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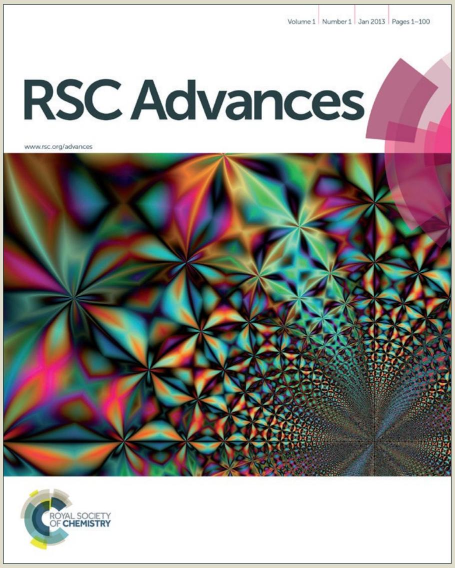

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Synthesis of a phosphinated tetracyanate ester and its miscible blend with 4,4'-oxydianiline/phenol-based benzoxazine

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Abstract

A phosphinated tetracyanate ester **(4)** was prepared by a three-step procedure, including nucleophilic addition of DOPO on 5,5'-methylenebis(2-hydroxybenzaldehyde), electrophilic substitution of phenol, and nucleophilic substitution with cyanobromide. Tetracyanate ester **(4)** was applied to copolymerize with a 4,4'-oxydianiline/phenol-based benzoxazine (P-oda) to enhance the properties of P-oda thermoset. We discussed the miscibility, microstructure, as well as the thermal and dielectric properties of the reactive blends of **(4)** with a P-oda. A miscible blend can be achieved in all compositions, as judged by thermal analysis. The co-reactions between **(4)** and P-oda, as observed in the IR analysis, explain the single-T_g phenomenon. The experimental data show that the thermal, dielectric and flame retardant properties of polybenzoxazine are enhanced through the reactive blends.

Introduction

Cyanate ester is known for its high glass transition temperature, high thermal stability, low water absorption, and low dielectric constant after being fully cured to form a triazine network.[1-5] The high-performance properties make it attractive for advanced copper clad laminate. Recently, cyanate esters containing silicon,[6-9] oligodimehylsiloxane,[10] phenolphthalein,[11] fluoromethylene,[12] dipentene,[13] perfluorocyclobutane,[14] and triazole[15] have been developed. However, the lack of flame retardancy hindered the application of cyanate ester in copper clad laminate, in which flame retardancy (UL-94 V-0) is required. It has been reported that the flame retardancy of dicyanate ester of bisphenol A (BADCY) can be drastically enhanced by the incorporation of a low concentration of the phosphorus element.[16-19]

The curing of cyanate ester is carried out through the trimerization of cyanate ester to a triazine structure. However, Wang et al. pointed out that the high cross-linking density and high viscosity during the final curing stage hindered the mobility of the residual cyanate groups.[20] Thus, a complete reaction of the cyanate groups could not be accomplished, and the remaining polar cyanate ester increased the dielectric constant. Therefore, they used monofunctional cyanate to reduce the crosslink density, and thus reduced the dielectric constant. Although the approach successfully reduced the dielectric constant, T_g was remarkably reduced due to the reduced crosslink density resulting from the incorporation of the monofunctional cyanate.

Benzoxazines are resins that can be polymerized to thermosets by means of thermally activated ring-opening reactions.[21] Thermosets with low water absorption, superior thermal and electrical properties[22] and low surface energy[23, 24] can be obtained after curing. Although polybenzoxazine has better properties than phenolic novolac and epoxy thermosets,[25] a further enhancement in performance is highly attractive.[26] In our previous work,[27] we reported that a copolymer with a lower dielectric constant than neat polybenzoxazine and poly(cyanate ester) was achieved because rare residual cyanate ester remained in the copolymers. In this work, continuing our efforts in the area of phosphinated thermosets, we synthesized a tetracyanate ester (4) and discussed the miscibility, microstructure, as well as the thermal and dielectric properties of its reactive blends with a 4,4’-oxydianiline/phenol-based benzoxazine (P-oda).

Experimental

Materials. s-Trioxane (from Acros), 2-hydroxybenzaldehyde (from Showa), sulfuric acid (from Scharlau), acetic acid (from Scharlau), 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO, from TCI),phenol (from Acros), p-toluenesulfonic acid (p-TSA, from Showa), cyanogen bromide (from TCI), and triethylamine (from Showa) were used as received. 5,5'-methylenebis(2-hydroxybenzaldehyde) **(1)** was prepared according to our previous work.[28] 4,4'-Oxydianiline /phenol-based benzoxazine (P-oda) was prepared in our lab, according a previously reported procedure.[29]

Characterization. Differential scanning calorimetry (DSC) scans were obtained using a Perkin-Elmer DSC 7 in a nitrogen atmosphere at a heating rate of 10^{o}C/min. Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris1 at a heating rate of 20 ^{o}C/min in an atmosphere of nitrogen or air. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer Pyris Diamond DMA with a sample size of 5.0 cm x1.0 cm x0.2 cm. The storage modulus E' and tan δ were determined as the sample was subjected to the temperature scan mode at a programmed heating rate of 5 ^{o}C/min at a frequency of 1Hz. The test was performed by a bending mode with an amplitude of 5 μm. Thermal mechanical analysis (TMA) was performed with a Perkin-Elmer Pyris Diamond at a heating rate of 5 ^{o}C/min. IR spectra were obtained from at least 32 scans in the standard wavenumber range of 400–4000 cm^{-1}using a Perkin-Elmer RX1 infrared spectrophotometer. The dielectric constant was measured by an Agilent E49991A with a sample size of 1 cm x1 cm x0.08 cm. The UL-94 vertical test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with a test specimen bar of 127 mm in length, 12.7 mm in width and about 1.27 mm in thickness. In the test, the polymer specimen was subjected to two 10 s ignitions. 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 when 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. The flame test was performed on five specimens. If the average t_1 plus t_2 is less than 10 s without any dripping, the polymer is considered to be a V-0 material. If t_1 plus t_2 is in the range of 10–30 s without any dripping, the polymer is considered to be a V-1 material.

Synthesis of (2). DOPO 50.5 g (0.23 mole)**, (1)** 20.0 g (0.08 mole), toluene 150 mL were introduced into a 500-mL round-bottom glass flask equipped with a nitrogen inlet and a magnetic stirrer. The mixture was stirred at 80 ^{o}C for 12 h. The white precipitate was filtered, dissolved in methanol, and poured into water. After drying at 80 ^{o}C for 12 h, white powder (83 % yield) with a melting point of 169^{o}C (DSC) was obtained.^{1}H-NMR (DMSO-d_6), δ= 3.5 (2H, CH_2), 5.4-5.6 (2H, P-CH), 6.1 (2H, C-OH), 6.5-8.2 (22H, Ar-H), 9.3 (2H, Ph-OH).

Synthesis of (3). Phenol 13.7 g (0.15 mole), p-TSA 0.4 g, and **(2)** 10.0 g (0.01 mole) were introduced into a 250-mL round-bottom glass flask equipped with a nitrogen inlet and a magnetic stirrer. The mixture was stirred at 130 ^{o}C for 7 h. After that, methanol 100 mL was added, and the mixture was poured into water to precipitate the product. After recrystallization by isopropanol/DMAc (1/1, V/V), white crystal (76% yield) with a melting point of 239 ^{o}C (DSC) was obtained.^{1}H-NMR (DMSO-d_6), δ= 3.9 (2H, CH_2), 4.8 (2H,P-CH), 6.6-8.2 (30H, Ar-H), 9.2 (2H, Ph-OH), 9.3 (2H, Ph-OH).

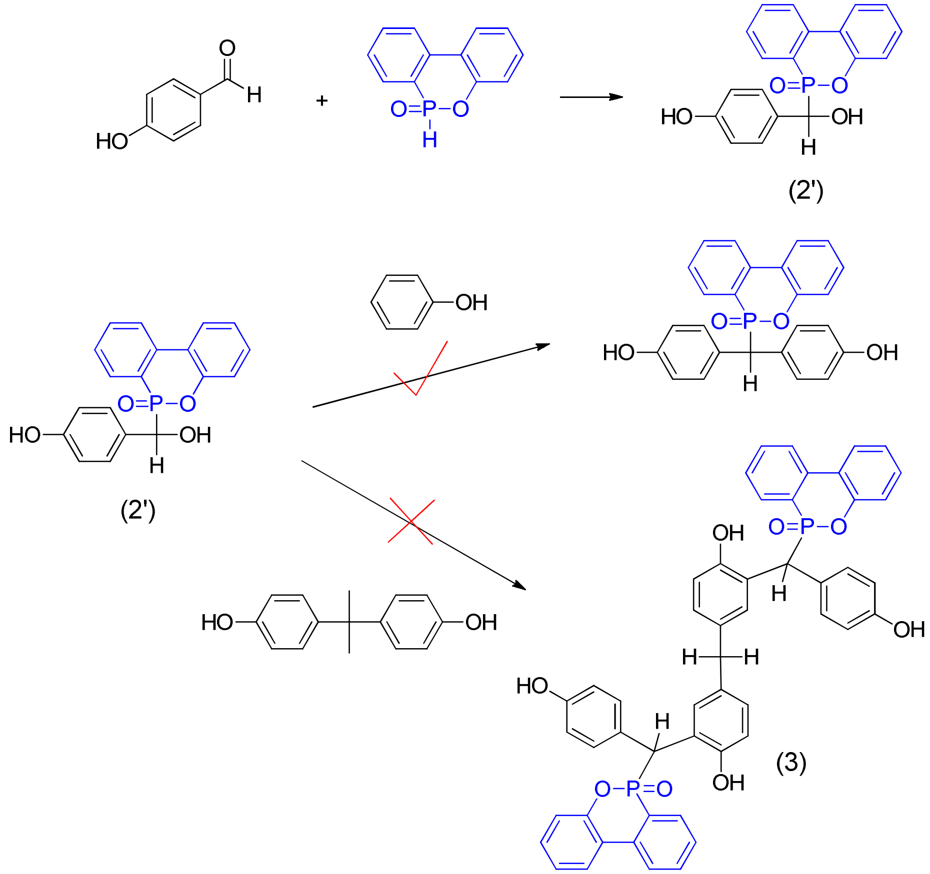
Synthesis of (4). (3) 5.0 g (5.95 mmole), and DMAc 100 mL were added to a 100 mL round-bottom flask equipped with a nitrogen inlet and magnetic stirrer. The reaction system was gradually cooled to −15 °C. Cyanogen bromide 3.149 g (29.75mmole) was added. Triethylamine 3.009g (29.75 mmole) in 10 mL DMAc was added gradually over 2 h. The mixture was kept at that temperature for another 10 h. After that, the white $Et_3N \cdot HBr$ salt was filtered. The filtrate solution was then poured into stirring water to precipitate the product. The precipitate was filtered and dried at 80 °C for 24 h. White powder 10.0 g (70% yield) of was obtained. FTIR (KBr): 1203 cm^{-1} (P O), 2273 cm^{-1} and

2237 cm^{-1} (cyanate stretch). ^{1}H-NMR (ppm, DMSO-d_6), δ = 4.2 (2H, CH$_2$), 5.1 (2H, P-CH), 7.0-8.3 (30H, Ar-H).

Sample preparation and curing procedure. (4)/P-oda with various molar ratios were prepared by melt blending. The blend was crushed into fine powder and then heated on a hot plate at about 150 ^{o}C with continuous stirring until a homogeneous solution was obtained. The solution was poured into aluminum modes with dimensions of 5.0 cm x1.0 cm x0.2 cm (for DMA measurement) and 1.0 cm x1.0 cm x0.3 cm (for TMA and dielectric measurements), and was cured at 150 ^{o}C (2 h), followed by 180 ^{o}C (2h), 200 ^{o}C (2h), and 220 ^{o}C (2 h). After that, the samples were allowed to cool slowly to room temperature to prevent cracking. The sample ID odax means the content of P-oda is x mole% in the blend. Therefore, the sample ID oda25 means the content of P-oda is 25 mole% in the blend. The sample IDs for the polymer of odax, **(4)**, and P-oda are P(odax), P(4), and P(P-oda), respectively.

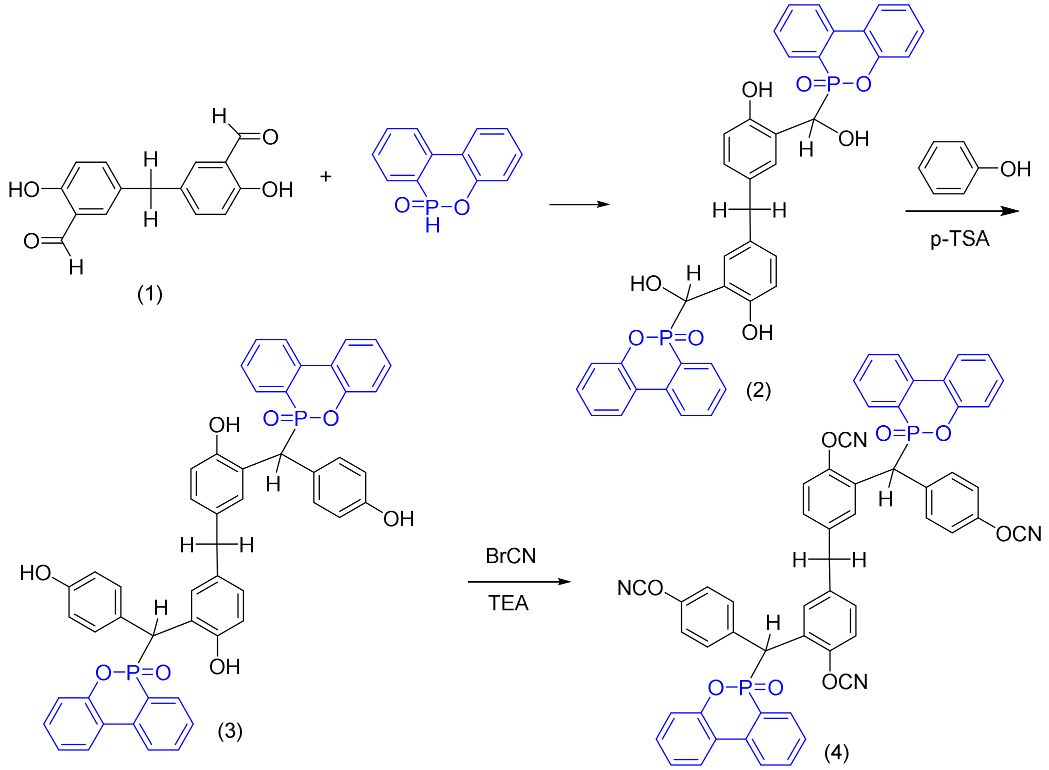
Results and Discussion

Synthesis of phosphinated tetraphenol (3). Initially, we attempted to prepare **(3)** by route I (Scheme 1). Two steps are required for the reaction. The first step is the nucleophilic addition of DOPO on aldehyde of 4-hydroxylbenzaldehyde, forming an intermediate (2') with a secondary alcohol structure. The second step is the electrophilic substitution bisphenol A on the protonated (2'). In our previous paper, we prepared a phosphinated bisphenol through the electrophilic substitution of phenol with (2’) using acid as the catalyst.[30] However, using bisphenol A as the electrophilic substitution agent was not successful under the various reaction conditions we applied. It is probably due to the electrophilic reactivity of the ortho-position of bisphenol A is not as active as the para-position of phenol.



Scheme 1. Synthesis of **(3)** through route I. Note that the electrophilic substitution of bisphenol A on (2') was not successful.

Since phenol is more reactive than bisphenol A in electrophilic substitution, we designed route II (Scheme 2) using phenol as the electrophilic substitution agent to prepare **(3)**. Two steps are required to the synthesis. The first step is nucleophilic addition of DOPO on the aldehyde of 5,5'-methylenebis(2-hydroxybenzaldehyde) **(1)**, forming **(2)** with a secondary alcohol structure. The second step is electrophilic substitution of phenol on **(2)**, releasing water and forming **(3)**.



Scheme 2. Synthesis of (2-4) through route II.

Figure 1(a) shows the ^{1}H-NMR spectrum of **(3)**. Signals of phenolic OH at 9.2 and 9.3 ppm (note that two types of phenolic OH existed), the signal of P-CH at 4.8 ppm and the signal of CH_2 at 3.9 support the structure of **(3)**. ^{13}C spectrum of compound **3** was shown in Figure S1. However, the pattern is too complex to assign due to both the P and methine are chiral centers. Phosphinated tetracyanate (4) was prepared by nucleophilic substitution of **(3)** with cyanogen bromide in the presence of triethylamine. Figure 1(b) shows the ^{1}H-NMR spectrum of **(4)**. Signals of phenolic OH disappeared completely in Figure 1(b). An absorption at 2273 and 2237 cm^{-1} corresponding to cyanate ester was clearly observed in the IR spectrum. The results support the complete transformation of phenolic OH to cyanate ester.

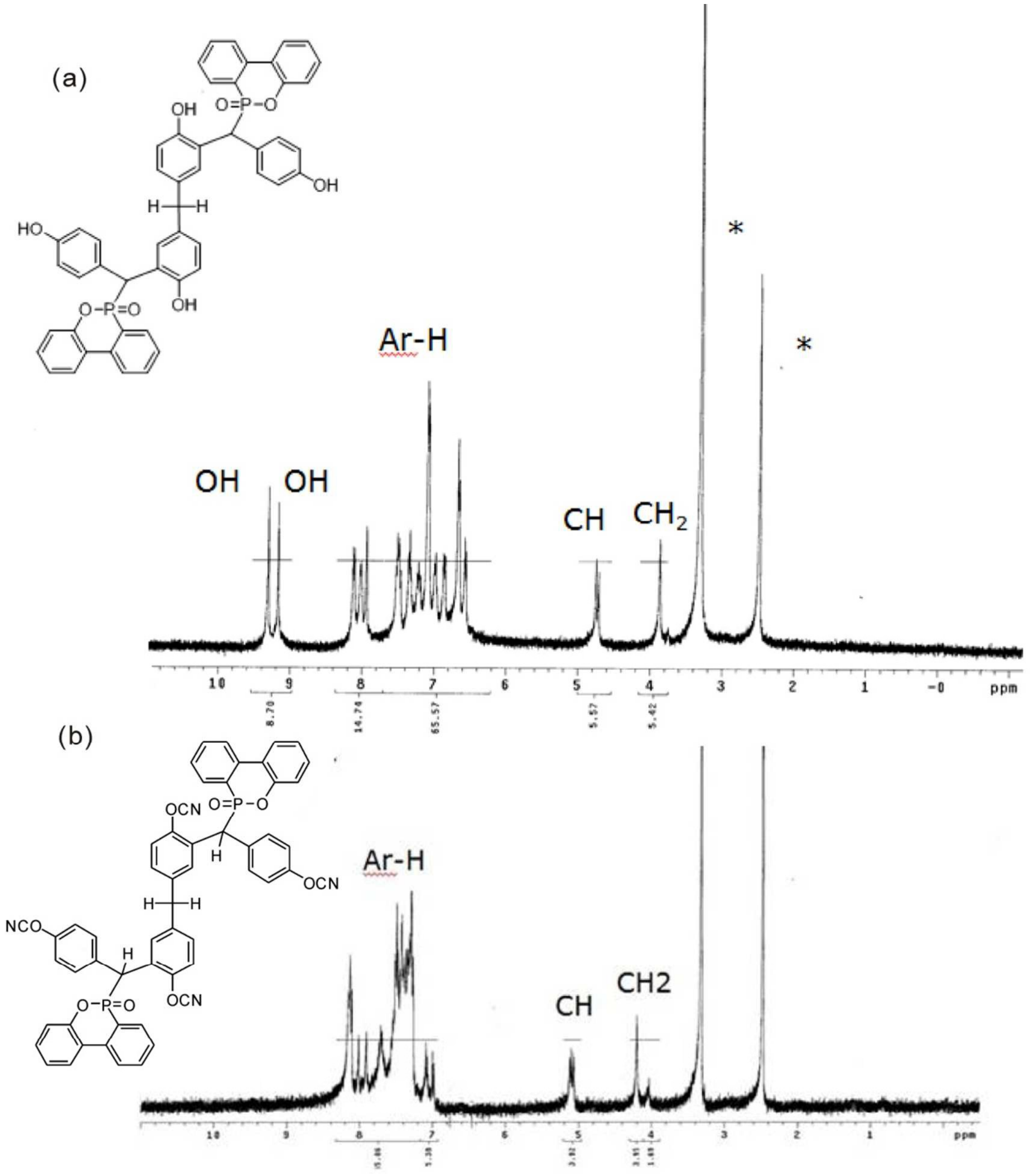


Figure 1. ^{1}H NMR spectrum of **(3)** and **(4)** in DMSO-d_6.

Microstructure of (4)/P-oda blend. Figure 2 shows the DSC thermograms of **(4)**, P-oda, and **(4)**/P-oda blends at a heating rate of 10 °C/min. Based on our previous work[27], the cyclotrimerization of cyanate ester is faster than ring-opening polymerization of benzoxazine. So the first exothermic peak of oda50 is about the cyclotrimerization of cyanate ester, and the other peak is about ring-opening polymerization of benzoxazine. Both exothermic temperature of oda50 is much lower than those of neat **(4)** and P-oda, showing a forward polymerization. IR was used to monitor the reactions, and explain the forward exothermic peak.

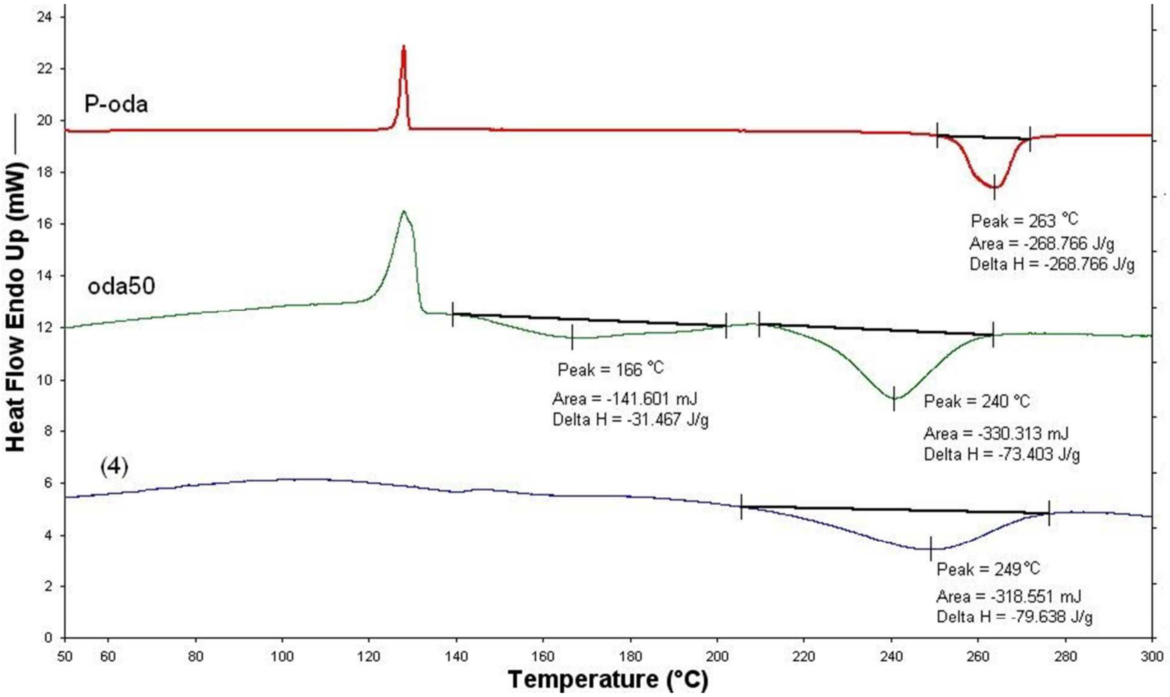
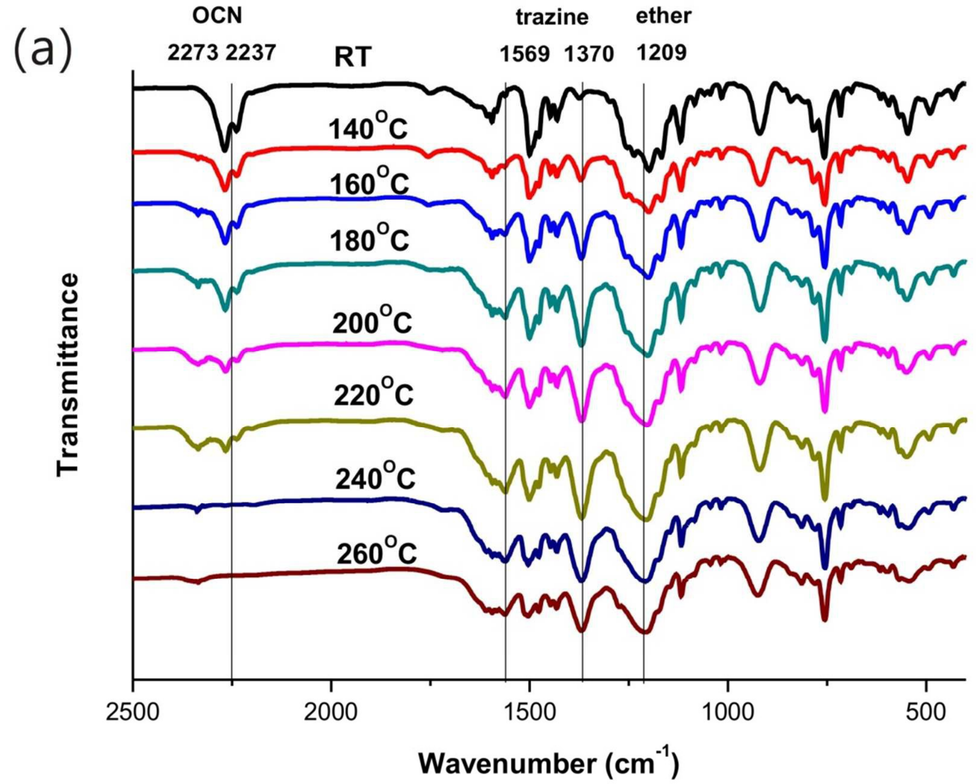


Figure 2. DSC thermograms of P-oda, oda50, and **(4)** at a heating rate of 10 ^{o}C/min.

Figure 3 shows the IR spectra of (a) **(4)** and (b) oda50 after accumulative curing at each stage for 20 min. For **(4)**, cyanate ester absorptions (2273 and 2237 cm^{-1}) decreased gradually at 180 ^{o}C and disappeared completely at 240 ^{o}C. Triazine absorptions (1370 and 1569 cm^{-1}) appeared after curing at 160 ^{o}C. For oda50, cyanate absorptions apparently disappeared at 140 ^{o}C. Compared with the cyanate ester absorption in Figure 3(a) in which cyanate ester absorptions remained at 200 ^{o}C, this result indicates that the cyclotrimerization of the cyanate ester of **(4)** was prompted in the presence of P-oda. This result is consistent with those reported by Nair et al.,[31]Kimura et al.,[32]Gu et al.[33], and Lin et al.[27] in the studies of cyanate ester/benzoxazine blend. It has been reported that the cyclotrimerization of cyanate ester can be catalyzed by the phenol group.[34-36] Therefore, it is speculated that the phenol, resulting from the ring-opened benzoxazine during preparation or during thermal curing, catalyzed the cyclotrimerization. However, in our recent work, we found that the tertiary amine of benzoxazine catalyzes the trimerization of cyanate ester.[37] These factors explain the forward trimerization of cyanate ester.



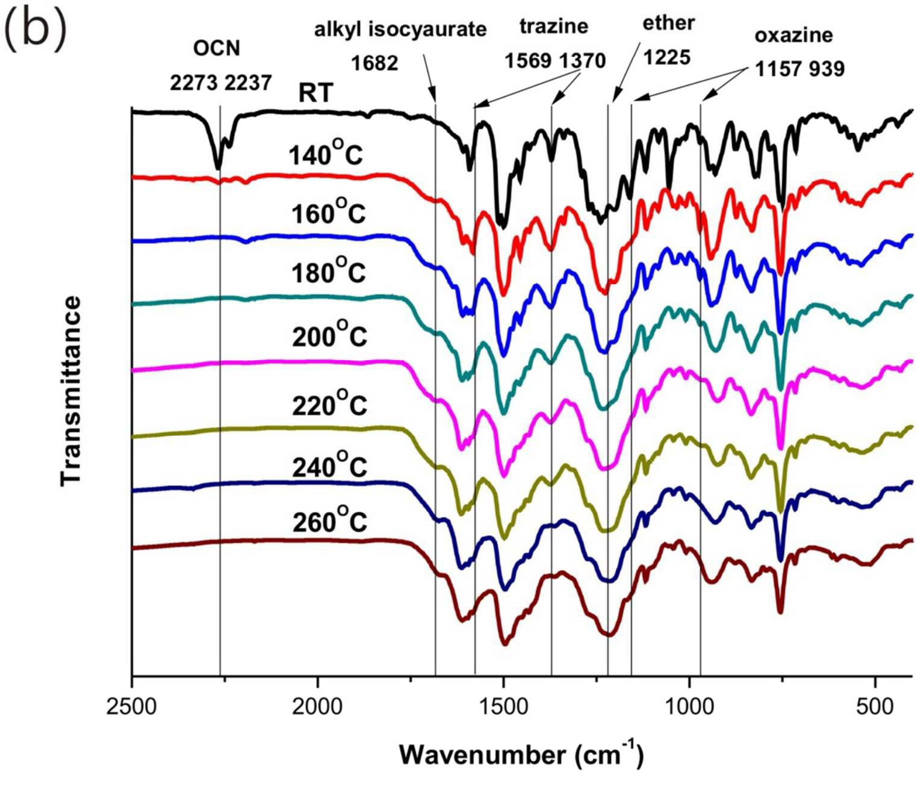
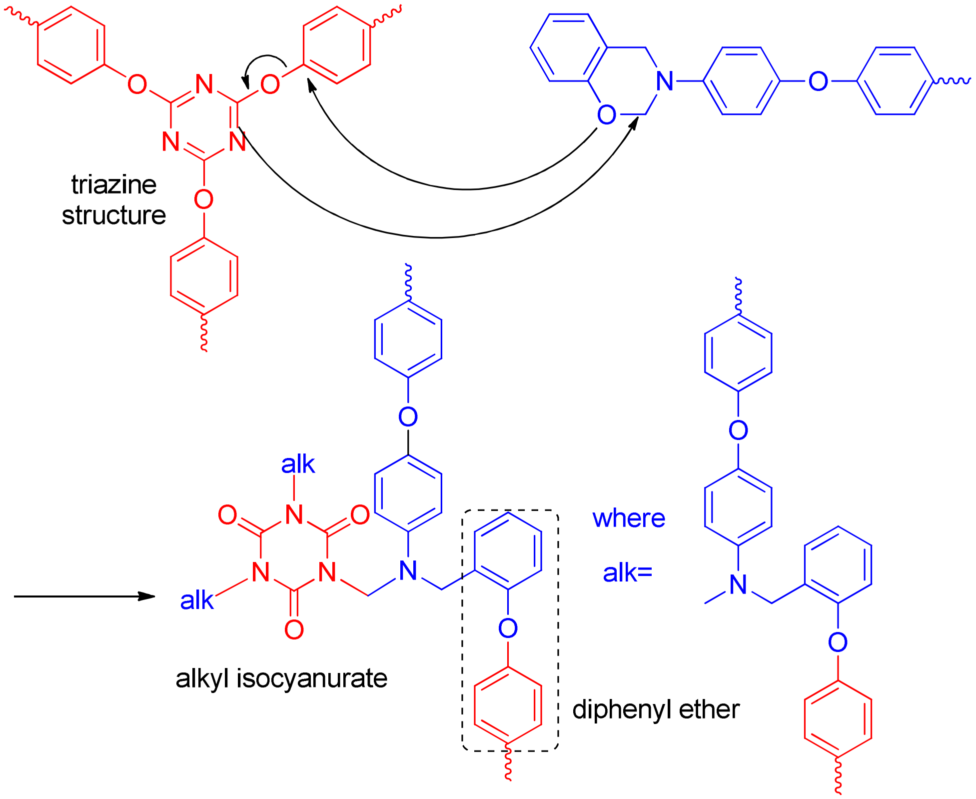


Figure 3. IR spectra of (a) **(4)** and (b) oda50 after accumulative curing at each stage for 20 min.

DMA data show a single T_g for the **(4)**/P-oda blend (see Figure 4), suggesting it is a homogeneous blend. As shown in Figure 3(b), triazine absorption (1370 cm^{-1}) of oda50 increased initially, but decreased gradually after 180 °C. In addition, new absorption was observed at 1682 cm^{-1} after curing at 140 °C. In contrast, strong triazine absorption at 1370 cm^{-1} remained after curing for **(4)**, and no absorption at around 1682 cm^{-1} was observed, as shown in Figure 3(a). The IR data support the concerted reaction between triazine and benzoxazine that has been suggested in our previous work.[27] As shown in Scheme 3, the electron-rich nitrogen of triazine attacks the electron-deficient methylene (O-**C**H_2-N) of benzoxazine, then, the electron-rich oxygen (CH_2-**O**-ph) attacks the aromatic carbon (Ar-O, which is electron-deficient due to the electron-withdrawing characterization of oxygen and triazine structure), forming an alkyl isocyanurate and a diphenyl ether (ph-o-ph) structure.



Scheme 3. Proposed concerted reaction mechanism between triazine and benzoxazine.

Figure 4 shows the DMA thermograms of **(4)**/P-oda copolymers. T_g taken from the peak temperature of tanδ increases with the content of **(4)**. A composition-dependent T_g indicates that **(4)**/P-oda blends are miscible blends, not composed of two immiscible IPN networks. In addition, the peak width of tanδ is reasonably narrow, further suggesting the homogeneous structure of the blends. The TAM thermograms (Figure 5) also support the miscibility. The co-reaction between triazine and benzoxazine, as shown in Scheme 3, is thought to be responsible for the miscibility.

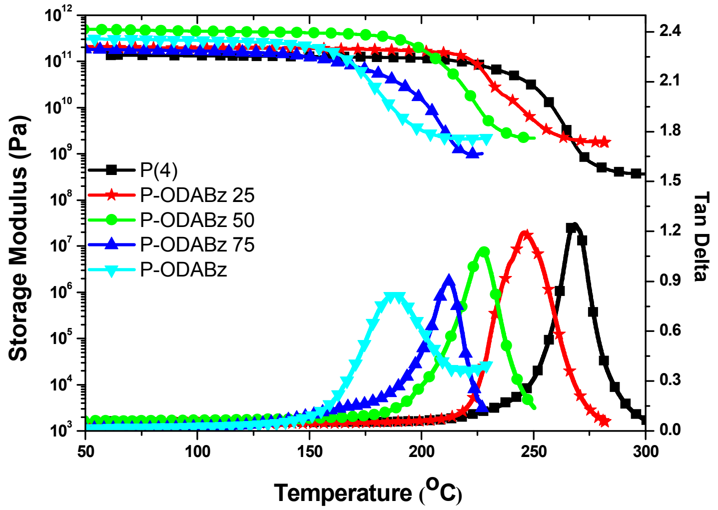


Figure 4. DMA thermograms of **(4)**/P-oda copolymers.

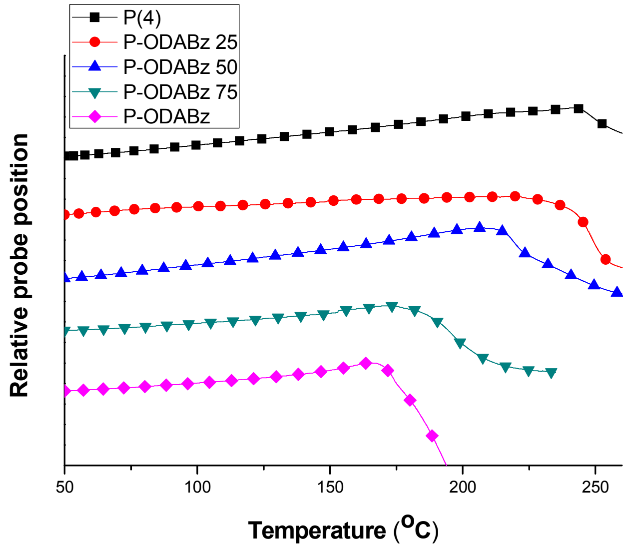


Figure 5. TMA thermograms of **(4)**/P-oda copolymers.

Thermal Stability and flame retardancy. Table 1 lists the TGA data of **(4)**/P-oda copolymers. The range of 5 wt% decomposition temperature ($T_{d5\%}$) and char yield of **(4)**/P-oda copolymers in a nitrogen atmosphere are 399-421^{o}C, and 41-45%, respectively. Char yield ranges from 41 to 49%. Generally, cyanate ester thermosets exhibit higher thermal stability than polybenzoxazines. TGA data show that the phosphorus element in **(4)** reduces the thermal stability slightly, due to the P-C bond possess a lower bonding energy. However, the value of 399 ^{o}C is relatively high compared with other phosphorus-containing polymers. Therefore, no obvious thermal stability-structure trend was observed. However, they all show moderate-to-high thermal stability. Table 1 also list the data of UL-94 measurement. The t_1 plus t_2 of copolymers decrease with the content of **(4)**, suggesting that the flame retardancy of copolymers was increased with the increase of phosphorus content. UL-94 V-0 grade can be obtained for Poda75, which contains 1.5 wt% of phosphorus element, demonstrating the excellent flame retardant characteristics of the blends.

Table 1. Thermal properties of **(4)**/P-oda copolymers.

Sample ID	T_g (^{o}C) (DMA)^{a}	T_g (^{o}C) (TMA)^{b}	$T_{d5\%}$ (^{o}C)^{c}	Char yield(%)^{d}	t_1^{e} (sec)	t_2^{f} (sec)	dripping	UL-94 grade
P**(4)**	268	242	399	49	1.5	1.2	No	V-0
Poda25	245	227	402	42	1.9	1.1	No	V-0
Poda50	227	213	407	44	2.2	1.4	No	V-0
Poda75	212	190	421	41	2.7	1.4	No	V-0
P(P-oda)	187	172	413	46	>60	-	No	Burning

a: Measured by DMA at heating rate of 5 ^{o}C/min; T_g were determined from a peak temperature of the tan δ curve.
b: Measured by TMA at a heating rate of 5^{o}C/min.
c: Temperature corresponding to 5% weight loss by thermogravimetry at a heating rate of 20 ^{o}C/min.
d:Residual weight % at 800 ^{o}C.
f: 1st burning time
g:2nd burning time

Dielectric constant and moisture absorption. Material with a low dielectric constant is known to enhance the signal propagating speed and reduce the signal propagating loss. Table 2 lists the dielectric constant of the **(4)**/P-oda copolymers. The dielectric constant at 1 GHz is 3.04 for P**(4)**, and 3.48 for P(P-oda). Incorporating 25 mole% P-oda in **(4)** results in the lowest D_k in the copolymers. According to the DSC thermograms (Figure 2) and IR spectra (Figure 3), the forward cyclotrimerization of cyanate ester leads the residual of high-polar cyanate ester to be rare in the copolymers, and explains the D_k being lower for Poda25 than P**(4)**.

Table 2. Dielectric constant and dissipation factor properties of copolymers.

Sample ID	1GHz		0.1GHz	
	D_k (U)[a]	D_f (mU)[b]	D_k (U)[a]	D_f (mU)[b]
P**(4)**	3.04±0.04	4.42±0.05	3.11±0.06	4.56±0.01
Poda25	2.95±0.06	3.61±0.01	3.01±0.02	3.69±0.12
Poda50	3.15±0.07	4.44±0.02	3.23±0.06	4.56±0.06
Poda75	3.24±0.01	6.31±0.03	3.30±0.01	6.37±0.07
P(P-oda)	3.48±0.02	7.99±0.10	3.49±0.01	8.09±0.10

a: Dielectric constant at 1GHz and 0.1 GHz, measured at 25 °C.
b: Dissipation factor at 1GHz and 0.1 GHz, measured at 25 °C.

Conclusion

We prepared a phosphinated tetracyanate ester **(4)** using two reaction routes (Schemes 1 and 2). The approach in Scheme 1 failed, probably due to the lower reactivity of bisphenol A in electrophilic substitution. Tetracyanate ester **(4)** was successfully prepared using the reaction route shown in Scheme 2, in which phenol was used as the electrophilic substitution. We investigated the curing behaviors, thermal, and dielectric properties of **(4)**/P-oda blends. DMA and TMA thermograms show one composition-dependent T_g, suggesting that the blends are miscible. According to DSC (Figure 2) and IR (Figure 3) analyses, we thought that the reactions between benzoxazine and cyanate ester, as shown Scheme 3, are responsible for the miscibility. Dielectric data show that Poda25 has the lower D_k and D_f than P**(4)**. The trimerization of cyanester ester in oda25 occurred at an early stage, so residual high-polar cyanate ester is rare in Poda25, explaining the lower D_k and D_f of Poda25 than those of P**(4)**. A UL-94 V-0 grade can be obtained for Poda75, which contains 1.5 wt% of phosphorus element, demonstrating excellent flame retardant characteristics of the blends.

Acknowledgment. The authors thank the Ministry of Science and Technologyof Taiwan for financial support.

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Graphical Abstract

Synthesis of a phosphinated tetracyanate ester and its miscible blend with 4,4’-oxydianiline/phenol-based benzoxazine

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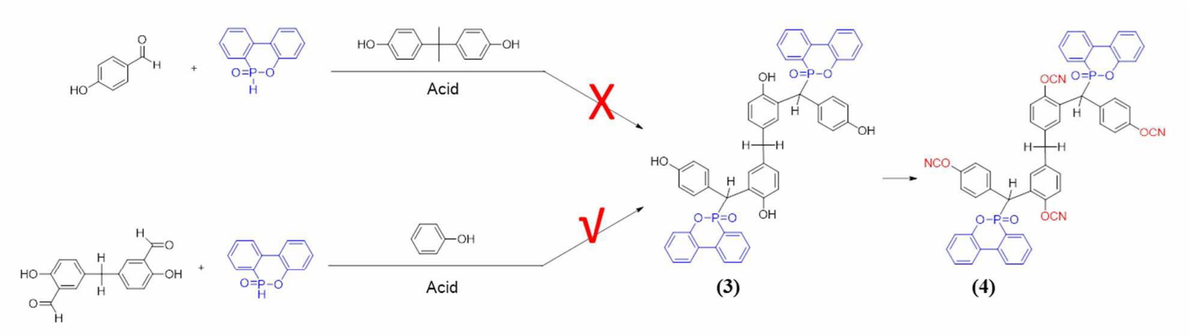

A phosphinated tetracyanate ester **(4)** was prepared and applied to copolymerize with a 4,4’-oxydianiline/phenol-based benzoxazine (P-oda) to enhance the properties of P-oda thermoset. We discussed the miscibility, microstructure, as well as the thermal and dielectric properties of the reactive blends of **(4)** with a P-oda. The experimental data show that the thermal, dielectric and flame retardant properties of polybenzoxazine are enhanced through the reactive blends.