Synthesis of Bisphenol A-Free Oligomeric Phthalonitrile Resins with Sulfone and Sulfone-Ketone Containing Backbones

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ABSTRACT: Two new oligomeric sulfone and sulfone-ketone containing phthalonitrile (PN) resins with excellent processability have been developed. The PN monomers were prepared from the reaction of an excess amount of bisphenol S with 4-(chlorophenyl)sulfone or 4,4-dichlorobenzophenone in the presence of a base in a solvent mixture (dimethylsulfoxide/toluene), followed by end-capping with 4-nitro-PN in a two-step, one-pot reaction. These PN resins exhibited good viscosities and cure times for molding into various shapes. After being thermally cured to yield crosslinked polymers, these polymers demonstrated superb mechanical properties, thermo-oxidative stability, and maintained good dielectric properties. Published 2016.[†] J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 1639–1646

KEYWORDS: resins; thermal properties; thermosets

INTRODUCTION Polysulfone thermoplastics containing sulfonyl linkages are widely used in high temperature applications due to their high glass transition temperatures (T_g) and outstanding thermal, oxidative, hydrolytic, and mechanical properties. They have several important applications such as membranes in fuel cells and in the manufacture of various composite structures.^{1–5} However, the presence of a T_g limits their full thermal potential for composite structural applications to around 250 °C.

High temperature thermosetting resins, which garner interest due the their high T_{σ} and ease of processing from small molecules, have been recently gaining popularity as replacements for metals in aerospace and marine applications.⁶ Three classes of resins have emerged from this research; cyanate esters,^{7,8} polyimides, and phthalonitriles (PN).^{9,10} Cyanate esters are a class of resins that are easy to process, cure at low temperatures, and can exhibit high T_{g} s, but suffer from long term hydrolytic stability issues and have upper temperature limits around 400 °C.¹¹ Polyimides, on the other hand, are more difficult to process than other resins, although they have a high T_{g} , long-term thermal stability and good mechanical properties. Typically, polyimides absorb a fair amount of water (>5%), which limits their use in some high temperature applications by effecting their structural integrity and mechanical properties.¹² PN resins, however, have excellent processability and the thermoset polymers exhibit outstanding thermal and mechanical properties, low water absorption (<1.5%), low flammability and have the potential to replace many current high temperature resins (e.g., PMR-15)¹³ so long as the cost of the resin is competitive with current technologies.

PN resins can be grouped into two distinct classes. The first generation PN resins, consisting of small crystalline molecules synthesized from the phenolate salts of bisphenols (e.g. 4, 4'biphenol, bisphenol A, bisphenol S, bisphenol A6F, etc.) and 4nitrophthalonitrile, exhibited high melting points (195-230 °C) and were difficult to process effectively.14-19 The second generation PN resins greatly improve upon the processing limitations of the first generation PN by using oligomeric aromatic ether spacers between the terminal PN groups. The PN resins are prepared through a two-step, one-pot nucleophilic displacement reaction between activated or unactivated dihaloaromatic compounds and an appropriate bisphenol, followed by end-capping with 4-nitrophthalonitrile. $^{10,20\mathchar`-23}$ More recently, we have developed an improved synthesis of a sulfonyl-containing PN resin composition by reacting 4-(chlorophenyl) sulfone with an excess of bisphenol A followed by end-capping with 4-nitrophthalonitrile.²³ Although this PN resin had excellent properties, the inclusion of bisphenol A limited the thermal stability to 400 °C. In addition, bisphenol

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FIGURE 1 Structure of PN resin 1 containing sulfonyl linkages.

A is a known endocrine disruptor, which may limit its future usage in some applications.

Due to the excellent physical properties exhibited by the incorporation of sulfonyl linkages into PN resins, we sought to determine what effect replacing bisphenol A with bisphenol S had on the overall properties of the resin and resulting thermosetting polymer (Fig. 1). Additionally, knowing that a polysulfone backbone has a high affinity for self-interaction between the sulfonyl linkages, we also incorporated a ketone linkage to disrupt the symmetry and reduce the interaction between the polar sulfonyl units. The synthesis of these two new resins systems will be reported in this paper along with a comparison of the rheological properties. The effect of structural changes within the PN resin on the processing parameters as well as the thermal, mechanical, and other physical properties will be discussed in detail.

EXPERIMENTAL

All starting materials were of reagent grade and used without further purification. Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min⁻¹ and a nitrogen purge of 50 cm³ min⁻¹ Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min⁻¹ under a nitrogen or air purge of 100 cm³ min⁻¹. Infrared (IR) spectra were recorded on films deposited on NaCl plates using a Nicolet iS50 FTIR spectrometer. Solution NMR was performed on a Brüker ADVANCE 300 spectrometer.

Rheometric measurements from 25 to 400 °C were performed on a TA Instruments AR-2000 Rheometer, in conjunction with an environmental testing chamber for temperature control and torsion fixtures to monitor the response of polymeric samples (50 \times 13 \times 2 mm³) to oscillatory testing. The measurements were made under a nitrogen atmosphere over the temperature range of \sim 25–400 °C. A temperature ramp of 3 °C min⁻¹ was used to determine the storage modulus and damping factor (tan δ) of the material at a frequency of 1 Hz and a strain of 2.5 \times 10⁻² %. Normal force control was used throughout the tests to keep the samples taut. Viscosity measurements were performed at various temperatures using a 25 mm top plate and 40 mm diameter cup shaped bottom plate at a frequency of 1 Hz and a strain of 2.5×10^{-2} %. The rheometric chamber was heated to the desired temperature and the resin placed onto the bottom plate, melted and the gap was set to 100 μ m. The chamber was allowed to equilibrate for 1-4 min depending on the experiment.

Dielectric measurements were performed on precast films using a HP 4291A Network Analyzer sweeping between 1 MHz and 1.8 GHz and calibrated with HP Kit 4291A. Sample thicknesses were 1.0794 mm (**6a**), 1.543 mm (**6b**), and 1.653 mm (**6c**) while a parallel plate (HP 16453A) cell was calibrated to Teflon.

Mass spectrometry data were recorded on a QTRAP 5500 mass spectrometer (AB Sciex, Foster City, CA) under control of the Analyst 1.6.2 software. Polymers were reconstituted in a solution of 0.1% trifluoracetic acid in acetonitrile and infused via a TurboV electrospray ionization source (ESI) at a flow rate of 2 μ L min⁻¹. Liquid connections between the on-board syringe pump and the ionization source were constructed of 100 μ m i.d. fused silica coupled to an in-line filter fitting (M-520, IDEX/Upchurch) as previously described.²⁴ Mass spectra were acquired in positive mode ESI.

Synthesis of the PN Resin 1a

To a 1000 mL, three-necked flask fitted with a thermometer, a Dean-Stark trap with condenser and a nitrogen inlet, were added bisphenol S 2 (30 mol % excess relative to 3a) (50.0 g, 0.200 mol), bis(4-chlorophenyl) sulfone 3a (20.0 g, 0.070 mol), sodium hydroxide (14.4 g, 0.360 mol), potassium carbonate (11.0 g, 0.080 mol), toluene (50 mL), and dimethylsulfoxide (DMSO) (300 mL). Toluene was added to control the refluxing azeotropic removal of water and to control the temperature of the reaction content. The resulting mixture was degassed with nitrogen at ambient temperature and the Dean-Stark trap was filled with toluene. The mixture was refluxed at 150 - 160 °C under a nitrogen atmosphere for 12 h or until no more water was observed being collected in the Dean-Stark trap. The toluene was then slowly distilled off causing the temperature to rise in the reaction vessel, which caused an enhancement of the yield, and high conversion of the intermediate hydroxyl salt 4a. After the mixture was cooled to 50 °C, 4-nitrophthalonitrile 5 (46.2 g, 0.267 mol) was added in one portion and the reaction mixture was heated at 80 $^\circ\!C$ for 6 - 8 h. The mixture was allowed to cool to ambient temperature and poured into a 5% (w/w) aqueous HCl solution resulting in the formation of a solid. The material was broken up and collected using a Bűchner funnel. The solid was washed with 200 mL portions of distilled water mixed with 20% ethanol until a neutral pH was reached. The isolated solid was vacuum dried to yield the 2:1 oligomeric sulfone containing PN composition 1a (88.8 g, 97%) as an off-white amorphous solid, which is a mixture of $\sim 70\%$ n = 1 and $\sim 30\%$ n = 0. ¹H NMR (300) MHz, CDCl₃, δ): 7.93 (m, aromatic-H), 7.85 (m, aromatic-H), 7.70 (d, aromatic-H), 7.24 (d, aromatic-H), 7.16 (s, aromatic-H), 7.10 (m, aromatic-H), 7.01 (d, aromatic-H), 7.01 (s, aromatic-H). IR (NaCl): λ 3059 (s; C=C), 2236 (s; CN), 1596 (w; C=C), 1507 (s; aromatic), 1490 (s; aromatic), 1315 (w, -0-), 1125 (s, SO₂). Calc. For M+ (C₂₈H₁₄N₄O₄S) 502.50

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(n = 0), $(C_{52}H_{30}N_4O_{10}S_3)$ 967.01 (n = 1). Observed ESI-MS m/z ratios for the singly-charged n=0 and n=1 species were 503.0 and 967.9, respectively.

Synthesis of the PN Resin 1b

To a 2000 mL, three-necked flask fitted with a thermometer, a Dean-Stark trap with condenser and a nitrogen inlet, were added bisphenol S 2 (30 mol % excess relative to 3b) (100 g, 0.400 mol), 4, 4'-dichlorobenzophenone **3b** (35.12 g, 0.140 mol), potassium carbonate (115.80 g, 0.839 mol), toluene (200 mL), and DMSO (1000 mL). The nitrogen degassed mixture was refluxed at 150-160 °C under a nitrogen atmosphere for 16 h or until no more water was observed being collected in the Dean-Stark trap. The toluene was then slowly distilled off causing the temperature to rise in the reaction vessel, which resulted in an enhancement of the yield, and high conversion of the intermediate hydroxyl salt 4b. After the mixture was cooled to 50 °C, 4nitrophthalonitrile 5 (91.5 g, 0.529 mol) was added in one portion and the reaction mixture was heated at 80 °C for 6-8 h. The mixture was allowed to cool to ambient temperature and the aqueous workup was performed identical to 1a. The isolated solid was convection dried at 50 °C to yield the 2:1 oligomeric sulfone-ketone containing PN composition 1b (186.6 g, 98%), which is a mixture of \sim 70% *n* = 1 and ~30% n = 0. ¹H NMR (300 MHz, CDCl₃, δ): 8.05 (s, aromatic-H), 8.01 (d, aromatic-H), 7.95 (d, aromatic-H), 7.88 (d, aromatic-H), 7.84 (d, aromatic-H), 7.78 (m, aromatic-H), 7.32 (s, aromatic-H), 7.30 (s, aromatic-H), 7.29 (s, aromatic-H), 7.24 (s, aromatic-H), 7.20 (s, aromatic-H), 7.15 (m, aromatic-H), 7.09 (s, aromatic-H). IR (NaCl): λ 3060 (w; C=C), 2235 (s; CN), 1652 (s, C=0), 1597 (s; C=C), 1508 (s; aromatic), 1492 (s; aromatic), 1315 (w, -0-), 1174 (w, C-0), 1126 (s, SO₂). Calc. For M+ ($C_{28}H_{14}N_4O_4S$) 502.50 (n = 0), $(C_{53}H_{30}N_4O_9S_2)$ 930.96 (*n* = 1). Observed ESI-MS *m*/*z* ratios were for the singly charged n = 0 and n = 1 species were 503.0 and 931.2, respectively.

Preparation of Monomer/m-BAPS Mixtures for DSC Analysis

To the melt of **1a** or **1b** at 200 °C was added 2.7 or 5.0 mol % of bis[4-(3-aminophenoxy)phenyl]sulfone (*m*-BAPS). Once the curing additive had been evenly dispersed by stirring for 2 min, the sample was cooled and used in the DSC studies.

Sample Preparation for Rheometric Measurements

Samples for rheometric measurements were prepared by degassing **1a** or **1b** under vacuum at 200 °C for 4 h in an aluminum mold with cavity dimensions of $50 \times 13 \text{ mm}^2$. *m*-BAPS was added with stirring. The samples were cooled, placed in an oven, and heated to gelation under argon at 200 °C for 16 h (overnight), then heated to 375 °C for 8h (ramped at 3 °C min⁻¹). Selected samples were postcured for an additional 2 h at 415 °C. The cured polymers **6** were removed from the mold and sanded to a thickness of ~2 mm before testing using 220 and 600 grit sandpapers.

Sample Preparation for Dielectric Measurements

Samples for dielectric measurements were prepared by degassing **1a** or **1b** under vacuum at 200 °C for 4 h in a 25 mm round metal pan. *m*-BAPS (2.7 mol %) was added with stirring and the samples were cooled, placed in an oven, and heated to gelation under argon at 200 °C for 16 h (overnight), then heated to 375 °C for 8 h (ramped at 3 °C min⁻¹). The cured polymer 6 were removed from the mold and sanded to a uniform thickness (\sim 1 mm) using 220 and 600 grit sandpapers.

Sample Preparation for Water Uptake and Oxidative Aging Studies

Samples for water uptake studies measured $\sim 20 \times 13 \times 2 \text{ mm}^3$. The previously dried samples were heated in distilled water for 24 h at 100 °C before weighing.

Samples for oxidative aging studies measured ${\sim}50 \times 13 \times 2 \text{ mm}^3$ for all experiments. The samples were placed in a 330 °C muffle furnace under a flow of air and periodically removed and weighed.

RESULTS AND DISCUSSION

The synthesis of the amorphous multiple aromatic ether sulfonvl-linked PN resin **1a** was achieved via a nucleophilic displacement reaction between bisphenol S 2 (30% excess) and bis(4-chlorophenyl) sulfone 3a under basic conditions in dimethylsulfoxide (DMSO) using toluene as an azeotropic solvent to remove the water formed during the reaction (Scheme 1). In this reaction, the chlorine group in compound **3a** is extremely easy to displace due to the highly activating nature of the sulfonyl moiety. We also used a mixed base system of 90 mol % sodium hydroxide to 20 mol % potassium carbonate (K₂CO₃) relative to each reactive hydroxyl group on 2. This first reaction was heated at 150-160 °C for 16 h and contained an excess amount of 2 relative to 3a yields a dimetallic phenolate intermediate 4a, which is composed of a mixture of oligomeric sulfonyl-containing phenolates (n = 1) and bisphenol S diphenolate (n = 0) in an \sim 70:30 ratio. Formation of this intermediate was considered complete when ¹H-NMR spectroscopy confirmed that all of 3a had reacted. However, the synthesis of the sulfonylketone containing PN resin 4b was not as simple. First attempts using the NaOH and K₂CO₃ mixed base system failed. This is presumably due to the chlorine group in compound **3b** being more difficult to displace than the one on **3a**, In addition, the hydrolytic side reactions seen previously in the synthesis of high molecular weight polysulfones appears to be a factor that alters the reaction stoichiometry involving 3b.25 This was determined by the presence of a doublet in the ¹H-NMR around 6.9 ppm, which has been identified as the protons α to the OH group on an aromatic phenol. Upon cooling to below 50 °C, 4-nitrophthalonitrile 5 was slowly added to the dimetallic phenolate intermediate mixture 4 producing the PN 1a and 1b in nearly quantitative yields after heating at 80 °C for 6-8 h, in which there is theoretically around 70% of n = 1 (oligometric PN) and 30% of n = 0 (bisphenol S PN). The PN resin compositions **1a** and







SCHEME 1 Synthesis of PN monomers 1a and 1b and polymers 6.

1b were soluble in common organic solvents such as toluene, acetone, methylene chloride, and DMSO. The structures of resins **1a** and **1b** were confirmed by FTIR, ¹H-NMR, and mass spectroscopy. The mass spectrometry of both resins indicated the composition contained both n = 0 and n = 1with no higher oligomers. The ratio of n = 1 to n = 0 can be readily varied by changing the amount of excess **2** relative to **3** but for the scope of this article, we chose to study the composition containing ~70% of the n = 1 PN resin and 30% of the n = 0 PN resin.

The viscosity of the PN resin compositions 1 at various temperatures is an important factor in determining the processing parameters needed to mold the resin into various shapes. Upon heating 1a to 150 °C, a viscosity of 180,000 cP was observed, which quickly dropped with further heating to 7,000 cP at 175 °C, 800 cP at 200 °C, and 250 cP at 225 °C. As a comparison, we performed viscosity measurements on samples of 1b, which contained a ketone moiety instead of a sulfone moiety in the oligomeric structure. In this case, viscosity values of 7,400, 1,100, 475, and 175 cP were observed at 150, 175, 200, and 225 °C, which is markedly lower than 1a at any temperature. This difference is most likely a result of the ketone group in **1b** being less polar relative to the highly polar, self-interacting sulfone groups in 1a, which apparently is strong enough to act as a physical crosslinking center. These newly synthesized compositions containing an excess of

the n = 0 which significantly alters the viscosity profile by acting as a reactive plasticizer, should also make the thermoset more rigid by increasing the crosslinking density. The viscosity values for both PN resin compositions **1** rival resins such as cyanate ester and polyimides that are currently used in the manufacture of composites by resin transfer molding (RTM) under similar thermal conditions.

Polymerization studies of PN resins 1a and 1b were achieved by DSC analyses up to 400 °C in the presence of either 2.7 or 5.0 wt % of bis(3-[4-aminophenoxy]phenyl)sulfone (m-BAPS) to afford thermoset 6. Since the molecular weights of both resins are very similar, the use of wt % versus mol % of catalyst did not affect the results. Upon melting, 1a had a higher viscosity than 1b which affected the polymerization rate. The PN resin mixture 1a containing 2.7 wt % of *m*-BAPS exhibited two $T_{\rm g}$ s around 100 and 145 °C (Fig. 2), followed by an exothermic transition peaking at 245 °C. The appearance of two $T_{\rm g}$ s transitions are likely due to the two different components (n = 1 and n = 0) contained within the resin. Samples containing 5.0 wt % of m-BAPS showed a two stage $T_{\rm g}$ at around 100 and 135 °C followed by a stronger exothermic transition peaking at 235 °C. The lower viscous PN resin mixture 1b containing 2.7 wt % of m-BAPS, exhibited T_gs around 80 and 138 °C (Fig. 3), followed by a rather broad complex exothermic transition peaking at 235 °C. Similarly, samples of 1b containing 5.0 wt % of *m*-BAPS showed slightly higher $T_{g}s$ at 92 and 145 °C, likely due to some reaction of the curing additive with 1b during mixing, followed by a much stronger but similarly shaped exothermic transition peaking at 235 °C. These results indicate that a higher amount of *m*-BAPS appears necessary to cure 1a at a faster rate than 1b, which could be a result of **1a** having a higher viscosity and less mobility than **1b** at all temperatures.

Rheometric viscosity analysis of resin **1a** and **1b** containing 2.7 and 5.0 wt % of *m*-BAPS was performed at 200 and 225 °C. As with most high temperature thermosetting resins, the PN resin pot-life can be controlled as a function of



FIGURE 2 DSC curves of 1a with 2.7 wt % (top) and 5.0 wt % *m*-BAPS (Bottom).



FIGURE 3 DSC curves of 1b with 2.7 wt % (top) and 5.0 wt % *m*-BAPS (Bottom).

heating time at various temperatures (Figs. 4 and 5). As shown previously, the initiation reaction (early/flat part of curve) and the propagation reaction (part of curve where the viscosity increases exponentially) were clearly visible (Fig. 4).²⁶ Heating above 150 °C initiates a chemical cross-linking reaction resulting in a liquid to rubbery phase change. The intersection of storage (*G'*) and loss (*G''*) moduli, which we take as the gel point, corresponds to ~100,000 cP on the viscosity plots of **1a** and **1b** (Figs. 4 and 5).²³

The time to gelation for 1a and 1b were found to be a function of the curing temperature. Samples 1a and 1b containing 2.7 and 5.0 wt % of m-BAPS reached the gel point at 200 °C after 45 and 25 min and 33 and 25 min, respectively. For example, 1a took longer to gel at the lower concentration (2.7 wt %) of catalyst relative to 1b, which parallels the observed lower intensity of the exotherm in the DSC analysis indicating a slower rate of curing (Figs. 2 and 3). However, at the higher concentration (5.0 wt %), the gel times are the same for **1a** and **1b** but the shape of the exothermic curves are different. For 1a, the initiation step is just a few minutes longer than 1b but they both eventually catch up to one another and gel at around 25 min. At 225 °C, all gel times are significantly shorter for both 1a and 1b. Samples containing 2.7 and 5.0 wt % of m-BAPS, reaching the gel points at 225 °C after around 15 and 7 min for 1a and around 6 and 3.5 min for **1b**, respectively. Again, we observe a longer gel time at both catalyst concentrations for 1a when compared to 1b. This phenomenon can be explained by the higher viscosity of 1a vs. 1b, where the catalyst and resin are less mobile and also due to the strong self-interactions of the sulfone linkages in 1b that inhibits the movement of the resin and curing additive to find neighboring molecules in which to react. As seen in the data for both systems, the resin can be exploited and utilized using various processing conditions and catalyst concentrations to achieve the desired cure times depending on the application. Overall, resins 1a and 1b demonstrate excellent viscosity parameters and reasonable cure times for potential component fabrication.



FIGURE 4 Rheometric viscosity plot at 200 °C with 2.7 wt % of *m*-BAPS; resin **1a** (A) and **1b** (B) and with 5.0 wt % of *m*-BAPS; resin **1a** (C) and **1b** (D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Rectangular shaped samples were prepared for 6a and 6b post-cured at a maximum temperature of 375 °C and analyzed mechanically using a rheometer from 25 to 400 °C. We observed (Fig. 6) that the storage modulus for **6a** cured with either 2.7 (Plot A) or 5.0 (Plot C) wt % of m-BAPS showed a glass transition (T_g) at approximately 325 and 375 °C, respectively. This transition is also observed as a spike in the tan δ values near those temperatures (Fig. 7). The higher amount of *m*-BAPS did result in a higher T_{g} . Unlike **6a**, **6b** showed a gradual decreased in the storage modulus from ambient temperature to 400 °C indicating some flexibility within the thermoset with a rise in the temperature. However, this mobility does not result in complete loss of mechanical stability. When heated from 25 to 400 $^\circ \text{C},$ the storage modulus values for 6b that had been post-cured to 375 °C gradually changed from 1230 to 500 MPa and 1300



FIGURE 5 Rheometric viscosity plot at 225 °C with 2.7 wt % of m-BAPS; resin **1a** (A) and **1b** (B) and with 5.0 wt % of m-BAPS; resin **1a** (C) and **1b** (D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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FIGURE 6 Rheometric analysis of polymers **6** with 2.7 wt % of *m*-BAPS; **6a** (A) and **6b** (B) and with 5.0 wt % of *m*-BAPS; **6a** (C) and **6b** (D) post-cured to 375 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

to 400 MPa for the 2.7 and 5.0 wt % of *m*-BAPS cured samples, respectively. From these data, we can conclude that **6b**, regardless of the amount of curing additive and thermal curing conditions, is more fully cured than **6a** reflecting what was observed during the DSC studies.

Upon postcuring to 415 °C for 2h, the storage modulus values for **6a** gradually changed from 1230 to 500 MPa and 885 to 300 MPa for the 2.7 and 5.0 wt % of *m*-BAPS cured samples, respectively (Fig. 8). Polymer **6b**, however, gradually changed from 1285 to 620 MPa and 1125 to 530 MPa for the 2.7 and 5.0 wt % *m*-BAPS cured samples, respectively. In both samples, the tan δ plots were featureless over the entire temperature range. From this data, we can conclude that post-curing above 400 °C is necessary to achieve



FIGURE 7 Tan δ plot of polymer **6** with 2.7 wt % of *m*-BAPS; **6a** (A) and **6b** (B) and with 5.0 wt % of *m*-BAPS; **6a** (C) and **6b** (D) post-cured to 375 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 8 Rheometric analysis of polymers **6** with 2.7 wt % of *m*-BAPS; **6a** (A) and **6b** (B) and with 5.0 wt % of *m*-BAPS; **6a** (C) and **6b** (D) post-cured to 415 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

a full cure and the absence of a $T_{\rm g}$ for **6a**. However, the increased amount of curing additive (5.0 wt % of *m*-BAPS) affected the mechanical integrity of the thermoset **6a** and **6b**, especially after curing above 400 °C, indicated by the lower storage modulus for both samples.

The thermal and thermo-oxidative properties were investigated between 25 and 1000 °C in a TGA chamber. Figure 9 shows the TGA thermograms for polymers **6a** and **6b** cured to 375 °C with 2.7 mol % of *m*-BAPS. The thermal and oxidative stabilities were determined on powdered samples, which represent a worst case scenario in thermal performance but is the most accurate way to compare the two systems since thermal stability is highly dependent on sample surface area.



FIGURE 9 TGA of polymer **6a** and **6b** with 2.7 wt % of *m*-BAPS; **6a** (A) and **6b** (B) under nitrogen and **6a** (C) and **6b** (D) under air after postcuring to 375 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymers **6a** and **6b** retained 95% weight at 450 and 480 °C and exhibited char yields of 60 and 52%, respectively, when heated under inert conditions. Both polymers showed weight retention in air of 95% at 450 °C, with catastrophic decomposition occurring slowly between 500 and 700 °C. Additional postcuring of **6a** to 415 °C improved the weight retention to 480 °C and the char yield to 58%. This postcuring had little effect on the properties of **6b**. These values are consistent with what is seen for most PN resin systems, which is a significant improvement over traditional thermoplastic polysulfones, which illustrates the unique effects that the PN crosslinking unit has on the thermal and oxidative properties.^{27,28}

To simulate the use of polymer **6** under real environmental conditions, we assessed the effect of long-term heating or aging at high temperatures under air. By subjecting polymers **6a** and **6b** to continuous heating at 329 °C (625 °F), a cumulative weight loss of 10 and 8.5 % and 16 and 18 % was observed for polymers **6a** and **6b**, postcured at 375 °C, for 100 and 150 h, respectively. These values are exceptional considering these are all organic polymeric systems. These weight loss values would be expected to be considerable better for fiber reinforced composites where the resin content is around 30%.

High temperature polymeric materials have potential use in many electronic applications including radomes, which require the polymer to be transparent to microwaves measured by a low dielectric constant (D_k) , low dissipation factor or tan δ ($D_{\rm f}$), and low water absorption.²⁹ The $D_{\rm k}$ values for samples of 6 postcured at 375 °C were measured from 1 MHz to 1.8 GHz and found to be 3.4 with the $D_{\rm f}$ in the range of 0.01. These values are similar to other resins currently being used in the fabrication of radomes and other electrical components.²⁴ They are slightly higher than previously reported PN polymers,^{30,31} which were closer to 3.0 but the presence of the highly polar SO₂ groups in the backbone of **6a** and **6b** could account for the higher D_k values. Additionally, samples of thermosets 6 were heated in distilled water at 100 °C for 24 h, dried, and weighed. The maximum amount of water absorption for polymers 6a and 6b over that time was around 4.8 and 3.9% by weight, respectively. The water absorption for these systems is higher than other PN polymers, which are closer to 1 to 2% by weight, but is not surprising due to the presence of many polar groups in the backbone. In a composite, the overall water absorption would be far less.

CONCLUSIONS

The synthesis of two PN resins compositions **1a** and **1b** containing sulfone and sulfone-ketone groups in the backbone has been achieved in high yield by reaction of 4-(chlorophenyl) sulfone **3a** or 4, 4'-dichorobenzophene **3b** with an excess of bisphenol S **2**. The excess bisphenol S creates resins in which there is approximately 30 mol % of a bisphenol S PN resin, which acts as a reactive plasticizer and lowers the overall viscosity of the two resin systems. Both PN resins **1a** and **1b** exhibit excellent viscosity parameters under processing conditions that rivals current technologies with resin **1b** showing the lower viscosity of the two systems at any given temperature. The thermal, oxidative, and mechanical properties of polymers **6** can be controlled as a function of the curing additive concentration and the post-curing conditions. Although, the substitution of bisphenol A with bisphenol S in these resin systems has a detrimental effect on most of the physical properties of the reported resins and polymers, these systems exhibit properties that are still far superior than current resin systems and the benefit of removing bisphenol A can outweigh the slight reduction in performance.

When the PN resins 1a and 1b are fully cured, polymers 6 displays many important attributes including the absence of a T_{g} when fully cured, which translates to minimal loss of structural integrity at elevated temperatures. Additionally, 6 displays excellent thermo-oxidative properties, low dielectric constants and relatively low water absorption. One aspect of all oligomeric PN resins including 1a and 1b is that B-staged prepolymers exhibit indefinite shelf-life under ambient conditions but flow above 150 °C and cure above 200 °C, which enhances its importance in the fabrication of composite components by emerging cost effective manufacturing methods such as RTM, resin infusion molding (RIM), filament winding, etc. Due to their physical properties, polymers 6 have the potential to be used in structural components for ships, missiles, aircraft, high temperature tooling, and many other military and domestic applications where the properties exhibited by the PN polymers are essential.

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