES <sub>OH</sub> 6000	5270			6195	1.08 : 1	
PES <sub>OH</sub> 9000	8047			8014	1.05 : 1	

RI, GPC data detected using refractive index detector; UV, GPC data detected using ultra-violet-visible spectrometer; PMMA, data acquired using narrow molecular weight poly(methyl methacrylate) standards; PS, data acquired using narrow molecular weight polystyrene standards.

round-bottom-flask under nitrogen was charged with chloroform ( $200 \text{ cm}^3$ ) to which aniline (6.21 g) and paraformaldehyde (4.00 g) were added and stirred until dissolved before adding PSU<sub>OH</sub>3000 (20 g), rinsing the container with a small amount of chloroform. The mixture was heated to reflux and maintained for 24 h. The solution was then allowed to cool before pouring into methanol to yield a solid. This was not always successful, and in these cases the solvent was removed using rotary evaporation and the resulting crude solid broken up and washed with copious amounts of water, followed by methanol, then dried at  $60^\circ\text{C}$  *in vacuo* for 24 h, to yield a white solid. Molecular weight by GPC (PS standard), ( $M_n$ ):  $2,842 \text{ g mol}^{-1}$ , ( $M_w$ )  $3,504 \text{ g mol}^{-1}$ .

#### Blending and Cure of Polymer Samples for Thermo-Mechanical Analyses

Monomers were first degassed at  $100\text{--}120^\circ\text{C}$  (2–3 h depending on the level of foaming) and cured in aluminum dishes (55 mm diameter, depth 10 mm) in a fan-assisted oven: heating at 2 K/min to  $180^\circ\text{C}$  (2 h isothermal) + heating at 2 K/min to  $200^\circ\text{C}$  (2 h isothermal) followed by a gradual cool to room temperature. Cured samples were cut to the correct token size for analysis using a diamond saw.

#### Characterization and Measurements

Nuclear magnetic resonance (NMR) spectra (including DEPT-135, HSQC and HMBC pulse sequences to assign individual environments) were obtained for  $^1\text{H}$  (500 MHz) using a Bruker DRX500 FT-NMR at 298K in  $\text{CDCl}_3$  with TMS as an internal standard.

Vibrational spectra were obtained using a Perkin-Elmer FTIR system 2000 spectrometer. Samples for FTIR analysis were cast from chloroform (GPR) on KBr disks and the solvent removed in a fan oven ( $50^\circ\text{C}$ , 30 min). For each measurement, 16 spectra

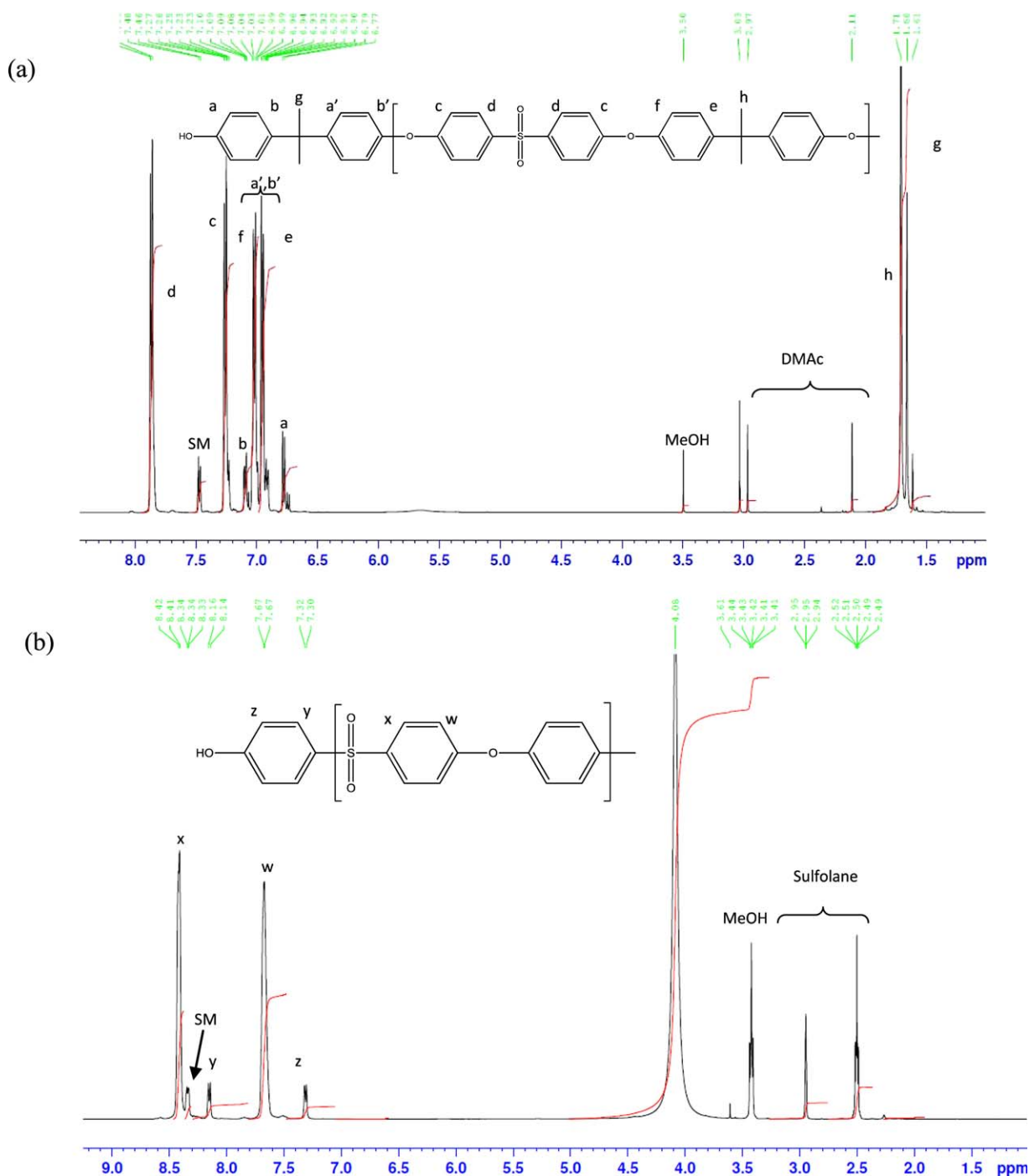
were obtained at a resolution of  $4 \text{ cm}^{-1}$  and coadded to produce the final spectrum.

Gel permeation chromatography (GPC) was conducted on a Polymer Laboratory PL-GPC50 integrated GPC system equipped with micro-volume double piston pump ( $100 \mu\text{m}$  loop with micro injection) and PL gel ( $5 \mu\text{m}$ ) mixed bed D ( $300 \times 7.5 \text{ mm}^2$ ) column maintained at  $50^\circ\text{C}$ . The detector was a Filter photometer UV (Deuterium lamp–280 nm). Narrow PDI polystyrene (PS) or poly(methyl methacrylate) (PMMA) standards were used and oligomer samples were dissolved in dimethylformamide (DMF) with 0.01M LiBr. Data were analyzed using Cirrus GPC/SEC software v. 3.0 (Varian, 2006).

DSC thermograms were obtained using a TA Instruments DSC Q1000 Thermal analyzer. Samples ( $3 \pm 1 \text{ mg}$ ) were heated under dry nitrogen ( $40 \text{ cm}^3/\text{min}$ ) in hermetically-sealed, aluminum pans at 10 K/min from 20 to  $300^\circ\text{C}$  (represented by “Heat 1”). After the first excursion to  $250^\circ\text{C}$ , the sample was quenched and rapidly cooled to ambient temperature before being rescanned over the same temperature range to demonstrate that reaction had been completed in the first scan. The second scan (Heat 2) was again quenched at  $250^\circ\text{C}$  and the final rescan (Heat 3) was performed to demonstrate the influence on  $T_g$ , which was minimal indicating complete reaction.

TGA thermograms were obtained using a TA Instruments TGA Q500 Thermal analyzer. Samples ( $3 \pm 1 \text{ mg}$ ) were heated under dry nitrogen ( $40 \text{ cm}^3/\text{min}$ ) in a platinum pan at 10 K/min from 20 to  $900^\circ\text{C}$ .

Dynamic mechanical thermal analysis (DMTA) (in single cantilever mode at a frequency of 1 Hz) was carried out on cured neat resin samples ( $2 \times 10 \times 17 \text{ mm}^3$ ) using a TA Q800 in static air.



**Figure 3.** General assignment of <sup>1</sup>H NMR spectra of (a) PSU (e.g., using PSU<sub>OH</sub> 9000) and (b) PES (e.g., using PES<sub>OH</sub>3000). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Thermoplastic Oligomers

By varying the ratio of the BPA or BPS to the DCDPS, it was possible to obtain oligomers of different molecular weights and the development of the chain length of the PSU<sub>OH</sub> oligomer via step growth polymerization is shown in Figure 2.

The different ratios and the functionality and molecular weights produced are tabulated in Table I. The nomenclature employed

for the thermoplastics (TPs) is as follows: the first three letters designate the polymer backbone, where PSU is polyarylethersulfone and PES is poly(ether sulfone), the subscript designates the main terminal group, where —Cl = chloro, —OH = hydroxyl, and —Bz = benzoxazine, the number is an approximation of the molecular weight based on the number average molecular weight values in Table I and also the estimated molecular weight from the stoichiometry. Thus, PES<sub>OH</sub>6000 is a poly(ether



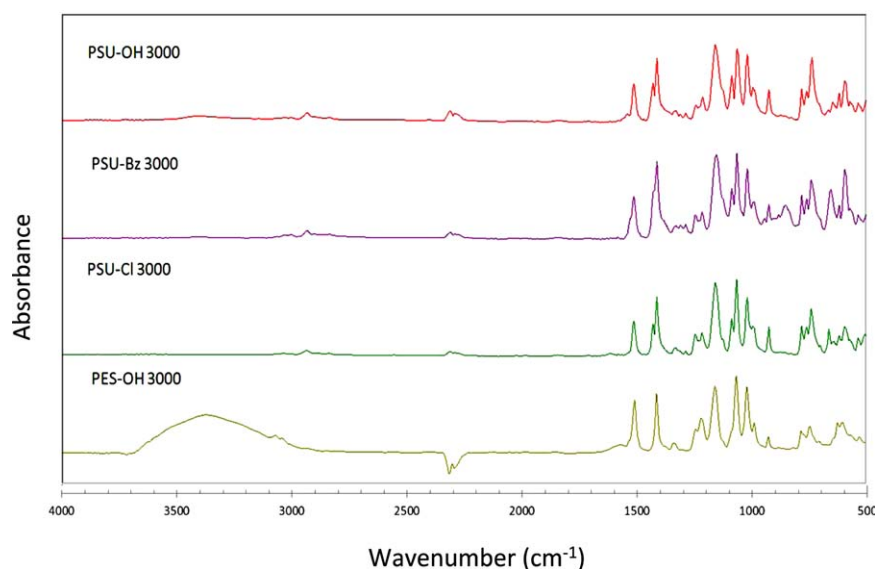
**Table II.**  $^1\text{H}$  NMR Assignments for Synthesized Thermoplastics

Polymer	$^1\text{H}$ NMR Chemical Shift (ppm) designations refer to Figure 2												
	$H_a$	$H_b$	$H_c$	$H_d$	$H_e$	$H_f$	$H_g$	$H_h$	$H_w$	$H_x$	$H_y$	$H_z$	
PSU <sub>OH</sub> 3000	6.74	7.10	7.23	7.84	6.93	7.01	1.65	1.69					
PSU <sub>OH</sub> 6000	6.79	7.10	7.23	7.85	6.93	7.01	1.65	1.70					
PSU <sub>OH</sub> 10000	6.74	7.08	7.25	7.85	6.94	7.00	1.65	1.69					
PSU <sub>Cl</sub> 3000			7.25	7.85	6.94	7.00		1.69					
PSU <sub>Cl</sub> 6000	6.75	7.09	7.22	7.84	6.94	6.99		1.69					
PSU <sub>Cl</sub> 9000			7.25	7.85	6.93	6.99		1.69					
PSU <sub>Bz</sub> 3000	6.72	7.10	7.25	7.84	6.91	7.00	1.64	1.69	O-CH <sub>2</sub> -N 5.35		Ar-CH <sub>2</sub> -N 4.61		
PSU <sub>Bz</sub> 9000	6.70		7.25	7.85	6.94	7.01	1.64	1.69	O-CH <sub>2</sub> -N 5.33		Ar-CH <sub>2</sub> -N 4.60		
PSU <sub>Bz</sub> 12000	6.75	7.09	7.25	7.85	6.95	7.01	1.64	1.69	O-CH <sub>2</sub> -N 5.20		Ar-CH <sub>2</sub> -N 5.02		
PES <sub>OH</sub> 3000										7.25	7.98	7.70	6.85
PES <sub>OH</sub> 6000										7.27	7.98	7.74	6.90
PES <sub>OH</sub> 9000										7.27	7.98	7.75	6.89

The differences in chemical shifts in benzoxazine groups, as compared with the work of Yagci et al.<sup>31</sup> on similar compounds, are presumed to be caused by ring opening of the benzoxazine ring. Aromatic protons are not assigned due to the overlap in chemical shifts; this may also impact the assignment of the backbone aromatic protons.

sulfone) with hydroxyl end groups and has a number average molecular weight of  $6000 \text{ g mol}^{-1}$ , the structures of the different polymers can be seen in Figure 1. The values achieved for molecular weight show disparity in the method chosen for analysis, and the general problem in determining molecular weight due to polydispersity. To maintain consistency in the samples, the number average molecular weight achieved from GPC is quoted throughout the text (except in the case of PES<sub>OH</sub>3000 where a value could not be obtained so the value reported is that obtained from the NMR data).

$^1\text{H}$  NMR spectroscopy was used to determine the purity of each system and chemical shifts were assigned for each thermoplastic backbone.<sup>16,21,25–30</sup> One example of each dihydroxy oligomer is given for comparison in Figure 3, and there was some ambiguity with the assignment as the shifts are very close in the aromatic region and it is hard to differentiate unambiguously between the hydroxyl- and chloro-terminated chains, but it is clear that the desired material has been produced (molecular weight and functionality were confirmed using chromatographic and vibrational spectroscopic techniques) and assignment has



**Figure 4.** Comparison of FTIR spectra of different oligomers all at nominally  $3000 \text{ g mol}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.** Assignment of Key Peaks in ATR-IR Spectra of the Oligomers

Wavenumber (cm <sup>-1</sup> )	Assignment	Band observed in
3500-3300	OH stretch <sup>22</sup>	PSU <sub>OH</sub> , PES <sub>OH</sub> , and PSU <sub>Bz</sub> (All)
3100-3000	Aromatic C-H stretch <sup>28</sup>	All
2965	CH <sub>3</sub> asymmetric C-H stretch <sup>28</sup>	All
2865	CH <sub>3</sub> asymmetric C-H stretch <sup>28</sup>	All
1585-1565	C=C aromatic ring (mono-, di-, and tri-substituted) <sup>28</sup>	All
1502	C=C aromatic ring (mono-, di-, and tri-substituted) <sup>28</sup>	PSU <sub>Cl</sub> , PSU <sub>OH</sub>
1485	C-C aromatic ring (mono-, <i>ortho</i> -, and <i>meta</i> -disubstituted) <sup>28</sup>	All
1410	C-H symmetric deformation of CH <sub>3</sub> <sup>33</sup>	PES <sub>OH</sub>
1320-1315	O=S=O asymmetric stretch <sup>23</sup>	All
1290	O=S=O symmetric stretch <sup>23</sup>	All
1240-1230	C-O-C stretch of aryl ether <sup>32</sup>	All
1165-1170	O=S=O symmetric stretch <sup>23</sup>	All
1150-1145	O=S=O symmetric stretch <sup>23</sup>	All
1105-1100	C=C aromatic ring ( <i>para</i> -disubstituted) <sup>28</sup>	All
1080-1070	Possibly Ar-Cl <sup>28</sup>	All
1015-1010	C=C aromatic ring ( <i>para</i> -disubstituted) <sup>23,28</sup>	All
940	Out of plane C-H deformation of trisubstituted ring (corresponds to benzoxazine ring) <sup>5,16,23,34</sup>	PSU <sub>Bz</sub>
872	Out of plane C-H deformation of trisubstituted ring <sup>28</sup>	All
852	C-H wag, aromatic <sup>28</sup>	All except PES <sub>OH</sub>
750-740	Out of plane C-H deformation of trisubstituted ring <sup>28</sup>	All
714	Out of plane C-H deformation of trisubstituted ring <sup>28</sup>	All
700-688	Out of plane C-H deformation of trisubstituted ring <sup>28</sup>	All

been carried out as accurately as possible using the published literature.

There is a degree of contamination from residual DMAc, despite several washings using water and methanol, and possibly some unreacted starting material as the integration shows some discrepancy between peaks. However, owing to the complexity of the aromatic region of the NMR spectrum (caused by the similarity of the chemical shifts of the starting material and the polymer chain end group protons), this is difficult to quantify. The assigned chemical shifts for each different polymer are given in Table II. Determination of the conversion of hydroxyl end groups to benzoxazine rings was carried out by examining the ratio of

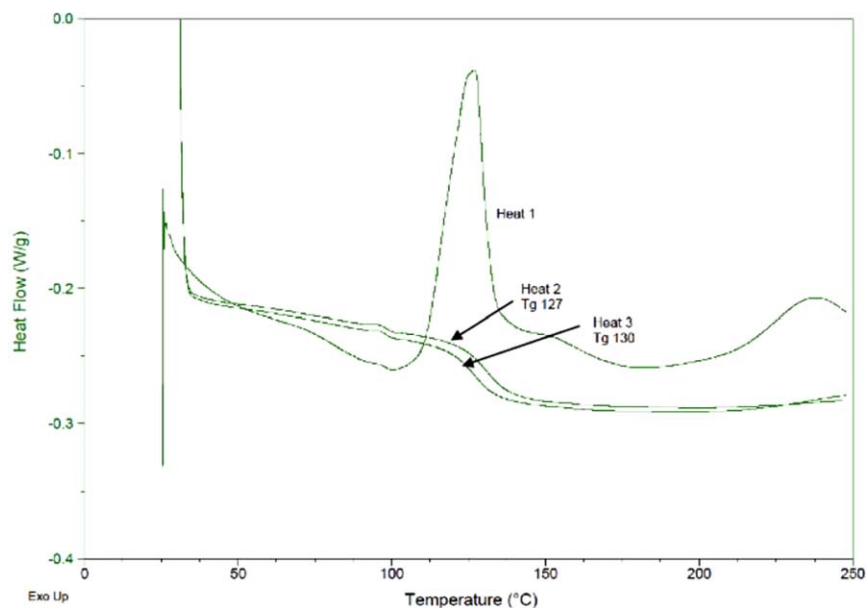
methylene groups in the benzoxazine ring, to the aromatic protons of the PSU end group. It is accepted that this is only a rough estimate as some ring opening might have occurred as there were three peaks in the methylene range, that were at a slightly higher shift than the values given for the methylene groups by other groups.<sup>31</sup> Evaluation of the FTIR spectrum of a PSU<sub>Bz</sub>3000 (Figure 4) shows evidence of a “polymeric” hydroxyl peak (involving hydrogen-bonding), which might indicate either the presence of unconverted PSU-OH or could also indicate that some ring opening might have occurred.

FTIR spectral analysis was performed in order to determine whether the desired end group had been incorporated.

**Table IV.** Glass Transition Temperatures for Thermoplastic Oligomers and Selected Cured Thermoplastic-Polybenzoxazine Blends

Sample	[PBZ:TP] (wt %)	$\Delta H_p$ (J g <sup>-1</sup> )	$T_{5\%}$ (°C)	$Y_{C800}$ (%)	$E''_{max}$ (°C)
BA-a	100 : 0	309.9	222	25	165
PES <sub>OH</sub> 6000	90 : 10	280.0	250	28	182
PSU <sub>OH</sub> 6000	90 : 10	271.4	258	28	175
PSU <sub>Bz</sub> 6000	90 : 10	271.4	248	27	149
PSU <sub>Cl</sub> 6000	90 : 10	261.4	255	28	140

TP, concentration of thermoplastic oligomer in the blend; PBZ, concentration of polybenzoxazine in the blend;  $\Delta H_p$ , polymerization enthalpy (from DSC ‘Heat 1’ scan, heated at 10 K/min under nitrogen 50 cm<sup>3</sup>/min.);  $T_{5\%}$ , temperature at which a mass loss of 5% is recorded;  $Y_{C800}$ , char yield recorded at 800°C;  $E''_{max}$ , Temperature of maximum response in loss modulus (from DMTA).



**Figure 5.** Overlay of the three consecutive heating scans for PSU<sub>Bz</sub>9000. Heat 1 indicates the exotherm caused by the curing of the benzoxazine end groups. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Consequently, stacked plots of the different oligomers of approximately the same molecular weight (nominally 3000 g mol<sup>-1</sup>) are given in Figure 4 and as the polymers are largely the same, there are only subtle peak changes and these are highlighted in the assignments in Table III.

Several key peaks of interest are examined to determine whether the polymer has the desired end group. For example, the observation of a peak about 940 cm<sup>-1</sup> indicates conversion to a terminal benzoxazine ring, although a broad band at 3300–3400 cm<sup>-1</sup> is also characteristic of the presence of “polymeric” hydroxyl groups (hydrogen bonded) either from PSU<sub>OH</sub> that is not fully converted or arising from ring opening of the benzoxazine end group (the chloro end group is inferred by a lack of these features along with data from vibrational spectroscopy). From knowledge of the molecular weight of the thermoplastic, the percentage conversion from chloro end groups can also be estimated.

The free *ortho* position of the PSU phenol end group is believed to act as an additional potential crosslinking site for the benzoxazine polymerization reaction. The benzoxazine-terminated thermoplastic (a telechelic) undergoes its own curing reaction, which is responsible for the exotherm observed in the first heating scan on the DSC in Figure 4, hence two further temperature sweeps were undertaken to determine the  $T_g$  of the thermoplastic alone. The glass transition temperature values for PES are within the expected region for these types of polymers.<sup>7</sup> The glass transition values for PSU<sub>Bz</sub>, especially the 3000 and 9000, are of a lower magnitude compared with the value of 170°C achieved by Yagci et al.<sup>21</sup> for PSU<sub>Bz</sub> with molecular weights of 2150 and 4000 g mol<sup>-1</sup>, but there is a chemical shift at 6.77 ppm in the <sup>1</sup>H NMR spectrum, which might be associated with unconverted phenolic groups.

Furthermore, the FTIR spectrum shows the presence of O—H stretches from hydroxyl groups, so the degree of conversion may not be as high as the value given in Table I, nor as high as

the figure quoted by Ates et al. who reported conversions of terminal hydroxyl groups to benzoxazine rings in excess of 90%; this would, in turn, reduce the maximum  $T_g$  achievable. The  $T_g$  values obtained for the other PSUs (Table IV) are similar to those achieved for PSUs of similar molecular weights<sup>22,25,28,35–38</sup> and a general trend for these thermoplastics is that  $T_g$  increases with molecular weight of the polymer, due to increased secondary interactions between the polymer chain such as hydrogen bonding and  $\pi$ – $\pi$  stacking of the aromatic rings reducing the mobility of the polymer chain.<sup>39</sup>

When blended (at a loading of 10 wt %) in the benzoxazine monomer based on bisphenol A and aniline (BA-a), the effects of the oligomers ( $M_n = 6000$  g mol<sup>-1</sup>) are shown in Table IV. Modest enhancements in the char yield observed at 800°C ( $Y_{C800}$ ) when compared with the polybenzoxazine of BA-a. The general influence on the thermal stability is to raise the initial temperature of degradation from 222°C to 248–255°C depending on the oligomer, with the polyethersulfone diol (PSU<sub>OH</sub>6000) displaying the greatest effect. The incorporation of the functional oligomers (hydroxyl-terminated) serves to increase the glass transition temperature ( $T_g$ ) of the cured blend from 165 to 175°C and 182°C respectively. The introduction of the less reactive benzoxazinyl-terminated oligomer (PSU<sub>Bz</sub>6000) actually leads to a reduction in the  $T_g$  of the cured blend, as a result of the reduction in crosslink density. The lowest  $T_g$  is observed for the cured blend incorporating PSU<sub>Cl</sub>6000, which is not coreactive with the BA-a, leading to an interpenetrating polymer network (IPN).

The ultimate purpose of investigating different functionalities is to determine whether any interaction or reaction between the benzoxazine and the thermoplastic can be observed and ultimately whether this influences the resin toughness (as has been found for epoxy blends containing similar polymers). It has been proposed that increased interaction between the



thermoplastic and benzoxazine will prevent “pulling out” of the thermoplastic at the crack front, so increasing the force required to progress a crack or diverting the crack front and dissipating its energy that way.<sup>14,15</sup> It is proposed that the hydroxyl terminated thermoplastic may not only potentially improve toughness through hydrogen bonding interaction with the benzoxazine polymer network, but that the acidic protons of the hydroxyl terminated systems could also improve the reactivity of the benzoxazine curing reaction due to the protons initiating the ring opening reaction.

Although the terminal functionalization has the greatest influence on the reactivity of the oligomers (for a given molecular weight), it is noted that the phenyl rings in the oligomer backbones are also potential sites for crosslinking as Chang et al. have identified in their studies of PBZs and polybenzimidazoles,<sup>40</sup> albeit to a lesser degree than the conventional mechanism. Thus, from a consideration of the terminal functional groups the ostensibly nonreactive chloro-terminated oligomer (PSU<sub>Cl</sub>) would ultimately yield predominantly a semi-interpenetrating network<sup>41</sup>; the hydroxyl-terminated oligomer (PSU<sub>OH</sub>) would yield an interpenetrating network yielding both hydrogen bonded species and hydroxyl-mediated ring opening; the full benzoxazine telechelic (PSU<sub>Bz</sub>) would be fully coreactive in a copolymeric network.

PSU<sub>Bz</sub> could also undergo homopolymerization, which results in the exotherm observed in the first heating scan on the DSC in Figure 5, hence two further temperature sweeps were performed to determine the  $T_g$  of the telechelic oligomer alone. When blended with benzoxazine monomers the Bz-terminated oligomer should also react with these benzoxazine groups forming a coreacted network of benzoxazine and PSU. This increased linkage between the polymer networks should improve the toughness the most out of these three systems due to increased interfacial adhesion and stronger physical interactions leading potentially to one crosslinked network as seen in other systems,<sup>21,42</sup> rather than two interacting polymers.

## CONCLUSIONS

The thermoplastics were successfully synthesized with different functionality and molecular weight, they will be blended with the benzoxazines to examine toughness but also the effect they may have on the reactivity of the benzoxazine system, which will be discussed in a future publication. These blended systems will be investigated for thermal and mechanical properties in this work, but due to the difficulty in producing void free resins it was only possible to take the BA-a forward for blending with the synthesized thermoplastics and the following thermal analysis and fracture toughness testing.

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