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# Low Dielectric Thermoset from Redistributed Poly(phenylene oxide)

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A curable low-molecular-weight poly(phenylene oxide) (PPO) was prepared by the redistribution of regular PPO with bisphenol-A (BPA) followed by etherification of the redistributed-PPO (BPA-PPO) with N,N-diallyl-2-chloroacetamide. The redistributed-PPO with allyl group (AL-PPO) was characterized by proton nuclear magnetic resonance, and Fourier transform infrared spectroscopy. The AL-PPO oligomers with reactive double bonds were cured with triallylisocyanurate (TAIC) and/or phosphorus-containing allyl-functionalized monomer (allyl-DOPO). The glass transition temperatures were measured by dynamic mechanical analysis (DMA). Electrical properties of cured resins were studied using dielectric analyzer (DEA). The flame retardancy was determined by a UL-94 vertical test. The effects of curing accelerator, amount of TAIC and allyl-DOPO incorporated into the network on the glass transition temperatures, dielectric properties, and flame retardancy of the resulting systems were investigated. The results indicated that AL-PPO cured with TAIC exhibited high glass-transition temperature (162–198°C), low dielectric constants (2.36–2.57 at 1 GHz) and dissipation factors (0.0039–0.0043 at 1 GHz). The AL-PPO/TAIC copolymerized with allyl-DOPO could achieve a flame retardancy rating of UL-94 V-0 at about 1.35% phosphorus content. The AL-PPO/TAIC resins have potential applications in the fabrication of printed circuit board.

**Keywords:** Poly(phenylene oxide), curing of polymers, thermosets, dielectric properties, Thermal properties

## 1. Introduction

It is known that the signal propagating speed in an integrated circuit is inversely proportional to the square root of the dielectric constant, and the signal propagation loss is proportional to the square root of the dielectric constant and dissipation factor (1–2). In particular, for high frequency applications, printed wiring boards with low dielectric characteristics are required for the purpose of increasing signal transmission speed and minimizing signal transmission loss. Conventional printed circuit boards made from glass-fiber reinforced epoxy resins often fall short of the thermal and electric performance demands of many modern high-speed devices (1–5).

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has excellent physical properties such as mechanical properties, high dimensional stability, low moisture uptake, high thermal

stability, low flammability, along with exceptional electrical properties, such as low dielectric constant and a low dielectric dissipation factor. In view of these characteristics (6–9), thermoplastic PPO would be an excellent candidate as a material for high frequency electronic substrates. However, high-molecular-weight thermoplastic PPO resin has a number of deficiencies such as poor processability, high melt viscosity, poor solvent resistance, and fail to meet UL-94 V-0 rating (electronic grade) by itself (10).

In order to overcome these deficiencies of PPO resin for electronic applications, in this study, an allyl-containing low-molecular-weight PPO (AL-PPO) was prepared by the redistribution reaction between commercially available PPO and bisphenol-A (BPA) in the presence of a radical initiator benzoyl peroxide (BPO). The resulting low molecular weight PPO with terminal phenolic hydroxyl groups is further reacted with N,N-diallyl-2-chloroacetamide to form the allyl functionalized-PPO (AL-PPO). AL-PPO with reactive double bonds was cured with triallylisocyanurate (TAIC) at various weight ratios in the presence of triphenylphosphine (TPP) or cumene hydroperoxide (PO) as a curing promoter. The resulting crosslinked AL-PPO/TAIC resins were expected to have low dielectric constant and dissipation factor because of the incorporation of low

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dielectric PPO linkage while hoping to retain the attractive glass transition temperature ( $T_g$ ) of cured resin. Phosphorus-containing allyl-functionalized monomer (allyl-DOPO) with reactive allyl group and organophosphorus moiety was used as potential flame retardant and copolymerized with the above AL-PPO/TAIC through double bond reaction. Improvement in flame retardancy of cured AL-PPO/TAIC was expected by the incorporation of the additional nitrogen atom (from TAIC) and phosphorus atom (from allyl-DOPO) into cured resins.

## 2. Experimental

### 2.1. Materials

Chloroacetyl chloride from Ferak, diallylamine, benzoyl peroxide (BPO) from Lancaster, tetra-butylammonium hydrogen sulfate, allyl-bromide, triallylisocyanurate (TAIC), triphenylphosphine (TPP) from Acros, cumene hydroperoxide (PO) from Aldrich, 9,10-dihydro-oxaphosphaphenanthrene 10-oxide (DOPO) from Forte Chem., were all used as received. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) ( $M_n = 13000$ ,  $M_w/M_n = 2.1$ ) was kindly supplied by Chang Chun Chem. Co. All other solvents were obtained from various commercial sources and used without further purification.

### 2.2. Monomer synthesis

#### 2.2.1. Synthesis of *N,N*-diallyl-2-chloroacetamide (*N*-Cl)

To a 500-mL four-necked flask was charged chloroacetyl chloride (0.11 mol) and 100 ml toluene. The solution was stirred with a mechanical stirrer and maintained at 0°C. Under nitrogen atmosphere, diallylamine (0.1 mol) was added dropwise into a flask over a period of 1 h. After the addition was completed, the reaction was maintained at room temperature for another 18 h. The solution was washed with water and then the solvent was removed. *N*-Cl: IR (KBr)  $\text{cm}^{-1}$ : 3075 (olefinic C–H stretching), 1670–1640 (C=C and C=O stretching), 990, 930 (olefinic C–H bending), 640 (C–Cl stretching).  $^1\text{H-NMR}$   $\delta$  (ppm): 5.68–5.94 (m,  $-\text{CH}=\text{}$ , 2H), 5.19 (m,  $=\text{CH}_2$ , 4H), 4.25 (s,  $\text{Cl}-\text{CH}_2-$ , 2H), 3.99 (d,  $\text{N}-\text{CH}_2-$ , 4H). Elemental analyses for  $\text{C}_8\text{H}_{12}\text{ClNO}$  are as follows: C: 55.33%, H: 6.92%, N: 8.07%, O: 9.22% (theoretically) and C: 55.15%, H: 6.95%, N: 8.12%, O: 9.20% (experimentally).

#### 2.2.2. Redistribution of PPO with bisphenol-A (*BPA*-PPO)

40 g of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was dissolved in 100 ml toluene at 90°C in nitrogen. Subsequently, 4 g of bisphenol-A (BPA) was added, and then 4 g benzoyl peroxide (BPO) was added portionwise. After maintaining the reaction at 90°C for another 3 h, the mixture was allowed to cool to room temperature and was added to methanol to precipitate the product. The

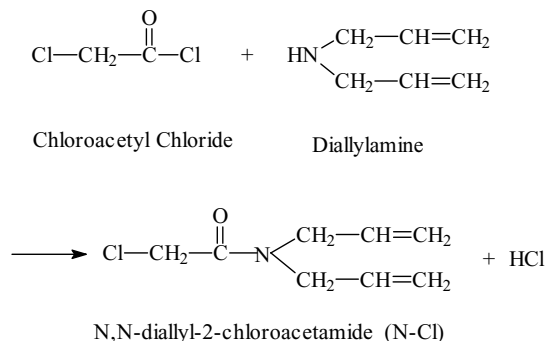
pale-yellow precipitate was collected by filtration, washed with aqueous  $\text{Na}_2\text{CO}_3$  solution and then dried in a vacuum oven at 110°C. The dried product was ground to powder, washed with methanol several times, and finally dried at 70°C in vacuum. *BPA*-PPO: IR (KBr)  $\text{cm}^{-1}$ : 1620 (aromatic C–C stretching), 1740, 1725 (C=O stretching), 1465 (methyl C–H bending), 1180, 1020 (C–O stretching).  $^1\text{H-NMR}$   $\delta$  (ppm): 8.22 (s, *BPA*-OH, 1H), 6.79–7.01 (m, Ar-H belong to *BPA*, 8H), 6.55 (s, Ar-H belong to PPO), 2.19 (s, PPO- $\text{CH}_3$ ), 1.7 (s, *BPA*- $\text{CH}_3$ , 6H).

#### 2.2.3. Preparation of allyl-containing redistributed-PPO (*AL*-PPO)

25 g of the above redistributed-PPO (*BPA*-PPO) was dissolved in 250 ml dichloromethane, and 5 g of 50% aqueous NaOH was added. Under vigorous stirring, 2.5 g of tetra-butylammonium hydrogen sulfate was added, followed by dropwise addition of 16.5 g of *N,N*-diallyl-2-chloroacetamide (*N*-Cl) at room temperature. After the addition was completed, the reaction mixture was maintained at room temperature for another 15 h. The organic layer was washed with water and saturated sodium chloride solution, followed by the removal of solvent under vacuum to obtain the product. The weight average molecular weight of the allyl-containing redistributed PPO was 3050 g/mol determined by using gel permeation chromatography (GPC). IR (KBr)  $\text{cm}^{-1}$ : 1620 (aromatic C–C stretching), 1655 (C=C and C=O stretching), 1465 (methyl C–H bending), 1180, 1020 (C–O stretching).  $^1\text{H-NMR}$   $\delta$  (ppm): 6.76–7.25 (m, Ar-H belong to *BPA*, 8H), 6.47 (s, Ar-H belong to PPO), 5.8 (m,  $-\text{CH}=\text{}$ , 2H), 5.2 (m,  $\text{H}_2\text{C}=\text{}$ , 4H), 4.41 (s,  $\text{O}-\text{CH}_2-\text{C}$ , 2H), 4.00 ( $\text{R}_2-\text{N}-\text{CH}_2-$ , 4H), 2.09 (s, PPO- $\text{CH}_3$ ), 1.69 (s, *BPA*- $\text{CH}_3$ ).

#### 2.2.4. Synthesis of allyl-DOPO

Into a reactor equipped with a stirrer, a reflux condenser, a thermometer, a Dean-Stark water separator, and a nitrogen inlet were charged 250 mL of xylene and 50 g DOPO. Under nitrogen atmosphere, water was removed from the system by azeotroping with xylene. After 3 h, no more removed water was collected. Anhydrous DOPO was obtained after the removal of solvent under vacuum. 0.1 mol of DOPO, 0.11 mol of allyl-bromide, 0.11 mol of triethylamine and 300ml of methanol were charged into a 500 mL four-necked flask. The reaction mixture was heated to reflux for 8 h under nitrogen atmosphere. After completion of the reaction, the solvent and unreacted monomers were removed under vacuum. The residual yellow solid was stirred with water and the suspending solid was collected by filtration and dried. Allyl-DOPO: IR (KBr)  $\text{cm}^{-1}$ : 3045 ( $=\text{C}-\text{H}$  stretching), 2910 ( $\text{CH}_2$ , C–H stretching), 1610 (C=C stretching), 1445 (P–C), 1195 (P=O), 945, 760 (P–O–Ph).  $^1\text{H-NMR}$   $\delta$  (ppm): 6.8–8.1 (m, Ar-H), 3.8 (d, P- $\text{CH}_2$ , 2H), 5.5 (m,  $=\text{CH}_2$ , 2H), 5.8 (m,  $-\text{CH}=\text{}$ , 1H). Elemental analyses for  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{P}$  are as follows: C: 70.31%, H: 5.08%, O: 12.50%



Sch. 1. The synthetic equation of N,N-diallyl-2-chloroacetamide.

(theoretically) and C: 70.18%, H: 5.17%, O: 12.62% (experimentally).

### 2.3. Characterization

The GPC measurements were obtained with Shimadzu gel permeation chromatography (GPC). Molecular weight of the samples was calculated on the basis of polystyrene standards.  $^1\text{H-NMR}$  spectra were registered using a Bruker AMX-400 spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magna-520 spectrometer. Spectra in the optical range of  $400\sim 4000\text{ cm}^{-1}$  were obtained by averaging 16 scans at a resolution of  $4\text{ cm}^{-1}$ . DMA was carried out with a Perkin-Elmer DMA 7e. The  $\tan \delta$  was determined as the sample subjected to

temperatures scan mode at a programmed heating rate of  $10^\circ\text{C}/\text{min}$  from ambient to  $200^\circ\text{C}$  at a frequency of 1 Hz and an amplitude of  $6\text{ }\mu\text{m}$ . Dielectric measurements were performed with an Agilent 4291B measurement system at 1 GHz. The applied voltage is 1 volt. Before testing, samples were dried under vacuum at  $100^\circ\text{C}$  for 8 h. The UL-94 vertical test was performed according to the testing procedure of FMVSS 302/ZSO 3975 with a test specimen bar 127 mm long, 12.7 mm wide, and about 1.27 mm thick.

### 2.4. Preparation of resin formulation and their curing procedure

The AL-PPO was dissolved in toluene, and then formulated with TAIC to various weight ratios (AL-PPO: TAIC=1:1, 1.5:1, 2:1), respectively, to evaluate the effect of the content on the physical properties of cured products. The mixture was heated with continuous stirring until a homogeneous solution was obtained. Finally, TPP or PO (by total weight) was added as accelerator at room temperature and stirred until a homogeneous solution was achieved. The mixture was vacuumed to drive off the toluene. The homogeneous mixture was poured into aluminum trays and cured in oven under atmospheric pressure at  $160^\circ\text{C}$  for 4 h,  $185^\circ\text{C}$  for 4 h, and further post cured at  $210^\circ\text{C}$  for 4 h for AL-PPO/TAIC series. The allyl-DOPO was formulated (12.5 wt% based on total weight of AL-PPO/TAIC) to study the flame retardant properties of cured products. The allyl-DOPO modified AL-PPO/TAIC systems were cured at  $100^\circ\text{C}$  for 4 h,  $130^\circ\text{C}$  for 4 h, and post cured at  $150^\circ\text{C}$  for 4 h.

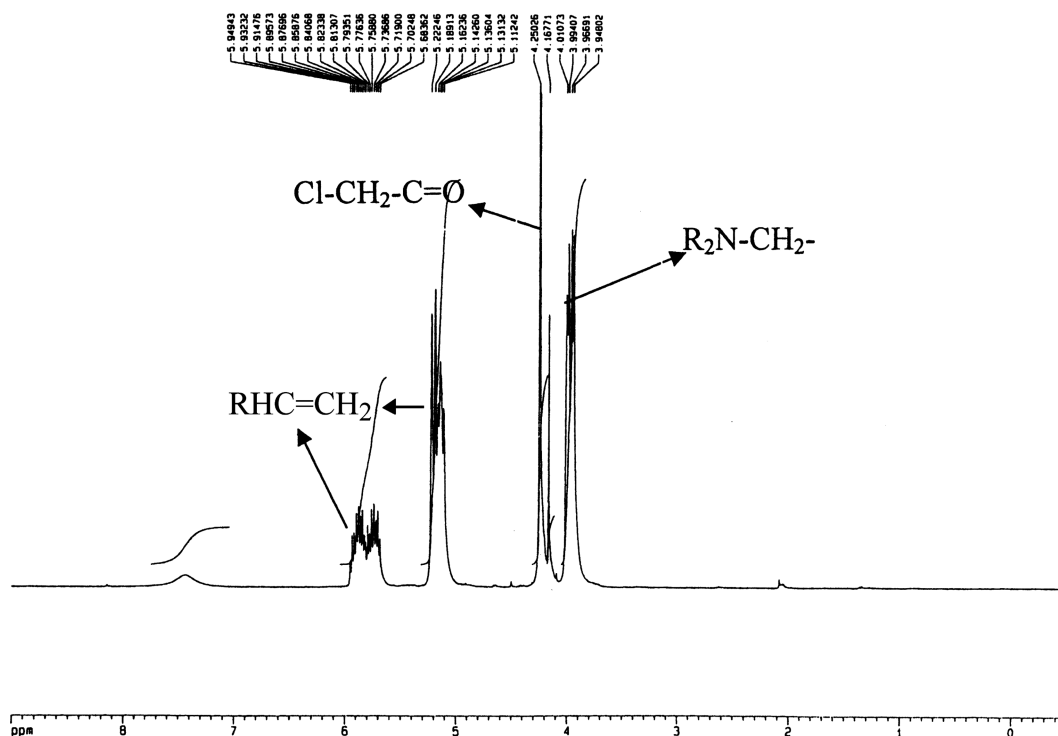
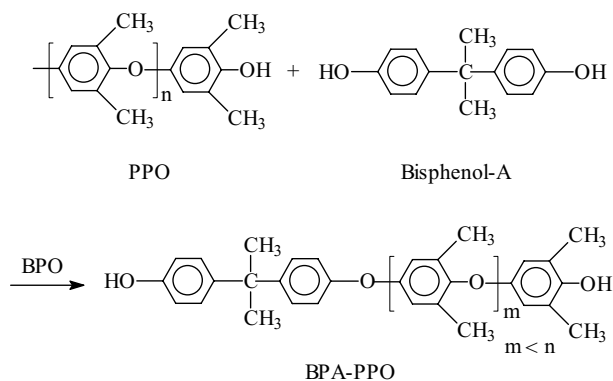


Fig. 1.  $^1\text{H-NMR}$  spectrum of N,N-diallyl-2-chloroacetamide (N-CL).



Sch. 2. The synthetic equation of redistributed-PPO(BPA-PPO).

### 3. Results and discussion

#### 3.1. Monomer synthesis

The *N,N*-diallyl-2-chloroacetamide (N-Cl) was synthesized from chloroacetyl chloride and diallylamine at low temperature as shown in Scheme 1. The diallylamine was fed slowly to maintain the reaction at the desired rate. The infrared spectrum of the *N,N*-diallyl-2-chloroacetamide exhibited several distinctive absorption. The *N,N*-diallyl-2-chloroacetamide showed strong overlap absorption at 1640–1670  $\text{cm}^{-1}$ , assigned to C=C and O=C stretching. The absorption associated with the O=C–Cl and HN-R<sub>2</sub>,

respectively, have disappeared, while 640  $\text{cm}^{-1}$  for C–Cl stretching has appeared. <sup>1</sup>H-NMR spectrum was shown in Figure 1. The integration matched the expected spectrum.

The redistributed-PPO (BPA-PPO) was synthesized in one step as shown in Scheme 2. Low-molecular-weight PPO can be prepared in the presence of BPO as an initiator for free-radical redistribution reaction (11–13). The decrease in molecular weight during the redistribution reaction was traced by GPC. The new peak appeared at higher retention time in comparison to the starting material PPO, being assigned to the redistributed-PPO with lower molecular weight. From Figure 2, the methyl proton (–CH<sub>3</sub>), the phenolic hydrogen (Ar–H) and OH proton at  $\delta$ 1.7,  $\delta$ 6.79~7.01 and  $\delta$ 8.22, respectively, were observed for the bisphenol-A tail-end group of the redistributed-PPO.

The allyl-functionalized PPO (AL-PPO) was obtained by the reaction between the terminal phenolic OH group of the redistributed PPO and *N,N*-diallyl-2-chloroacetamide in the presence of a phase transfer catalyst. The synthetic equation is shown in Scheme 3. The conversion of the BPA-PPO to the desired AL-PPO was confirmed by the <sup>1</sup>H-NMR spectrum as shown in Figure 3. The hydrogen proton of vinyl group appeared at  $\delta$ 5.2 ppm and  $\delta$ 5.8 ppm. The peak of (–Cl–CH<sub>2</sub>–C=O) at 4.25 ppm in Figure 1 is shifted downfield to 4.41 ppm in Figure 3, which indicates the formation of the (–O–CH<sub>2</sub>–C=O) in AL-PPO, while the phenolic hydroxy proton of BPA had disappeared. The redistributed-PPO possesses two characteristic bands of the

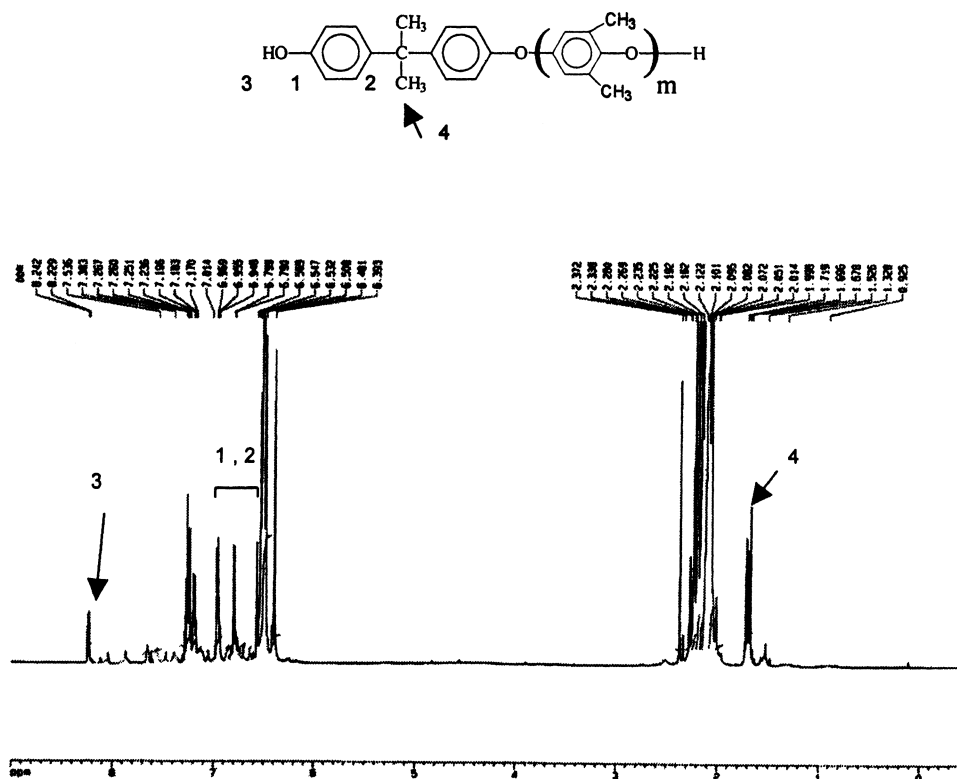
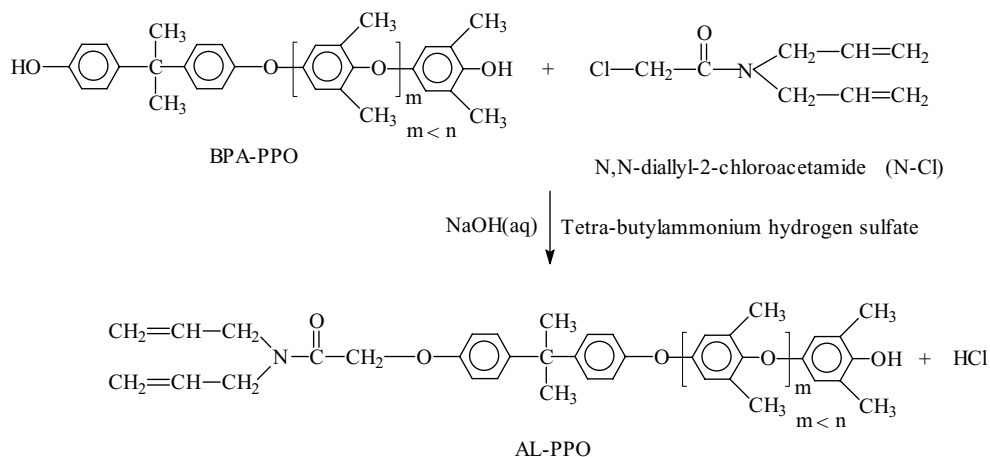


Fig. 2. <sup>1</sup>H-NMR spectrum of the redistributed-PPO (BPA-PPO).



**Sch. 3.** The synthetic equation of AL-PPO.

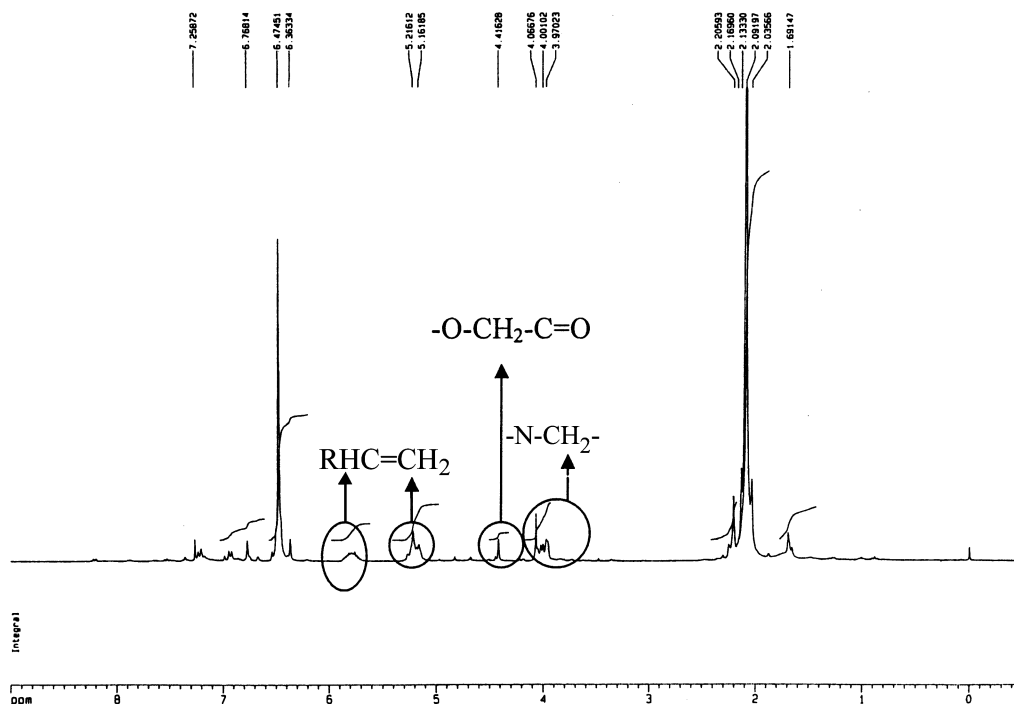
phenylene ether at 1020 and 1180  $\text{cm}^{-1}$ , corresponding to the C—O stretching. The aromatic ring stretching of these PPO give absorption at 1620  $\text{cm}^{-1}$ . Comparing the FT-IR spectrum of AL-PPO with that of the BPA-PPO, the small difference at around 1655  $\text{cm}^{-1}$  for C=C and C=O stretching was observed. The results were in good agreement with the proposed structures.

The synthetic equation of phosphorus-containing allyl-functionalized monomer (allyl-DOPO) is described in Scheme 4. The allyl-DOPO was synthesized from the DOPO and allyl bromide in the presence of triethylamine as an acid acceptor using methanol as a solvent. The infrared

spectra of DOPO and allyl-DOPO exhibited several distinctive differences. The P-H group absorption at 2350  $\text{cm}^{-1}$  for DOPO has disappeared. In addition, the peak assigned to P-C (aliphatic) stretching absorption at around 1445  $\text{cm}^{-1}$  appeared. Consequently, this reaction could be monitored by means of these absorptions.

### 3.2. Glass transition temperatures of polymers

The  $T_g$  values of all cured AL-PPO/TAIC resins with various weight ratios were listed in Table 1. The typical dynamic mechanical properties of the cured AL-PPO/TAIC



**Fig. 3.**  $^1\text{H-NMR}$  spectrum of the AL-PPO.

**Table 1.** Glass transition temperature and dielectric properties for various weight ratios of AL-PPO/TAIC resins

Sample ID	Catalyst	AL-PPO/TAIC (weight ratio)	Allyl-DOPO Content (wt%)	T <sub>g</sub> (°C)	Dielectric constant D <sub>k</sub> (U) at 1 GHz	Dissipation factor D <sub>f</sub> (U) at 1 GHz
AT-T1	TPP	1	0%	162	2.37	0.0042
AT-T2		1.5	0%	165	2.56	0.0041
AT-T3		2	0%	167	2.57	0.0043
AT-P1	PO	1	0%	178	2.36	0.0040
AT-P2		1.5	0%	184	2.43	0.0039
AT-P3		2	0%	198	2.55	0.0040
AT-P-T1	TPP	1	12.5%	134	3.23	0.0554
AT-P-T2		1.5	12.5%	145	3.42	0.0572
AT-P-T3		2	12.5%	148	3.61	0.0584
AT-P-P1	PO	1	12.5%	149	2.82	0.0528
AT-P-P2		1.5	12.5%	155	3.12	0.0542
AT-P-P3		2	12.5%	158	3.34	0.0559

are indicated in Figure 4. The T<sub>g</sub>s ranged from 162~167°C for TPP systems, 178~198°C for PO systems, respectively. The PO promoted systems exhibited higher curing efficiency than those of the corresponding TPP systems. Similar tendencies were observed in the allyl-DOPO containing systems. The glass transition temperatures of cured resins increased with the AL-PPO weight ratio. This result may be attributed to the rigid PPO structure.

The glass transition temperatures of allyl-DOPO modified resins (134~148°C for TPP systems, 149~158°C for PO systems) were lower than those of the corresponding AL-PPO/TAIC systems. The results may be attributed to the fact that the addition of monofunctional allyl-DOPO into AL-PPO/TAIC has reduced its crosslink density. The bulky phosphorus-containing cyclic structure of DOPO group also led to more spacing between the polymer molecules (14), and resulted in less efficient chain packaging and an increase in the free volume of the polymer, which reduced

the glass transition temperature of the allyl-DOPO modified AL-PPO/TAIC systems.

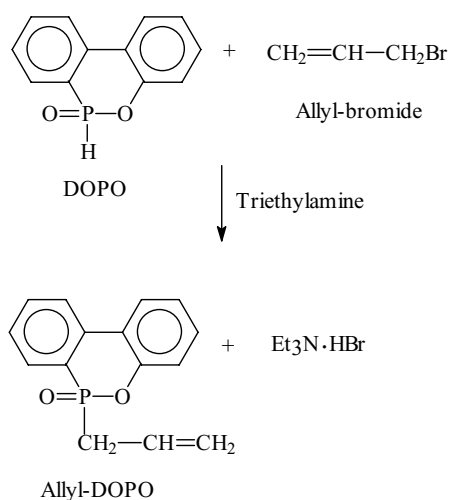
### 3.3. Dielectric constant and dissipation factor

From Table 1, the dielectric constants and dissipation factors of cured AL-PPO/TAIC resins at 1 GHz ranged from, 2.36–2.57 and 0.0039–0.0043, respectively. No matter how much weight ratio of AL-PPO/TAIC was used, the dielectric constant and dissipation factor of the PO systems were lower than those of the TPP systems. The dielectric characteristic of all AL-PPO/TAIC systems were significantly lower than that of the FR-4 resin (D<sub>k</sub> = 4.7–5.0 D<sub>f</sub> = 0.015–0.019) (7). This could be attributed to the low polar and hydrophobic structure of PPO chain.

The dielectric constant and dissipation factor slightly decreased with the increasing content of TAIC. The dielectric constant could be reduced by an increase in the free volume of the molecule or by a decrease in the polarization (15–17). TAIC monomer with reactive allyl group will self-polymerize to form linear linkage, which led to more spacing between the polymer molecules, and this may resulted in an increase in the free volume of the polymer (18), which reduced the dielectric constant and dissipation factor of the AL-PPO/TAIC system. The introduction of relatively high polar allyl-DOPO into AL-PPO/TAIC resin systems results in higher dielectric constant (D<sub>k</sub> = 2.82–3.42) and dissipation factor (D<sub>f</sub> = 0.0528–0.0584) than those of the other AL-PPO/TAIC resin systems. This may be attributed to the high polar sites (O=P–O groups) of allyl-DOPO in the cured resins.

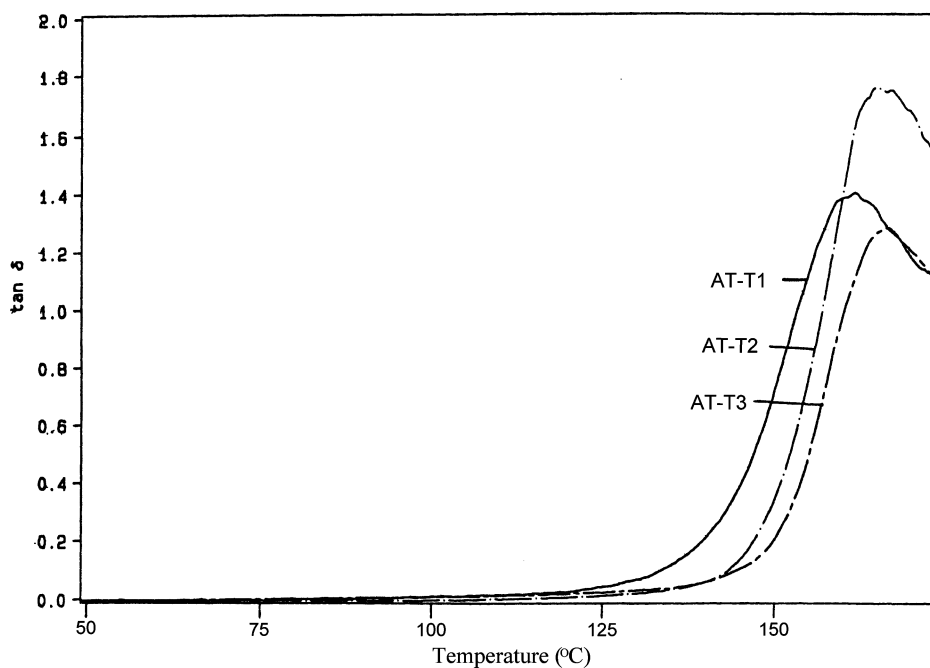
### 3.4. UL-94 measurements

UL-94 is a testing method for flame retardancy. As shown in Table 2, the UL-94 rating improves from V-1 grade for AL-PPO/TAIC series to V-0 grade for allyl-DOPO modified series. In the AL-PPO/TAIC series, the increase in

**Sch. 4.** The synthetic equation of Allyl-DOPO.

**Table 2.** UL-94 test for various weight ratios of AL-PPO/TAIC resins

Sample ID	Catalyst	AL-PPO/TAIC (weight ratio)	Allyl-DOPO Content (wt %)	P/N (wt%)	t1 (sec)	t2 (sec)	t1 + t2 (sec)	UL-94
AT-T1	TPP	1	0%	0/8.66	5	11	16	V-1
AT-T2		1.5	0%	0/7.02	4	10	14	V-1
AT-T3		2	0%	0/5.93	3	8	11	V-1
AT-P1	PO	1	0%	0/8.66	12	15	27	V-1
AT-P2		1.5	0%	0/7.02	10	14	24	V-1
AT-P3		2	0%	0/5.93	9	12	21	V-1
AT-P-T1	TPP	1	12.5%	1.35/7.70	0	1	1	V-0
AT-P-T2		1.5	12.5%	1.35/6.24	0	0	0	V-0
AT-P-T3		2	12.5%	1.35/5.27	0	0	0	V-0
AT-P-P1	PO	1	12.5%	1.35/7.70	0	3	3	V-0
AT-P-P2		1.5	12.5%	1.35/6.24	0	1	1	V-0
AT-P-P3		2	12.5%	1.35/5.27	0	0	0	V-0

**Fig. 4.** Typical DMA scans of AL-PPO/TAIC mixture cured at various weight ratios.

nitrogen content (from 5.93% to 8.66%) with increasing weight ratio of the TAIC (TAIC contains nitrogen atom) did not show a significant effect in increasing the flame retardancy by the UL-94 test. The UL-94 V-1 properties of AL-PPO/TAIC may be originated from PPO. As expected, the addition of allyl-DOPO had effectively enhanced the flame retardancy of AL-PPO/TAIC systems. A UL-94 V-0 rating can be achieved with phosphorus content of 1.35 wt% for the AL-PPO/TAIC system. However, it is especially noteworthy that the cured phosphorus-containing allyl-DOPO modified AL-PPO/TAIC resins have exhibited excellent flame retardancy, which may be attributed to the phosphorus-nitrogen synergistic effect.

#### 4. Conclusions

The redistributed-PPO with allyl group (AL-PPO) was synthesized. A series of thermally crosslinkable low-molecular-weight AL-PPO/TAIC resins were prepared. Because of the low polarity and hydrophobic nature of PPO, the cured AL-PPO/TAIC resins exhibited pretty low dielectric constant and dissipation factor. All AL-PPO/TAIC resins still retain good thermal properties. Furthermore, the AL-PPO/TAIC copolymerized with phosphorus-containing allyl-DOPO series had offered excellent flame retardancy. A UL-94 V-0 rating can be achieved with phosphorus content of 1.35% for AL-PPO/TAIC. The



combination of low dielectric constant, low dissipation factor, V-0 rating flame-retardancy with good thermal properties should make AL-PPO/TAIC resins attractive for practical application such as flame-retardant laminates.

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