

## High-Performance Thermosetting Films Based on an Amino-Functionalized Poly(ether sulfone)

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**ABSTRACT:** We have developed a sequence-dependent synthesis of the amino-functionalized poly(ether sulfone) **P2**. The amino groups of **P2** act as reactive sites toward epoxy resins. After curing **P2** with diglycidyl ether of bisphenol A (DGEBA) and cresol novolac epoxy (CNE), we obtained the flexible, light-yellow, transparent, epoxy thermosetting films **P2/DGEBA**, and **P2/CNE**, respectively, having glass transition temperatures ( $T_g$ ) of 258 and 274°C, respectively. In addition, we also prepared a flexible film after condensation of the amino groups of **P2** with the anhydride groups of 4,4'-oxydiphthalic anhydride (ODPA); after imidization at 300°C for 1 h, the resulting **P2/ODPA** thermosetting film possessed a value of  $T_g$  of 340°C. These three thermosetting films also exhibited flame retardancy with a UL-94 VTM-0 grade. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40980.

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### INTRODUCTION

Poly(ether sulfone)s (PESs) possess high glass transition temperatures ( $T_g$ ), exhibit resistance toward acids, bases, and oxidants, and display high impact strength; accordingly, they can be considered as high-performance thermoplastics.<sup>1–3</sup> Modification of PESs further broadens their applications in fuel cells and ultrafiltration membranes (or separation technology) and increases their antibiofouling performance.<sup>4–16</sup> Such modification can be achieved through copolymerization with a monomer possessing appropriate functional groups<sup>17–23</sup> or through postfunctionalization using, for example, phosphonation,<sup>24</sup> amidoalkylation,<sup>25</sup> bromination,<sup>22,26,27</sup> vinylation,<sup>28–30</sup> sulfonation,<sup>31–35</sup> borylation,<sup>36–38</sup> and click chemistry.<sup>39</sup> To the best of our knowledge, however, amino-functionalized PESs have rarely been reported. Abate et al. prepared an amino-terminated PES by end-capping a corresponding chloro-terminated PES with *m*-aminophenol,<sup>40</sup> but thermosets based on this amino-terminated PES and epoxy generally exhibited low crosslinking densities because of their high active hydrogen equivalent weight (AHEW). Klapper and coworkers<sup>41</sup> prepared amino-functionalized poly(arylene ether ketone)s through nucleophilic substitution of bisphenol A with 2-amino-1,4-bis(4-fluorobenzoyl)benzene or 5-amino-1,3-bis(4-fluorobenzoyl)benzene in the presence of  $K_2CO_3$ , revealing that such amino linkages are stable under such reaction

conditions. Recently Zhu and coworkers<sup>42</sup> prepared an amino-functionalized PES through polymerization of bis(3-amino-4-hydroxyphenyl)sulfone, 4,4'-sulfonyldiphenol, and 4,4'-difluorodiphenylsulfone (DFDPS) in the presence of  $K_2CO_3$ .

Recently, we reported a phenol-functionalized poly(aryl ether)<sup>43</sup> and a poly(aryl sulfone)<sup>44</sup> and their application in the preparation of high-performance epoxy thermosetting films. Continuing our quest for high-performance thermosets, in this study we examined two strategies for the preparation of the phosphinated PES **P2** presenting an amino group in each repeating unit. The first, unsuccessful, approach involved postfunctionalization of DHBP-PES, a PES prepared from 4,4'-dihydroxybenzophenone (DHBP) and DFDPS. The second, successful, approach involved polymerization of DFDPS with an amino-functionalized bisphenol (DOPO-diphenolaniline), the preparation of which we have reported previously.<sup>45</sup> The amino linkages of **P2** behaved as reactive sites toward epoxy resins; in other words, **P2** served as an epoxy curing agent. Indeed, we could use **P2** to prepare homogeneous, light-yellow epoxy thermosetting films exhibiting high values of  $T_g$  and flexibility. In addition, we also prepared a high-performance poly(sulfone imide) thermosetting film through the reaction of **P2** with 4,4'-oxydiphthalic anhydride (ODPA). After thermal imidization, the resulting poly(sulfone imide) thermosetting film (**P2/ODPA**) displayed a high value of  $T_g$  and low thermal expansion. Herein, we describe the

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**Table I.** Thermal Properties of P<sub>2</sub> and Resulting Epoxy Thermosetting Films

Sample	T <sub>g</sub> (°C) (DSC) <sup>a</sup>	T <sub>g</sub> (°C) (DMA) <sup>b</sup>	T <sub>g</sub> (°C) (TMA) <sup>c</sup>	CTE (ppm/°C) <sup>d</sup>	T <sub>d5%</sub> <sup>e</sup>	CY <sup>f</sup>
DHBP-PES	204	-	-	-	500	40
<b>P2</b>	238	-	-	-	418	50
<b>P2/DGEBA</b>	244 (224) <sup>g</sup>	258 (238) <sup>g</sup>	234 (227) <sup>g</sup>	50	373	37
<b>P2/CNE</b>	254 (236) <sup>g</sup>	274 (247) <sup>g</sup>	255 (241) <sup>g</sup>	48	383	46
<b>P2/OPDA</b>	315	340	324	33	419	57

<sup>a</sup> Measured by DSC at a heating rate of 10°C/min.<sup>b</sup> Measured by DMA at a heating rate of 5°C/min.<sup>c</sup> Measured by TMA at a heating rate of 5°C/min.<sup>d</sup> Coefficient of thermal expansion, recorded from 50 to 150°C.<sup>e</sup> 5% Decomposition temperature (°C) under a N<sub>2</sub> atmosphere.<sup>f</sup> Char yield, residual weight percentage at 800°C under a N<sub>2</sub> atmosphere.<sup>g</sup> Data in parentheses are those of thermosets based on a phenol-functionalized poly(ether sulfone) and an epoxy, as reported in Ref. 44.

polymerization in detail and provide the structure–property relationships of the resulting thermosetting films.

## EXPERIMENTAL

### Materials

DHBP (Showa), DFDPS (Acros), K<sub>2</sub>CO<sub>3</sub> (Acros), phenol (TCI), 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO; TCI), *p*-toluenesulfonic acid monohydrate (*p*-TSA; Showa), ODPDA (TCI), and H<sub>2</sub>SO<sub>4</sub> (Acros) were used as received. Diglycidyl ether of bisphenol A (DGEBA; epoxy equivalent weight [EEW]: 187 g/eq) and cresol novolac epoxy (CNE; EEW: 200 g/eq) were kindly supplied by Chang Chun Plastics (Taiwan). *N*-Methylpyrrolidone (NMP; TEDIA) was purified by distillation under reduced pressure over CaH<sub>2</sub> (Acros) and stored over molecular sieves. The other solvents were commercial products (HPLC grade) used without further purification.

### Characterization

Nuclear magnetic resonance (NMR) spectra were recorded for samples in DMSO-*d*<sub>6</sub> using a Varian Inova 600 NMR spectrometer; the signals were calibrated by setting the chemical shift of DMSO-*d*<sub>6</sub> as 2.49 ppm. Differential scanning calorimetry (DSC) was performed using a PerkinElmer DSC 7 instrument, under a N<sub>2</sub> atmosphere and at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed using a PerkinElmer Pyris1 apparatus operated at a heating rate of 20°C/min under a N<sub>2</sub> atmosphere. Dynamic mechanical analysis (DMA) was performed using a PerkinElmer Pyris Diamond DMA instrument with a sample size of 5.0 cm × 1.0 cm × 0.2 cm. The storage modulus (*E'*) and tan  $\delta$  were determined from samples subjected to the temperature scan mode at a programmed heating rate of 5°C/min and a frequency of 1 Hz. These tests were performed using a tension mode with an amplitude of 5  $\mu$ m. Thermomechanical analysis (TMA) was performed using a SII TMA/SS6100 instrument operated at a heating rate of 5°C/min. The coefficient of thermal expansion (CTE) was recorded at temperatures within the range from 50 to 150°C. Infrared spectra were recorded using a Nicolet Avatar 320 FTIR spectrophotometer; 32 scans were collected with a spectral resolution of 1 cm<sup>-1</sup>. Gel permeation chromatography (GPC) was performed at 60°C using a PerkinElmer series 200a apparatus, with *N,N*-dimethylformamide as the eluent at a flow rate of 1.0 mL/min; data

were calibrated with polystyrene standards. The flame retardancy of the thermosetting films was measured using a UL-94VTM vertical thin film test. In each test, an 8 in. × 2 in. sample was wrapped around a 1/2 in. mandrel, and then taped on one end; the mandrel was removed, leaving a cone-shaped sample that was relatively rigid. The two flame applications lasted for 3 s for the UL-94 VTM vertical thin film. After the first ignition, the flame was removed and the time for the polymer to self-extinguish (*t*<sub>1</sub>) was recorded. Cotton ignition was noted if polymer dripping occurred during the test. After cooling, the second ignition was performed on the same sample and the self-extinguishing time (*t*<sub>2</sub>) and dripping characteristics were recorded. If the sum of *t*<sub>1</sub> and *t*<sub>2</sub> was less than 10 s without any dripping, the polymer was considered to be a VTM-0 material. If the sum of *t*<sub>1</sub> and *t*<sub>2</sub> was in the range 10–30 s without any dripping, the polymer was considered to be a VTM-1 material.

### DHBP-PES

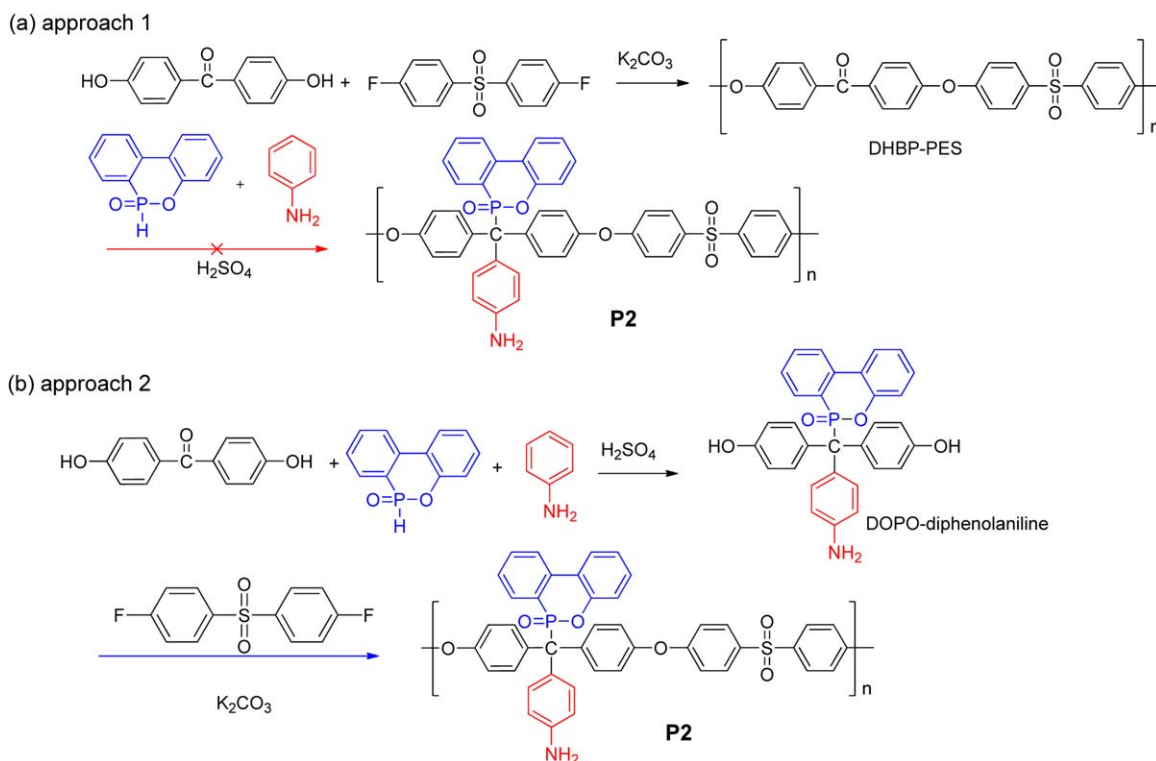
DHBP (6.00 g, 28.0 mmol), DFDPS (7.12 g, 28.0 mmol), K<sub>2</sub>CO<sub>3</sub> (8.13 g, 58.8 mmol), NMP (52 mL), and xylene (10 mL) were placed in a 100-mL round-bottomed glass flask equipped with a N<sub>2</sub> inlet, a magnetic stirrer, and a Dean–Stark trap. The reaction mixture was stirred at 130°C for 12 h and then the xylene was distilled off and the reaction mixture poured into MeOH. The light-yellow precipitate (94% yield) was filtered off and dried in a vacuum oven at 100°C for 8 h.

### P2 Through Approach 1

DHBP-PES (1.000 g, 2.183 mmol of repeating units), DOPO (0.472 g, 2.183 mmol), aniline (2.030 g, 21.83 mmol), and H<sub>2</sub>SO<sub>4</sub> (0.0188 g, 4 wt % relative to DOPO) were placed in a 100-mL round-bottomed glass flask equipped with a N<sub>2</sub> inlet, a magnetic stirrer, and a condenser. The reaction mixture was stirred at 140°C for 24 h and then it was poured into MeOH. The light-orange precipitate was filtered off and dried in a vacuum oven at 100°C for 8 h. The other reaction conditions for the synthesis of P2 are listed in Table I.

### P2 Through Approach 2

DOPO-diphenolaniline (10.00 g, 19.78 mmol), DFDPS (5.030 g, 19.78 mmol), DMAc (75 g), and K<sub>2</sub>CO<sub>3</sub> (5.732 g, 41.54 mmol) were placed in a 250-mL round-bottomed glass flask equipped with a N<sub>2</sub> inlet, a magnetic stirrer, and a condenser. The



**Scheme 1.** Synthesis of **P2**. The reactants in each approach were the same, but the reaction sequence was switched. Approach 2 was successful, but approach 1 was not. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

reaction mixture was stirred at 130°C for 12 h and then it was poured into MeOH. The light-red precipitate (92% yield) was filtered off and dried in a vacuum oven at 100°C for 8 h.

#### P2-Cured Epoxy Thermosetting Films

**P2** was cured with DGEBA and CNE, two commercially available epoxy resins, at an equivalent ratio of amine to oxirane of 1 : 1; the corresponding thermosetting films are named herein as **P2/DGEBA** and **P2/CNE**, respectively. **P2** (1.9122 g) and DGEBA (0.50 g) (or **P2** [1.7975 g] and CNE [0.50 g]) were dissolved in DMAc to give a solution with a 30 wt % solid content. The viscous solution was cast onto glass using an automatic film applicator. The resulting thin film was dried at 60°C for 12 h and then cured at 150°C (1 h), 180°C (1 h), 200°C (1 h), and 220°C (1 h).

#### Poly(sulfone imide) Thermosetting Film (P2/OPDA)

A solution of ODPA (0.215 g, 0.693 mmol) in NMP (2 mL) was added to a solution of **P2** (0.50 g, 0.693 mmol of repeating units) in NMP (3 mL). The viscosity of the resulting solution increased rapidly; to avoid gelation, it was quickly cast onto glass using an automatic film applicator. The resulting thin film was dried at 60°C for 12 h and then cured at 100°C (1 h), 200°C (1 h), 260°C (1 h), and 300°C (1 h).

## RESULTS AND DISCUSSION

### Synthesis of P2

We tested two approaches for the synthesis of **P2** (Scheme 1). In approach 1, we prepared a poly(ether sulfone), poly(oxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene-sulfonyl-1,4-

phenylene (DHBP-PES), through nucleophilic substitution of DHBP and DFDPS. We then prepared **P2** through the reaction of DHBP-PES, DOPO, and aniline in the presence of H<sub>2</sub>SO<sub>4</sub>. Supporting Information Table S1 lists the various reaction conditions that we tested for the synthesis of **P2** through approach 1; <sup>1</sup>H-NMR spectra (not shown) did not feature an amino signal and displayed the incorrect ArH patterns after each of these tested reaction conditions. In other words, this postfunctionalization approach was unsuccessful.

In approach 2, we first prepared an intermediate, DOPO-diphenolaniline, through the reaction of DOPO, DHBP, and aniline in the presence of H<sub>2</sub>SO<sub>4</sub>, according to our previously reported procedure.<sup>45</sup> We then reacted DOPO-diphenolaniline with DFDPS in the presence of K<sub>2</sub>CO<sub>3</sub>. Figure 1 presents the <sup>1</sup>H-NMR spectra of DOPO-diphenolaniline and **P2**. In the spectrum of **P2**, the signal for the phenol protons of DOPO-diphenolaniline (9.4 ppm) had disappeared completely, while the signal for the amino protons (5.1 ppm) remained, revealing the stability of the amino groups in the K<sub>2</sub>CO<sub>3</sub>-catalyzed nucleophilic substitution. The assignment of the aromatic protons through <sup>1</sup>H-<sup>1</sup>H COSY (Supporting Information Figure S1) supported the proposed structure of **P2**. The <sup>13</sup>C-NMR spectrum of **P2** (Supporting Information Figure S2) features splitting of the C<sup>5</sup> peak at 64 ppm, due to <sup>1</sup>J<sub>P-C</sub> coupling with a coupling constant of 92 Hz; the signal for C<sup>10</sup> exhibited a similar effect. The assignment of the signals for the aromatic carbon nuclei, assisted by <sup>1</sup>H-<sup>13</sup>C HETERCOR spectroscopy (Supporting Information Figure S3), further supported the proposed structure of **P2**.

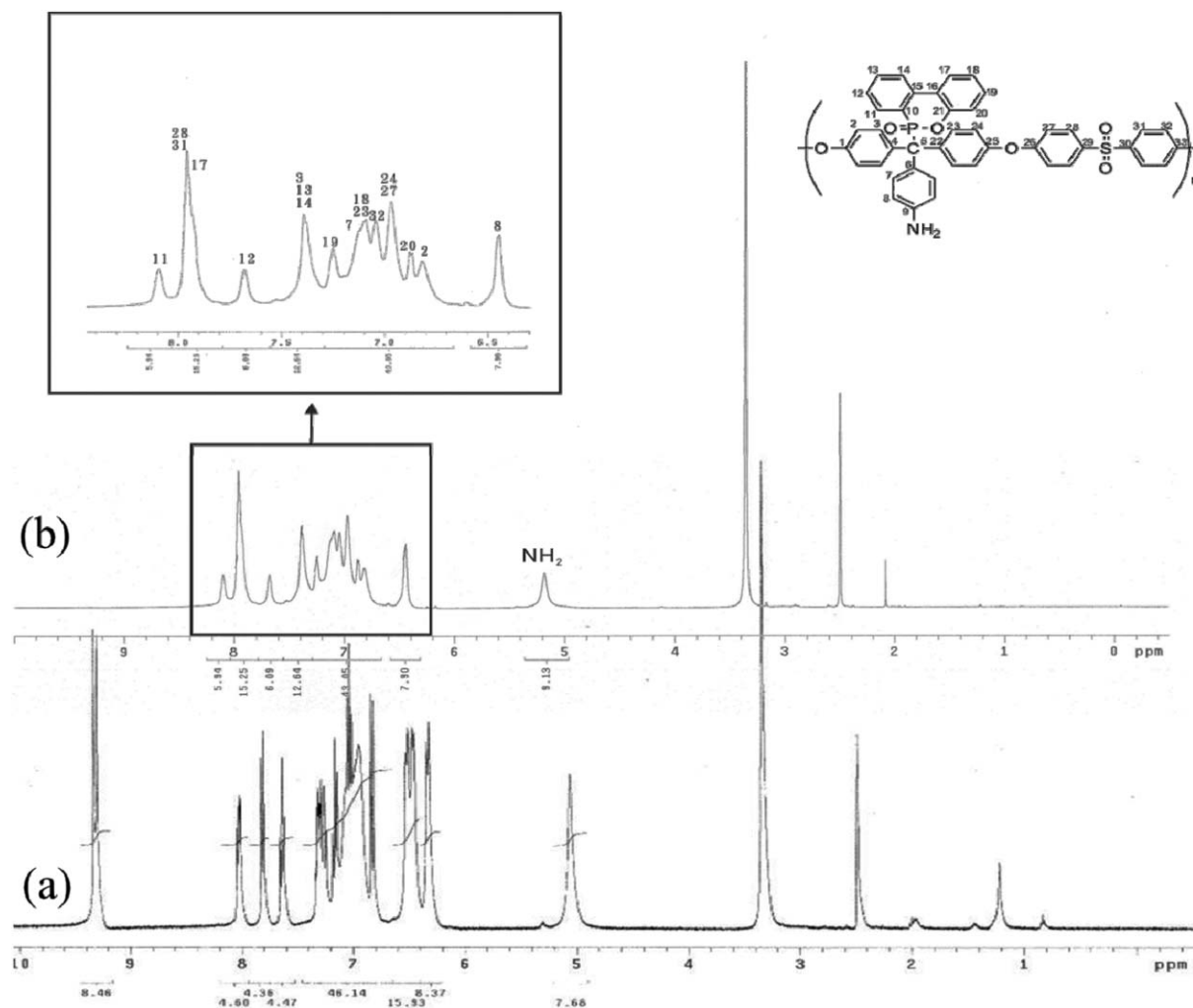


Figure 1.  $^1\text{H}$ -NMR spectra of (a) DOPO-diphenolaniline and (b) **P2**.

The synthesis of DOPO-diphenolaniline involved (i) nucleophilic addition of DOPO on the  $\text{C}=\text{O}$  group of DHBP, forming an intermediate possessing a tertiary OH group; (ii) protonation of the tertiary OH group by strong acid and subsequent dissociation of  $\text{H}_2\text{O}$  to yield a tertiary carbocation, stabilized through resonance with the electron-rich phenol group; and (iii) electrophilic substitution of aniline on the resulting carbocation. Therefore, we speculate that the electron donating ability of the phenoxy unit in DHBP-PES was not as strong as that of the phenol group in DHBP; as a result, the carbocation in approach 1 was not as stable as that in approach 2 and, therefore, the postfunctionalization of DHBP-PES was unsuccessful.

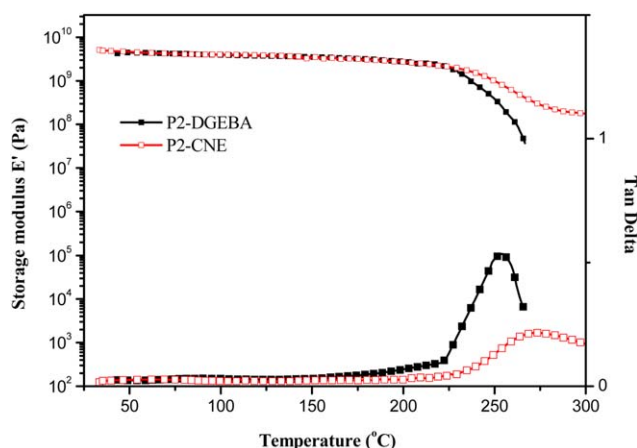
#### Thermal Properties of **P2**

DSC thermograms revealed that the glass transition temperatures of DHEP-PES and **P2** were 204 and 238°C, respectively. We presume that the bulky phosphinate pendent units, which hindered the rotation of the polymer chains, were responsible for the increased value of  $T_g$  for **P2**. In addition, the amino groups of **P2**, which presumably experienced polar interactions with the sulfonyl groups, might also have restricted molecular

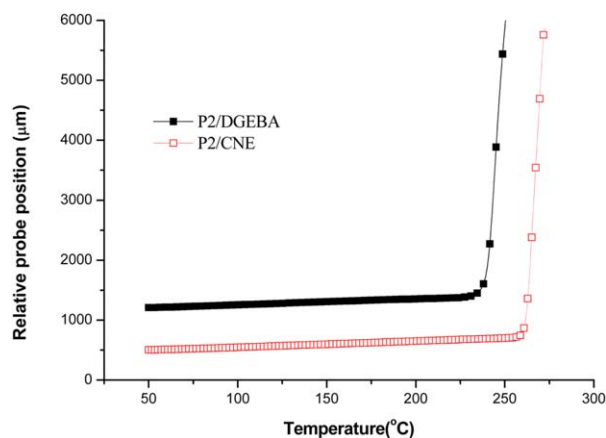
chain relaxation,<sup>46</sup> further enhancing the value of  $T_g$  of **P2**. The 5 wt % degradation temperature under a  $\text{N}_2$  atmosphere decreased from 500°C for DHEP-PES to 418°C for **P2**, but the char yield at 800°C increased from 40 to 50 wt % (Table I). Although the degradation temperature decreased after modification, the value of 418°C for **P2** is high relative to those of other phosphorus-containing polymers.

#### Thermal Properties of Epoxy Thermosetting Film

The high values of  $T_g$  (238°C by DSC) and  $T_d$  (418°C) make **P2** attractive for use as a high-performance epoxy curing agent for DGEBA and CNE. Supporting Information Scheme S1 presents the proposed structure of **P2**/CNE, in which the amino units of **P2** acted as curing sites for epoxy resins. Because **P2** and CNE are both multifunctional aromatic compounds, we supposed that they would form high-performance epoxy thermosets. DMA provided values of  $T_g$  for **P2**/DGEBA and **P2**/CNE of 258 and 274°C, respectively (Figure 2); TMA suggested values of  $T_g$  of 234 and 255°C, respectively, with coefficients of thermal expansion of 50 and 48 ppm/°C, respectively (Figure 3). The advantage of using **P2** as an epoxy curing agent is evident when comparing the values of  $T_g$  of the **P2**-cured epoxy



**Figure 2.** DMA thermograms of P2/DGEBA and P2/CNE. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** TMA thermograms of P2/DGEBA and P2/CNE. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** Photographs of (left) P2/DGEBA and (right) P2/CNE. Dimensions of the films: about 6 cm × 0.8 cm × 30 μm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

thermosets with those of the DOPO-diphenolamine-cured epoxy thermosets: 187 and 208°C (TMA) for DOPO-diphenolamine/DGEBA and DOPO-diphenolamine/CNE, respectively.<sup>45</sup> These values are 40–50°C lower than those of the P2-cured epoxy thermosets. Thus, our data suggest high- $T_g$  characteristics when using P2 as an epoxy curing agent. The 5 wt % degradation temperatures of P2/DGEBA and P2/CNE were 373 and 383°C, respectively (Table I); the corresponding char yields were 37 and 46 wt %, respectively. The thermal stabilities of the P2-

cured epoxy thermosetting films were high relative to those of other phosphorus-containing polymers, meeting the requirement of long-term stability at 288°C for application in printed circuit boards. In addition, the high char yields implied good flame retardancy of P2-cured epoxy thermosetting films (see below).

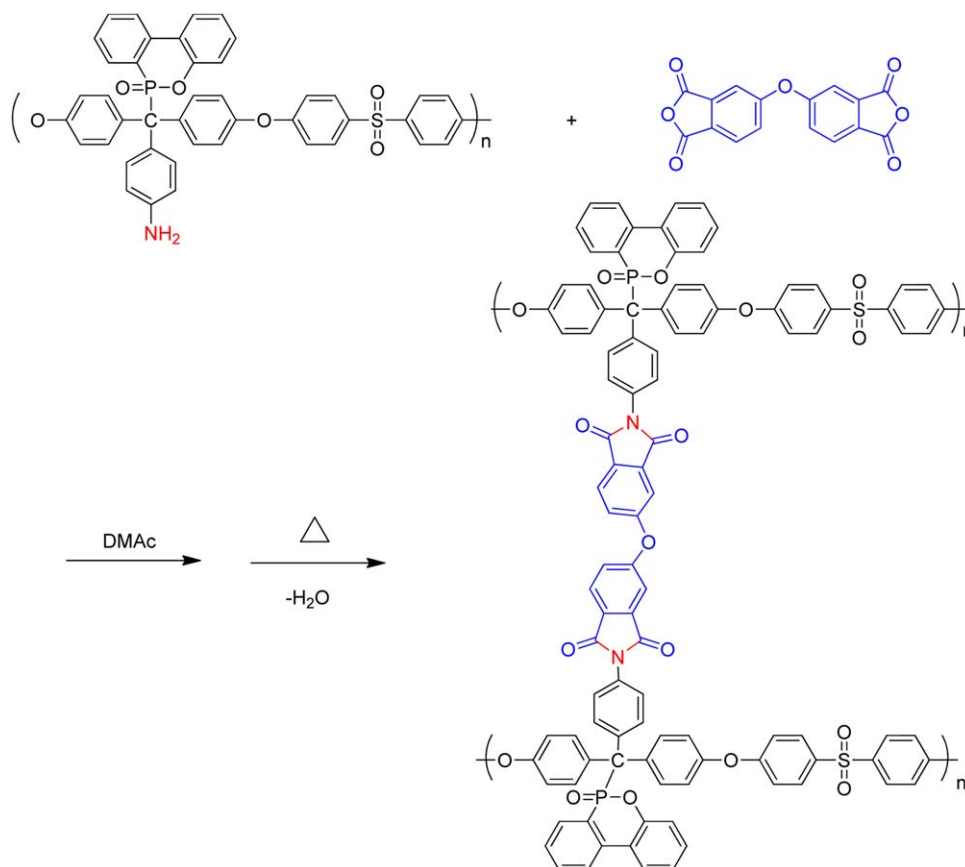
#### Quality of Cured Epoxy Thermosetting Films

GPC revealed that P2 possessed a moderate molecular weight (number-average molecular weight: 6500 g/mol; weight-average molecular weight: 14,300 g/mol). Therefore, we expected P2 to function as a curing and toughness agent for epoxy resins. Figure 4 displays photographs of the P2/DGEBA and P2/CNE thermosetting films, which were bendable, yellow, transparent films—that is, they displayed flexibility even though P2 itself was brittle. The properties of these films reveal the power of crosslinking. In addition, in contrast to the flexibility of the P2/DGEBA and P2/CNE films, the DOPO-diphenolamine-cured epoxy thermosets were brittle.<sup>45</sup> Combining the high- $T_g$  characteristics and flexibility, the thermosetting films prepared from P2 have promising potential applications.

**Table II.** UL-94VTM Data of the Thermosetting Films

Sample	First burning time (s) <sup>a</sup>	Second burning time (s) <sup>a</sup>	Dripping	UL-94 VTM grade
P2/DGEBA	2.3	3.7	No	VTM-0
P2/CNE	2.1	2.8	No	VTM-0
P2/ODPA	2.2	2.1	No	VTM-0

<sup>a</sup> Average burning time from five tests.



**Scheme 2.** Structure of the **P2**/ODPA thermosetting film. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

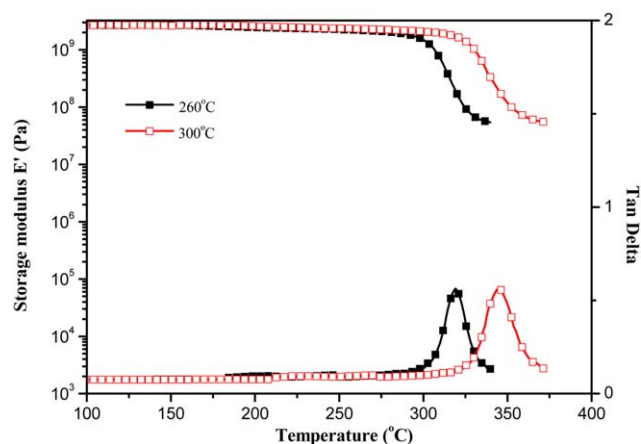
### Flame-Retardancy of Cured Epoxy Thermosetting Films

We applied a UL-94VTM vertical thin film test to measure the flame retardancy of the **P2**-cured epoxy thermosetting films. The total burning time, the sum of  $t_1$  and  $t_2$ , was less than 6 s for both of our **P2**-cured epoxy thermosetting films, making them of VTM-0 grade (Table II). We supposed that the presence of phosphorus atoms, which provide powerful flame-retardancy

in condensed phases and in the gas phase,<sup>47–50</sup> was responsible for the flame-retardant characteristic of the resulting epoxy thermosetting films derived from **P2**.

### Thermal Properties of Poly(ether imide sulfone) Thermosetting Film (**P2**/ODPA)

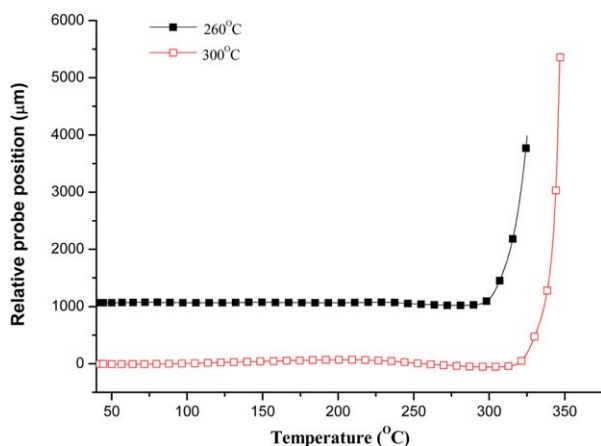
We obtained flexible films after condensation of the amino groups of **P2** with the anhydride groups of ODPA (Scheme 2). IR spectra featured the gradual appearance of signals for the imide units ( $1731$  and  $1785\text{ cm}^{-1}$ ) at temperatures higher than  $200^\circ\text{C}$ . DMA thermograms (Figure 5) revealed that the value of  $T_g$  of **P2**/ODPA imidized at  $300^\circ\text{C}$  (1 h) was higher than that of the sample imidized at  $260^\circ\text{C}$  (1 h), suggesting a greater degree of imidization at  $300^\circ\text{C}$ . The corresponding values of  $T_g$  reached as high as  $340^\circ\text{C}$ . TMA thermograms (Figure 6) revealed similar phenomena: the value of  $T_g$  after imidization at  $300^\circ\text{C}$  (1 h) was  $324^\circ\text{C}$ , with a coefficient of thermal expansion of  $33\text{ ppm}/^\circ\text{C}$ ; the 5 wt % degradation temperature was  $419^\circ\text{C}$  and the corresponding char yield was 57 wt % (Table I). Again, these good thermal properties confirm the power of crosslinking. In addition, Table II reveals that the total burning time, the sum of  $t_1$  and  $t_2$ , for **P2**/ODPA was less than 5 s, making it of VTM-0 grade.



**Figure 5.** DMA thermograms of **P2**/ODPA. Temperature marked on the figure is the final imidization temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### CONCLUSION

We have synthesized **P2**, an amino-functionalized phosphinated PES. Although this study is an extension of a previous



**Figure 6.** TMA thermograms of P2/ODPA. Temperature marked on the figure is the final imidization temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

examination,<sup>44</sup> we have observed some special characteristics for P2. First, the synthesis of this amino-functionalized poly(ether sulfone) is sequence-dependent—a new finding. Second, epoxy thermosets based on the amino-functionalized PES P2 possess better thermal properties than those based on phenol-functionalized PESs. Indeed, we obtained flexible and transparent epoxy thermosetting films with enhanced thermal properties. TMA revealed that P2/DGEBA and P2/CNE possessed high values of  $T_g$  (234 and 255°C, respectively) and moderate-to-low CTEs (50 and 48 ppm/°C, respectively). Third, using ODPA to crosslink the amino-functionalized PES P2 yielded flexible poly(sulfone imide) thermosetting films with values of  $T_g$  as high as 340°C and corresponding CTEs as low as 33 ppm/°C. To the best of our knowledge, thermosetting films possessing high values of  $T_g$  and flexibility are rare in the literature. Accordingly, our thermosetting films have potential applications in polymer membranes requiring high values of  $T_g$  and dimensional stability.

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