Soluble High- T_g Polyetherimides with Good Flame Retardancy Based on an Asymmetric Phosphinated Etherdiamine

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ABSTRACT: This study focuses on preparing soluble, high- T_g polyetherimides (PEIs) with good flame retardancy. To achieve this goal, a phosphinated aminophenol, 1-(4-hydroxyphenyl)-1-(4-aminophenyl)-1-(6-oxido-6H-dibenz $\langle c, e \rangle \langle 1, 2 \rangle$ oxaphosphorin-6-yl)ethane (1), was prepared. Then, an asymmetric etherdiamine, 1-(4-(4-aminophenoxy)phenyl)-1-(4-aminophenyl)-1-(6-oxido-6H-dibenz $\langle c, e \rangle \langle 1, 2 \rangle$ oxaphosphorin-6-yl)ethane (3), was prepared from the nucleophilic substitution of (1) with 4-chloronitrobenzene, followed by catalytic hydrogenation. Light colored, tough, and foldable PEIs (5) with good thermal stability, organo-solubility, and good flame retardancy were synthe-

sized from the condensation of (3) with various aromatic dianhydrides in *N*,*N*-dimethylacetamide, followed by thermal imidization. Properties of the resulting PEIs were evaluated and compared with those of symmetric PEIs (5') and polyimides (5"). The structure-property relationships were discussed. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1331–1340, 2011

KEYWORDS: asymmetric; phosphinate; polyimides; solubility; structure-property relationship

INTRODUCTION Polyimides (PIs) are useful high-performance electronic materials because of their high glass transition temperature, high thermal stability, and good mechanical properties.^{1–8} However, PIs are difficult to process due to their poor solubility in organic solvents. It has been reported that incorporating bulky pendants^{9–13} and flexible ether linkages^{14–16} can impart good solubility.

It has also been reported that phosphorus-functionalized polymers, whether in the phosphine oxide form,¹⁷⁻²¹ in the phosphonate^{22,23} or in the phosphinate form,²⁴⁻³³ can improve organo-solubility, adhesion to metal, flame retardancy, and atomic oxygen resistance.

In our previous work, we developed polyetherimides (PEIs) based on a dietheramine, 1,1-bis(4-(4-aminophenoxy)phenyl)-1-(6-oxido-6H-dibenz $\langle c, e \rangle \langle 1, 2 \rangle$ oxaphosphorin-6-yl)ethane.³⁴ Although the organo-solubility of the resulting PEIs was improved, their solvents were limited to high-boiling-point ones. Studies have shown that incorporating asymmetric structure into polymer chains can impart better organo-solubility because of the disturbed sequence distribution.^{35–40} Herein, continuing our work in organo-soluble phosphinated PIs, an asymmetric etherdiamine, 1-(4-(4-aminophenoxy)phenyl)-1-(4-aminophenyl)-1-(6-oxido-6H-dibenz $\langle c, e \rangle \langle 1, 2 \rangle$ oxaphosphorin-6-yl)ethane (3), was prepared from the nucleophilic substitution of a new phosphinated aminophenol, 1-(4-hydroxyphenyl)-1-(4-aminophenyl)-1-(6-oxido-6H-dibenz $\langle c, e \rangle \langle 1, 2 \rangle$ oxaphosphorin-6-yl)ethane (1), with 4-chloronitrobenzene, followed by

catalytic hydrogenation. Based on diamines (3), a series of PEIs (5) were prepared. The solubility, crystallinity, glass transition, dimensional stability, and thermal stability of the PEIs were investigated and compared with those of symmetric PEIs $(5')^{34}$ and PIs $(5'')^{41}$ (Fig. 1). As shown in Figure 1, PEIs (5') contain two phenoxy linkages, PEIs (5) contain one phenoxy linkage, but PI (5'') does not contain any phenoxy linkage.

EXPERIMENTAL

Materials

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, from TCI), 4-hydroxyacetophenone (from Acros), aniline (from Acros), p-toluenesulfonic acid monohydrate (p-TSA, from SHOWA), potassium carbonate, 10% palladium on carbon (Pd/C, from Acros), 4-chloronitrobenzene (from Acros), and calcium hydride (from Acros) were used as received. Pyromellitic dianhydride (PMDA, from Acros) was dried at 170 °C overnight before use. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA, from Acros), 4,4'-oxydiphthalic anhydride (ODPA, from Chriskev), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, from Chriskev) were recrystallized from acetic anhydride. N,N-Dimethylacetamide (DMAc, from TEDIA) was purified by distillation under reduced pressure over calcium hydride (from Acros) and stored over molecular sieves. The other solvents used are commercial products (HPLC grade) and were used without any further purification.

Additional Supporting Information may be found in the online version of this article. Correspondence to: C. H. Lin (E-mail: linch@nchu.edu.tw) Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 49, 1331–1340 (2011) © 2011 Wiley Periodicals, Inc.



FIGURE 1 Structures of PEIs (5), PEIs (5'),³⁴ and PIs (5").⁴¹

Characterization

NMR measurements were performed using a Varian Inova 600 NMR in DMSO- d_6 , and the chemical shift was calibrated by setting the chemical shift of DMSO- d_6 as 2.49 ppm. The assignment of the individual peak of (1-3) was assisted by the correlations shown in the ¹H-¹H COSY and ¹H-¹³C HET-COR NMR spectra. IR Spectra were measured by Perkin-Elmer RX1 infrared spectrophotometer. High-resolution mass measurements were performed by a Finnigan/Thermo Quest MAT 95XL mass spectrometer by fast atom bombardment. Elemental analysis was performed on an Elementar Vario EL III. Differential scanning calorimeter (DSC) scans were obtained by a Perkin-Elmer DSC 7 in a nitrogen atmosphere at a heating rate of 20 $^\circ\text{C}/\text{min.}$ $T_{\rm g}$ was taken as the midpoint of the heat capacity transition. Dynamic mechanical analysis (DMA) was performed by a Perkin-Elmer Pyris Diamond DMA at a heating rate of 5 °C/min. Thermo mechanical analysis (TMA) was performed by a SII TMA/SS6100 at a heating rate of 5 °C/min. The onset of transition in dimension was defined as T_{g} , and coefficient of thermal expansion (CTE) before $T_{\rm g}$ was defined by calculating the TMA data from 50 to $T_{\rm g}$ -20 °C. Thermal gravimetric analysis (TGA) was performed by a Seiko Exstar 600 at a heating rate of 20 °C/min in a nitrogen or air atmosphere. Flame retardancy of PIs was performed by a UL-94VTM vertical thin test. In that test, an $8^{\prime\prime}\,\times\,2^{\prime\prime}$ sample was wrapped around a $1/2^{\prime\prime}$ mandrel, and then taped on one end. The mandrel was removed, leaving a cone-shaped sample that was relatively rigid. The two flame applications were 3 s. After the first ignition, the flame was removed and the time for the polymer to self-extinguish (t_1) 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_2) and dripping characteristics were recorded. If t_1 plus t_2 was less than 10 s without any dripping, the polymer was considered to be a VTM-0 material. If t_1 plus t_2

was in the range of 10-30 s without any dripping, the polymer was considered to be a VTM-1 material.

Synthesis of (1)

DOPO 25.94 g (0.12 mol), 4-hydroxyacetophenone 16.34 g (0.12 mol), aniline 44.70 g (0.48 mol), and p-TSA 1.038 g (4 wt % of DOPO) were introduced into a 250-mL round-bottom glass flask equipped with a nitrogen inlet and a magnetic stirrer. The reaction mixture was stirred at 130 °C for 24 h. After that, the white precipitate was filtered and recrystallized from methanol, and then dried in a vacuum oven at 150 °C for 8 h. Light white crystal (55% yield) with a melting point of 294 °C (DSC) was obtained. HR-MS(EI) m/ z: calcd. for $C_{26}H_{22}O_3N_1P$ 427.1337; found 427.1332. ¹H NMR (DMSO- d_6), $\delta = 1.57$ (3H, H¹⁸), 4.99 (2H, NH₂), 6.41 (2H, H²), 6.57(2H, H²¹), 7.07 (2H, H³), 7.08 (2H, H²⁰),7.10 (1H,H¹⁵), 7.12(1H, H⁹), 7.17(1H, H¹³), 7.34 (1H, H¹⁴), 7.36 (1H, H⁸), 7.66 (1H, H⁷), 7.98 (1H, H¹²), 8.81 (1H, H⁶),9.36(1H,OH) ¹³C NMR (DMSO- d_6), $\delta = 24.17$ (C¹⁸), 51.62 (C¹⁷), 113.34 (C²¹), 114.37(C²), 118.98 (C⁹), 120.88 (C¹¹), 122.31 (C⁵), 123.34 (C¹⁰), 123.83(C¹³), 125.31 (C¹²), 127.78 (C^8) , 128.93 (C^3) , 128.97 (C^{21}) , 129.54 (C^4) , 130.54 (C^{14}) , 131.82 (C¹⁵), 133.20 (C⁷), 135.98 (C¹⁹), 147.03 (C¹), 150.73 (C^{22}), 156.18 (C^{16}). ³¹P NMR (DMSO- d_6), $\delta = 42.30$.



Synthesis of (2)

To a round-bottom 250-mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer, (1) 10.0g (23.3 mmol), 4-chloronitrobenzene 3.87 g (24.5 mmol), potassium carbonate 3.39 g (23 mmol), and DMAC 46 mL were introduced. The reaction mixture was heated to 120 °C and maintained at that temperature for 12 h. Then, the reaction mixture was filtered, and the filtrate was poured into 450 mL of enthanol/water (1/2, V/V) solution under stirring.

The yellow precipitate was filtered and recrystallized from ethyl acetate/DMAC, and then dried in a vacuum oven at 110 °C for 6 h. Light yellow crystals (66% yield) with a melting point of 180 °C (DSC) were obtained.HR-MS(EI) *m*/*z*: calcd. for $C_{32}H_{25}O_5N_2P$ 548.1501; found 548.1507. ¹H NMR (DMSO-*d*₆), $\delta = 1.73$ (3H, H¹⁸), 5.05 (2H, NH₂), 6.45 (2H, H²), 6.93 (2H, H²¹), 7.03 (2H,H²⁴), 7.12 (2H, H³), 7.21 (2H,H¹³), 7.29 (1H, H²⁰), 7.32 (1H, H¹⁵), 7.34 (1H, H⁹), 7.36 (1H, H¹⁴), 7.42 (1H, H⁸), 7.70 (1H, H⁷), 8.01 (1H, H¹²), 8.12 (1H, H⁶), 8.29 (1H, H²⁵).¹³C NMR (DMSO-*d*₆), $\delta = 24.31$ (C¹⁸), 52.43 (C¹⁷), 113.48 (C²), 117.30 (C²⁴), 119.26 (C²¹), 120.61 (C¹¹), 121.99 (C⁵), 123.38 (C⁶), 123.83 (C¹³), 125.31 (C¹²), 126.19 (C²⁵), 127.78 (C⁸), 128.93 (C³), 130.54 (C¹⁴), 131.58 (C²⁰), 131.82 (C¹⁵), 131.94 (C⁹), 133.20 (C⁷), 135.98 (C¹⁹), 136.21 (C⁴), 137.33 (C²²), 147.03 (C²⁶), 147.60 (C¹),



SCHEME 1 Synthesis of (1).

150.73 (C²²), 156.18 (C¹⁶), 162.10 (C²³). ³¹P NMR (DMSO- d_6), $\delta = 40.09$.



Synthesis of (3)

(2) 10 g, 10% Pd/C 0.15 g, and DMF 50 mL were introduced into a Parr autoclave at room temperature. The reaction system was purged with nitrogen for 30 min before introducing hydrogen. The pressure of the autoclave was maintained at about 140 psi under hydrogen atmosphere for 24 h. Then, the reaction mixture was filtered to remove Pd/C, and the filtrate was poured into 500 mL of water under stirring. The precipitate was filtered and then dried in a vacuum oven at 70 °C. Off-white powders (80% yield) were obtained. Mass spectra (FAB) (*m/e*, relative intensity): 507 (M + 1⁺ 78), 398 (M - 108⁺, 30), 154 (biphenyl, 100). HR-MS(EI) *m/z*: calcd. for C₃₂H₂₇O₃N₂P 518.1759; found 518.1763. ¹H NMR (ppm, DMSO-*d*₆), $\delta = 1.63$ (3H, H¹⁸), 5.02 (4H, NH₂), 6.40 (2H, H²), 6.58 (2H, H²⁵), 6.61 (2H, H²¹), 6.68 (2H, H²⁴), 7.04 (1H, H¹⁵), 7.06 (2H, H³), 7.08 (2H, H²⁰), 7.12 (1H, H¹³), 7.23

(1H, H⁹), 7.32 (1H, H¹⁴), 7.37 (1H, H⁸), 7.68 (1H, H⁷), 7.94 (1H, H¹²), 8.06 (1H, H⁶). ¹³C NMR (ppm, DMSO- d_6), $\delta = 30.51$ (C¹⁸), 52.09 (C¹⁷), 113.41 (C²), 114.81 (C²⁵), 115.43 (C²¹), 119.43 (C¹⁵), 122.22 (C²⁴), 122.86 (C⁵), 123.21 (C⁶), 123.84 (C¹³), 125.26 (C¹²), 128.04 (C⁸), 129.11 (C²⁰), 130.44 (C¹⁴), 130.85 (C³), 131.80 (C⁹), 132.66 (C¹⁰), 133.41 (C¹¹), 134.22 (C⁷), 136.78 (C⁴), 137.59 (C¹⁹), 145.61 (C²⁶), 146.23 (C¹), 147.87 (C²³), 151.22 (C¹⁶), 156.36 (C²²). ³¹P NMR (DMSO- d_6), $\delta = 40.48$.



Preparation of PEIs

Phosphinated PEIs were prepared by reacting (3) with equal molar dianhydrides (**a-d**). PEIs syntheses were exemplified by the specific synthesis of (**5a**) from the condensation of (3) and PMDA. To a 100-mL three-neck round-bottom flask equipped with a nitrogen inlet and magnetic stirrer, (3) 1.037 g (2 mmol) and CaH₂-dried DMAc 5.89 g were added. After the monomer had dissolved completely, the reactor was placed into an ice-bath cooling system. After the



FIGURE 2 ¹H NMR spectrum of (1).



carbocation

SCHEME 2 Proposed mechanism for the regio-selective electrophilic substitution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction mixture reached 3–5 °C, PMDA 0.436 g (2 mmol) was added quickly and reacted at that temperature for 2 h. Then, the viscous poly(amic acid) (**4a**) was diluted with DMAc 2.45 g (solid content 15 wt %) and then casted on glass by an automatic film applicator. The film was dried at 80 °C overnight, and then imidized at 100 °C (1 h), 200 °C (1 h), and 300 °C (1 h), respectively.

RESULTS AND DISCUSSION

Monomer Synthesis

Compound (1) was prepared by the reaction of DOPO, 4hydroxyacetophenone in excess aniline using p-TSA as catalyst via a one-pot procedure (Scheme 1). The excess aniline plays the roles of reactant and reaction medium. A nucleophilic addition, followed by electrophilic substitution mechanism for the synthesis of (1) was proposed (Supporting Information Scheme S1). In that mechanism, DOPO initially attacks the carbonyl group of 4-hydroxyacetophenone via a nucleophilic addition, forming an intermediate with a tertiary hydroxyl group. The tertiary hydroxyl group is then protonated by acid. Spontaneous dissociation of the protonated hydroxyl group occurs to yield a tertiary carbocation. Then, aniline reacts with the resulting carbocation via an electrophilic substitution, yielding (1). Figure 2 shows the ¹H NMR spectrum of (1). An amino peak at 5.0 ppm and a phenol peak at 9.4 ppm were observed. Signals of the methyl group at 1.5 ppm were split into two peaks with a coupling constant of 17.4 Hz because of a ${}^{3}J_{P-H}$ coupling. Signals from H² and H²¹ (ortho to the amino and ether group, respectively) show the smallest chemical shift at 6.4–6.6 ppm because of



SCHEME 3 Synthesis of (2) and (3).



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SCHEME 4 Synthesis of PEIs (5).

the shielding effect of the electron-donating amino and ether groups. The other spectroscopic data such as ¹³C NMR, ¹H-¹H COSY, and ¹H-¹³C HETCOR spectra (Supporting Information Figs. S1–S3) support the structure and purity of **(1)**.

Because the phosphorus and aliphatic carbon in (1) are both chiral centers, four stereoisomers should result. Theoretically, each stereocenter can be either R or S configuration, and hence, the possible combinations are RR, RS, SR, and SS configurations. The four stereoisomers can be grouped into two pairs of enantiomers, resulting in two pairs of diastereomers: RR + SS and RS + SR. The RR stereoisomer is the enantiomer of the SS stereoisomer and is diastereomerically related to the RS and SR stereoisomers. However, according to the spectroscopic data of (1), only racemic mixture with equal RR and SS configurations or equal RS and SR configurations was obtained. It is speculated that the electrophilic substitution of aniline on the 3° carbocation (Scheme 2) is limited to one direction, leading to regioselective reaction. However, a more detailed research is required to explain this phenomenon.

Compound (2) was easily synthesized from the nucleophilic substitution of (1) and 4-chloronitrobenzene at 120 °C using potassium carbonate as catalyst (Scheme 3). In our previous work,⁴² we reported that P-C (aliphatic carbon) is stable in an alkaline condition. That claim can be further supported in this case. Figure 3 shows the ¹H NMR spectrum of (2). Signals from H^{24} and H^{25} indicate that the nucleophilic substitution was successful. Because of the inductive and anisotropic deshielding effect of the nitro group, the signal from H²⁵ shows the largest chemical shift at around 8.3 ppm. In contrast, the signal from H^2 (ortho to the amino group) shows the smallest chemical shift at 6.4 ppm because of the shielding effect of the electron-donating amino group. The other spectroscopic data such as ¹³C NMR, ¹H-¹H COSY, and ¹H-¹³C HETCOR spectra (Supporting information Figs. S4–S6) also support the structure and purity of (2).

Compound (3) was readily obtained by catalytic reduction of (2). Figure 4 shows the ¹H NMR spectrum of (3). An amino peak corresponding to four hydrogen's at 5.02 ppm was observed, indicating that the two amino groups have almost the same chemical shift. Because of the shielding effect of



FIGURE 5 X-ray single crystal diffractogram of (2).

Polymer	η _{inh} (dL g ⁻¹) ^a	Solvent for Solubility Test ^b							
		NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	CH ₂ Cl ₂	CHCI ₃	THF
5a	0.51	$+h^{c}$	+h	+-	-	+h	-	_	_
5b	0.61	+h	+h	+h	±	+h	+	+	-
5c	0.58	+h	+h	+h	+h	±	±	_	_
5d	0.73	+h	+h	<u>+</u>	+h	+	±	+	-
5c′	0.64	+h	±	<u>+</u>	-	±	±	±	_

 TABLE 1 Inherent Viscosity and Solubility Data of PEIs (5)

 $^{\rm a}$ Measured at a polymer concentration of 0.5 g/dL in NMP at 30 $^\circ \rm C.$ $^{\rm b}$ Solubility was tested with a 5 mg sample in 0.5 g of solvent at room temperature.

the electron-donating amino groups, signals of H^{25} upshifted from 8.3 ppm in (2) to 6.6 ppm in (3), demonstrating the successful reduction of the nitro group. The other spectroscopic data such as ¹³C NMR, ³¹P, ¹H-¹H COSY, and ¹H-¹³C HETCOR spectra (Supporting Information Figs. S7–S9) support the structure and purity of (3).

Polyimide Synthesis

PEIs (5) were prepared by the reaction of (3) with various commercially available dianhydrides (a-d) in DMAc to form poly(amic acid)s (4), followed by thermal imidization (Scheme 4). According to the principle of NMR, a smaller chemical shift of an amino proton means a higher electron density of nitrogen, corresponding to a higher reactivity. The chemical shift of both amino groups of (3) is at 5.02 ppm. This suggests that the reactivity of the amine (next to C_1) is not affected by the electron-withdrawing P=O group. Although the single crystal data of (3) is not successfully prepared, the configuration of (3) might be approximately depicted by the single crystal data of (2), as shown in Figure 5. The bulky phosphinate pendant is oriented to the 4-(4-aminophenoxy)phenyl linkage. Therefore, little steric hindrance on the left 4-aminophenyl linkage is expected. As a result, PEIs with moderate-to-high inherent viscosity, ranging from 0.51 to 0.73 dL/g (Table 1), can be prepared. Supporting Information Figure S10 shows the IR spectra of (5), the characteristic imide absorption bands at 1773 cm^{-1} (C=0 asymmetric stretch), 1740 cm⁻¹ (C=0 symmetric stretch), 1370 cm⁻¹ (C–N stretch), 1116 and 717 cm⁻¹ (imide ring deformation) indicate the formation of the imide ring. Further, the absorptions of P—Ph absorption at 1594 cm⁻¹, P=O absorption at 1205 cm^{-1} , and P-O-Ph absorption at 922 cm^{-1} indicate no cleavage of the biphenylene phosphinate pendant after thermal imidization.

Properties of the PEIs Organosolubility

The solubility properties of PEIs (5) are listed in Table 1. When compared with the symmetric PEIs (5') with two flexible ether linkages, asymmetric PEIs (5), even with only one ether linkage, display much better solubility. For example, PEI (5c) is soluble in NMP, DMAc, DMF, and DMSO, but PEI (5c') is soluble only in NMP. The asymmetric structure, $^{\rm c}$ +, soluble at room temperature; +h, soluble on heating; ±, partially soluble on heating; –, insoluble on heating.

which leads to the formation of configuration isomers of the repeat unit and resulted in the disruption of the packing sequence, should be responsible for the improved solubility. In particular, PEI (**5b**), derived from flexible ODPA, is soluble in low-boiling solvents, such as CH_2Cl_2 and $CHCl_3$.

Film Quality and Thermal Properties

Supporting Information Figure S11 shows a picture of (5a), in which PEI (5a) displays light color and is foldable. The other PEIs also show light-color and foldable properties. Because all PEIs (5) are tough and foldable, DMA and TMA were applied to evaluate their thermal mechanical properties and dimensional stability. Figure 6 shows the DMA curves of PEIs (5), and the DMA data are listed in Table 2. The temperatures corresponding to 1 GPa were as high as 328, 288, 290, and 303 °C for (**5a-5d**), respectively, and the T_g 's obtained from the peak temperatures of tan δ are 336, 291, 300, and 311 °C for (5a-5d), respectively. Among the PEIs, (5a) shows the highest $T_{\rm g}$ due to the rigid pyromellitic moieties. In contrast, (5b) displays the lowest T_g because of the flexible ether linkage. Figure 7 shows the TMA curves of PEIs (5), and the TMA data are listed in Table 2. T_{σ} 's measured by TMA are in the range of 290-327 °C, which is slightly lower than those measured by DMA. The CTEs before T_g are in the range of 44–52 ppm/°C, displaying moderate dimensional stability. Figure 8 shows the structure- T_{g}



FIGURE 6 DMA curves of PEIs (5).

Sample	Film Quality	<i>E</i> ′ (GPa) ^a	Tan S	T _g (°C) (DSC) ^b		CTE (ppm/°C) ^d	<i>T</i> _{d 5%} (°C) ^e		Char Yield ^f	
			(°C)		(TMA) ^c		N_2	Air	N_2	Air
5a	Foldable	2.51	336	329	327	44	452	447	56	49
5b	Foldable	4.58	291	281	277	52	450	455	56	39
5c	Foldable	4.60	300	290	290	49	447	444	55	47
5d	Foldable	4.57	311	296	299	44	463	463	59	50

TABLE 2 Thermal Properties of PEIs (5)

^a Measured by DMA at a heating rate of 5 °C/min; storage modulus (*E*') are recorded at 50 °C.

^b From the second DSC heating scan at a heating rate of 20 °C/min.
^c Measured by TMA at a heating rate of 5 °C/min.

^e Temperature corresponding to 5% weight loss by thermogravimetry at a heating rate of 20 °C/min.

^f Residual wt % at 800 °C.

relationship of PEIs (**5**), PEIs (**5**'), and PIs (**5**''). Obviously, T_g is strongly related with the number of phenoxy linkages. For example, T_g reduced from 392 °C for (**5a**'') to 336 °C for (**5a**), and to 314 °C for (**5a**'). PEIs (**5**'), with two phenoxy linkages, show the lowest T_g . In contrast, PIs (**5**''), with no phenoxy linage, show the highest T_g . A 20–30 °C difference in T_g for a phenoxy linkage was observed for (b–d) series. Figure 9 shows the structure-CTE relationship of three series of phosphinated PIs. PEIs (**5**') show the highest CTE, and PIs (**5**'') show the lowest CTE. As expected, the trend of CTE is inversely related with that of T_g .

The thermal stability of PEIs (5) was evaluated by TGA (Table 2). The 5 wt % degradation temperatures of PEIs (5) in a nitrogen atmosphere range from 453 to 467 °C, and the char yields are in the range of 56–58 wt %. In an air atmosphere, the 5 wt % ($T_{\rm d}$ _{5%}) degradation temperatures range from 447 to 463 °C, and the char yields are in the range of 39–50 wt %. The degradation temperature is relatively high compared with those of main-chain type phosphinates.^{26,27}



^d Coefficient of thermal expansion are recorded from 50 °C to T_{α} –20 °C.











FIGURE 9 Structure-CTE relationship of PEIs (5), PEIs (5'), and PI (5").

stable than the main-chain type phosphinates. In addition, according to bonding energy, the P–C chain has a lower one, so the initial degradation of polymer occurred at that chain. In our previous studies,^{43,44} we reported that the thermal stability of phosphorus-containing thermosets is related to the electron density of the carbon adjacent to the phosphorus. The lower is the electron density of the carbon, the lower is its thermal stability. In this case, the high thermal stability of PEIs (**5**) can also be explained by the electron density of the aliphatic carbon adjacent to the phosphorus. The P=O group, an electron withdrawing group, reduced the electron density of the carbon, destabilizing the P–C bond. However, the methyl group, an electron donating group, increased the electron density of the Carbon, increasing the thermal stability of the P–C bond.

Figure 10 shows the structure- T_d relationship of the three series of phosphinated PIs. PEIs (**5**') show the highest T_d , and PIs (**5**'') show the lowest T_d . This trend is inversely related to the order in T_g . Generally, polymers with high T_g usually exhibit high thermal stability, so the trend is unexpected. According to the previous discussion, the density of the car-



FIGURE 10 Structure- T_d relationship of PEIs (5), PEIs (5'), and PI (5").

TABLE 3 Data of UL-94 Test for PEIs (5) Series and Kapt

Sample Code	Film Thickness (µm)	First Burning Time (s)	Second Burning Time (s)	Dripping	UL-94 Grade
5a	31	0.6	0.1	No	V-0
5b	33	1.2	0.3	No	V-0
5c	31	0.9	0.3	No	V-0
5d	35	0.7	0.2	No	V-0
Kapton	23	4.6	1.8	No	V-0

bon adjacent to the phosphorus is critical to the thermal stability of the resulting PIs. It is speculated that PEIs (5'), with two electron-donating ether groups, increased the electron density of the carbon next to phosphorus, so PEIs (5') display the highest T_{d} . In contrast, PIs (5"), with no electrondonating ether group to increase the electron density of the carbon, show the lowest T_{d} . As to the flame retardancy, according to the UL-94VTM vertical thin test (Table 3), the t_1 + t_2 is less than 2 s for PEIs (5), so they belong to the VTM-0 grade. In contrast, the $t_1 + t_2$ is higher than 6 s for Kapton. Although wholly aromatic PIs usually possess VTM-0 grade without halogen and phosphorus components, they are usually organo-insoluble. The combination of organo-solubility and flame retardancy makes PEIs (5) attractive for industrial application.

CONCLUSIONS

We report a facile procedure to prepare a phosphinated aminophenol (1). A "nucleophilic addition and then electrophilic substitution" mechanism was proposed for the preparation of (1). Then, an asymmetric etherdiamine (3) was then prepared from a K₂CO₃-catalyzed nucleophilic aromatic substitution of (1) and 4-chloronitrobenzene, followed by catalytic hydrogenation. PEIs (5) based on (3) are light colored, tough, and foldable. In the structure- T_{g} , and structure-CTE relationships, PIs (5") show the highest T_{g} and lowest CTE, whereas PEIs (5") display the lowest T_g and highest CTE. The values of $T_{\rm g}$ and CTE are strongly related with the number of phenoxy linkage in the repeating unit polymer backbone. In the structure- T_d relationships, PEIs (5') show the highest thermal stability, whereas PIs (5'') display the lowest one. It is speculated that electron-donating ether groups increased the electron density of the carbon next to phosphorus, and thus enhanced the P-C bond. As for the structure-solubility relationship, PEIs (5) show the best organosolubility. In particular, PEI (5b), derived from flexible ODPA, is soluble in low-boiling solvents, such as CH₂Cl₂ and CHCl₃. The asymmetric structure, which leads to the formation of configuration isomers of the repeat unit and results in the disruption of the packing sequence, might be responsible for the improved solubility. According to the UL-94VTM vertical test, PEIs (5) belong to the VTM-0 grade. The combination of organo-solubility and flame retardancy makes PEIs (5) attractive for industrial application.

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