Phosphinated Poly(aryl ether)s with Acetic/Phenyl Methacrylic/Vinylbenzyl Ether Moieties for High-\(T_g\) and Low-Dielectric Thermosets

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ABSTRACT: To achieve insulating materials with a low-dielectric characteristic for high-frequency communication applications, three phosphinated poly(aryl ether)s: P1-act (with acetic moiety), P1-mma (with phenyl methacrylic moiety), and P1-vbe (with vinylbenzyl ether moiety) were modified from a phenol-functionalized phosphinated poly(aryl ether) (P1). P1-act and P1-mma, both with active ester linkages (Ph−O−(C==O)−), were reacted with three commercial epoxy resins (diglycidyl ether of bisphenol A, HP7200, and cresol novolac epoxy) to obtain secondary hydroxyl-free epoxy thermosets. Because of the secondary hydroxyl-free structure, epoxy thermosets cured by P1-act and P1-mma show an 11–15% reduction in dielectric constant than those cured by P1. P1-vbe, with reactive vinylbenzyl ether moieties, was self-cured to a high-performance thermoset with a \(T_g\) value as high as 302 °C and a dielectric constant as low as 2.64\(U\). High-\(T_g\) and low-dielectric thermosets have been developed in this work.

INTRODUCTION

Epoxy resins are widely used in the electronic field such as encapsulation and printed circuit boards (PCBs) because of their good chemical resistance, adhesion, insulation, and dimensional stability after thermally curing. It is known that the propagating speed in an integrated circuit is inversely proportional to the square root of dielectric constant (\(D_s\)); the dielectric loss (\(L\)) is proportional to the product of square root of frequency, dielectric constant (\(D_s^{1/2}\)), and dissipation factor (\(D_f\)). Therefore, a material with a low dielectric value will exhibit a high signal propagating speed and a low signal propagating loss. Generally, epoxy resins are cured by reacting the epoxy groups with active hydrogen-containing compounds such as phenol novolac, diamine, or thiol. The reaction of active hydrogens with epoxy leads to secondary alcohol-free epoxy thermosets. Nishikubo et al. studied thermo-cross-linking reactions of active esters with epoxy-containing polymers. The resulting epoxy thermosets show better dielectric properties than those cured by active hydrogen-containing compounds. DIC (Dainippon Ink and Chemicals) has produced EPICLON HPC-8000, a dicyclo-di-pentadiene phenol novolac-based active ester for low-dielectric epoxy thermosets. Japan Epoxy Resins has developed DC808, a phenol novolac-based active ester for the same purpose. SABIC (Saudi Basic Industries Corporation) has developed a phenyl methacrylate end-capped oligo(2,6-dimethyl phenylene oxide), NORYL SA9000 (Figure 1a), for the low-dielectric PCB. The key application areas of NORYL SA9000 are in electronic packaging including PCB laminates, copper clad laminates, nonepoxy prepregs, and adhesives. NORYL SA9000 is designed to react with unsaturated monomers, styrenic, allylic, acrylic, maleimide, methacrylic, and unsaturated polyesters through free-radical reactions. It has an advantage in insulating materials, where very low dielectric constant and moisture absorption are required. Except phenyl methacrylate end capping, MGC (Mitsubishi gas chemical) has developed a vinylbenzyl ether end-capped oligo(2,6-dimethyl phenylene oxide), OPE-2st (Figure 1b). The thermostat of the OPE-2st exhibits a low dielectric constant of 2.65\(U\) and a very low dissipation factor of 0.005\(U\).

In our previous work, we have reacted phenyl methacrylate and glycidyl phenyl ether in the presence of 4-dimethylamino-pyridine (DMAP), and the reaction product is exclusive 1,3-diphenoxo-2-methacrylatepropane (Figure 2). On the basis of

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Figure 2, we understand the reaction mechanism of phenyl methacrylate and with epoxy in the presence of DMAP.

![Figure 1: Structure of (a) SA9000 and (b) OPE-2st.](image1)

For the low-dielectric PCB, poly (aryl ether)s also have low-dielectric characteristics compared to other polymer materials. For example, Wang et al. prepared a series of poly(aryl ether)s, and their dielectric constants are in the range of 2.5–3.0. In our previous work, we have successfully prepared a phenol-functionalized phosphinated poly (aryl ether) (P1). P1, with phenolic linkages, can react with cresol novolac epoxy (CNE) to get a transparent and flexible thermosetting film with a high Tg value (250 °C), a moderate dielectric constant (3.10), and flame retardancy (VTM-0). However, the secondary alcohols, resulted from the reaction of an epoxy group and the phenolic hydroxyl of P1, hinder P1-cured epoxy thermoset to be low-dielectric. To prepare epoxy thermosets with better dielectric properties, we modify P1 to polyether with acetic moieties (P1-act), with phenyl methacrylic moieties (P1-mma), and with vinylbenzyl ether moieties (P1-vbe) by respectively reacting P1 with acetic anhydride, methacrylic anhydride, and 4-chloromethyl styrene. P1-act, with an acetic structure, is definitely an active ester-type curing agent. P1-mma, with a phenyl methacrylic structure, can also react with epoxy resins (based on the finding of Figure 2). Therefore, in this work, P1-act and P1-mma are applied to react with epoxy resin to form secondary hydroxyl-free epoxy thermosets. P1-vbe, with reactive vinylbenzyl ether moiety, was self-cured to a low-dielectric thermoset. Detailed synthetic procedures, structure analysis, and thermal and dielectric properties of the resulting thermosets are provided.

## RESULTS AND DISCUSSION

**Synthesis of P1-act.** P1-act was synthesized from the reaction of P1 and acetic anhydride in the presence of a catalyst. Sodium acetate, DMAP, and pyridine have been tested as the catalyst for the synthesis (Table 1). We found that the optimal reaction is reacting in N,N-dimethyl acetamide (DMAc) at 130 °C for 12 h in the presence of 1 wt % sodium acetate (run 5). 1H NMR spectrum of P1-act (Figure 3b) shows the disappearance of the hydroxyl peak at 9.4 ppm and appearance of the acetic peak at 2.2 ppm. IR spectrum (Figure S1) shows

![Figure 2: Reaction of glycidyl phenyl ether with phenyl methacrylate in the presence of DMAP.](image2)

![Figure 3: 1H NMR spectra of (a) P1, (b) P1-act, (c) P1-mma, and (d) P1-vbe.](image3)

| run | catalyst (amount) | temperature (°C) | time (h) | solvent | ratio of integral area | result |
|-----|------------------|------------------|----------|---------|-----------------------|--------|
| 1   | sodium acetate (1 wt %) | 130 | 8 | acetic anhydride | 16/8.8 | some impurities and insoluble products |
| 2   | sodium acetate (1 wt %) | 90 | 8 | DMAc | 11.9/10.0 | some impurities |
| 3   | DMAP (2 mol %) | 90 | 12 | DMAc | 13.8/8.4 | incomplete reaction |
| 4   | DMAP (100 mol %) | 90 | 12 | DMAc | 16.8/6.8 | incomplete reaction |
| 5   | sodium acetate (1 wt %) | 130 | 12 | DMAc | 14.4/7.2 | pure P1-act (90% yield) |
| 6   | pyridine (4 wt %) | 90 | 12 | DMAc | 14.8/7.6 | pure P1-act (85% yield) |

*Based on P1. †The ratio of integral area between CH₃ signals of isopropyldiene and acetyl. The theoretical ratio is 2/1.
an obvious C=O absorption at 1761 cm$^{-1}$. Both NMR and IR spectra support the structure of P1-act.

**Synthesis of P1-mma.** P1-mma was prepared from the reaction of P1 with methacrylic anhydride in the presence of a catalyst. Table 2 lists the influence of reaction conditions on the preparation of P1-mma. The suitable reaction conditions are using sodium acetate (run 5) or DMAP (run 6) at 45 °C. $^1$H NMR spectrum of P1-mma (Figure 3c) shows the disappearance of the hydroxyl peak at 9.4 ppm and the appearance of new peaks at 6.2, 5.8, and 1.9 ppm, which evidences the methacrylic protons. IR spectrum (Figure S2) shows an obvious C=O and C=CH absorption at 1734 and 1649 cm$^{-1}$, respectively. Both NMR and IR spectra support the structure of P1-mma.

**Table 2. Effect of Reaction Conditions on the Preparation of P1-mma**

| run | catalyst (amount)$^b$ | temperature (°C) | result                    |
|-----|------------------------|------------------|--------------------------|
| 1   | pyridine (4 wt %)      | 45               | no reaction              |
| 2   | pyridine (4 wt%)       | 90               | incomplete reaction      |
| 3   | sodium acetate (1 wt %)| 90               | gelation at 12 h         |
| 4   | DMAP (2 mol %)         | 90               | gelation at 12 h         |
| 5   | sodium acetate (1 wt %)| 45               | pure P1-mma (85% yield)  |
| 6   | DMAP (2 mol %)         | 45               | pure P1-mma (85% yield)  |

$^a$The reaction solvent is DMAc, and the reaction time is 24 h for 1, 2, 5, and 6 runs. $^b$Based on P1.

**Thermomechanical Property of Thermosets.** Figure 4 shows the photos of (a) P1-act/epoxy, (b) P1-mma/epoxy, and (c) P1-vbe thermosets. All the films show flexibility. Because all the films are flexible, dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) are used to measure their thermal properties.

**Figure 5a** shows the DMA thermograms of P1-act/epoxy. The results are listed in Table 3. Recall that P1-act/epoxy cured at each temperature for 1 h is named P1-act/epoxy-1, while thermosets cured at each temperature for 2 h is named P1-act/epoxy-2. The $T_g$ values are dependent on the curing program. For example, the $T_g$ value of P1-act/CNE-2 is 238 °C, which is 15 °C higher than that of P1-act/CNE-1. Similar results are found for HP7200 and diglycidyl ether of bisphenol A (DGEBA) systems. **Figure 5b** shows TMA thermograms of P1-act/epoxy. The $T_g$ value of P1-act/CNE-2 is 214 °C, which is 17 °C higher than that of P1-act/CNE-1. The trend is similar to DMA data. The value in parenthesis is the data of P1/epoxy. $^{34}$ P1-act/epoxy displays lower $T_g$ values than P1/epoxy. This is the penalty of epoxy thermosets cured by active ester compared with those cured by active hydrogens because the secondary alcohol resulting from the reaction of active hydrogens provides the intermolecular interaction.

**Figure 5a** shows DMA thermograms of P1-mma/epoxy. An obvious increase in $T_g$ (25–36 °C) was observed when comparing with P1-act/epoxy. For example, the $T_g$ value of P1-mma/CNE is 274 °C, which is 36 °C higher than that of P1-act/CNE-2. This result suggests that the curing of methacrylic moiety contributes to the rigidity of epoxy thermosets.

**Figure 7a** shows DMA thermograms of P1-vbe-220 and P1-vbe-240. P1-vbe-240 exhibits a $T_g$ value as high as 302 °C, which is 55 °C higher than that of P1-vbe-220. In addition, the height of tan δ of P1-vbe-240 is much smaller than that of P1-vbe-220. Compared with the high modulus of P1-vbe-240 after $T_g$, the modulus of P1-vbe-220 after $T_g$ decreases rapidly. In

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**Figure 4. Photos of (a) P1-act/epoxy, (b) P1-mma/epoxy, and (c) P1-vbe thermosets.**
addition, the height of tan δ of P1-vbe-220 is 1.7. Both the modulus and tan δ indicate that a further curing is necessary. The height of tan δ of P1-vbe-240 is only 0.4, indicating that a rigid network was formed. Figure 7b shows TMA thermograms of P1-vbe-220 and P1-vbe-240. The $T_g$ value of P1-vbe-240 is 263 °C, which is also much higher than that (219 °C) of P1-vbe-220. The coefficient of thermal expansion (CTE) of P1-vbe-240 is 49 ppm/°C, which is much smaller than that (61 ppm/°C) of P1-vbe-220. Both DMA data ($T_g$ value and height of tan δ) and TMA data ($T_g$ value and CTE) suggest that curing at 240 °C leads to better thermal properties. However, to avoid thermal degradation, a further increase in curing temperature is not performed and discussed.

Thermal Stability. Table 3 lists the thermal stability data of the resulting thermosets. For P1-act/epoxy and P1-mma/epoxy, the 5 wt % degradation temperatures ($T_{d5}$) in a nitrogen atmosphere are in the range of 372−391 °C, and char yields range from 32 to 50%. These values are similar or slightly higher than typical epoxy thermosets. P1-vbe-240 is the only thermoset with $T_{d5}$ higher than 400 °C, demonstrating the best thermal stability.
Refractive Index and Dielectric Constant. Figure 8a shows the ellipsometry curves of P1-act/epoxy at various wavelengths. Table 3 lists the refractive index ($n$) at 633 nm. Table 3 also lists the dielectric constant ($\varepsilon$), calculated from the Maxwell’s equation, $\varepsilon = 1.1n^2$. P1-act/epoxy shows smaller dielectric constant than P1/epoxy. For example, the dielectric constant of P1-act/HP7200-2 is 2.71, which is much lower than that (3.07) of P1/HP7200. The value of 2.71, which is very low compared with general polyimide (Katpon around 3.2) and epoxy thermosets (around 3.5). The results in Table 3 indicate the low-dielectric characteristic of P1-act as a curing agent. Hougham et al. reported that the dielectric constant can be reduced by increasing the free volume and molecule’s hydrophobicity and by decreasing polarization. The less polarity of ester moiety in P1-act/epoxy than the secondary alcohol moiety in P1/epoxy is thought to be responsible for the lower dielectric constant. Moreover, the $T_g$ corresponding to the dielectric constant of 2.71 is as high as 225 °C, indicating that our approach can achieve epoxy thermosets with a low-dielectric and high-$T_g$ characteristic. Table 3 also shows the refractive index and the corresponding dielectric constant of P1-mma/epoxy (Figure 8b). Compared with P1-act/epoxy, a further reduction in refractive index was observed, probably because of the cross-linking and the aliphatic polymeric structure. The corresponding dielectric constant of P1-vbe-240 is as low as 2.64 (Figure 8c). The dielectric constant and dissipation factor of P1-vbe-240 have been measured by using an Agilent E5071C network analyzer at 10 GHz with a sample size of 9.0 cm × 9.0 cm × 80 μm. The value for dielectric constant and dissipation factor is 2.83$U$ and 0.008$U$, respectively. The dielectric properties of P1-vbe-240 are not as good as those (2.65$U$ and 0.005$U$) of thermoset of OPE-2st of MGC, probably because of the biphenylene phosphinate moiety, which exhibits a polar P=O moiety. Therefore, the values of 2.83$U$ and 0.008$U$ for a material with a built-in flame retardant element are still attractive.

CONCLUSIONS

Epoxy thermosts cured from phenolic hydroxyls lead to highly polar secondary alcohols, which hinder epoxy thermosts to be low-dielectric. To solve this problem, we have successfully prepared three phosphinated poly(aryl ethers): P1-act, P1-mma, and P1-vbe with acetic, phenyl methacrylic, and vinylbenzyl ether moiety, respectively, from a phenolic hydroxyl-containing polyether (P1). P1-act, exhibiting active
ester structures, can react with epoxy to form a secondary alcohol-free epoxy thermoset. Therefore, P1-act/epoxy shows a lower dielectric constant than P1/epoxy, indicating that the conversion of phenol OH to acetic moiety is a successful approach to prepare an epoxy thermoset with a low dielectric constant. However, compared with the $T_g$ of P1/epoxy, a penalty in $T_g$ (about 15 °C reduction) is found for P1-act/epoxy. Through the cross-linking of methacrylate linkage, P1-mma/epoxy shows an obvious increase in $T_g$ (25−36 °C) when comparing with P1-act/epoxy. A $T_g$ value as high as 274 °C can be achieved for P1-mma/CNE from the DMA thermogram. Furthermore, compared with the P1-act/epoxy, a further reduction in the dielectric constant is found for P1-mma/epoxy. A $D_k$ value as low as 2.71 U is found for P1-mma/CNE.

As to the self-curing of P1-vbe, P1-vbe-240 exhibits a $T_g$ as high as 302 °C (DMA data), a moderate-to-low CTE of 49 ppm/°C, and a low dielectric constant of 2.64 U. These properties make P1-act, P1-mma, and P1-vbe attractive for electronic application, especially in preparing high-performance PCBs.

### EXPERIMENTAL SECTION

**Materials.** The phenol-functionalized phosphinated polyether (P1) was prepared according to the procedure in our previous work. Acetic anhydride, DMAP, and sodium acetate were purchased from TCI. Methacrylic anhydride, t-butyl cumyl peroxide (TBCP), and 4-chloromethyl styrene were purchased from Acros. DGEBA with an epoxy equivalent weight (EEW) of 187 g/equiv, and CNE with an EEW of 200 g/equiv were kindly supplied by Chang Chun Plastics, Taiwan. Dicyclopentadiene epoxy (HP7200, DIC) with an EEW of 269 g/equiv was kindly supplied by Dainippon Ink and Chemicals Corporation under the commercial name of HP-7200. N-Methylpyrrolidone (NMP; HPLC grade from Showa) and DMAC (HPLC grade from Showa) were purified by distillation under reduced pressure over calcium hydride (from Acros) and stored over molecular sieves.

**Synthesis of P1-act.** P1 (10.0 g, repeat unit 14.3 mmol), sodium acetate (0.10 g), and DMAC (100 mL) were added into 250 mL flask and stirred under nitrogen. Acetic anhydride (10.22 g, 0.1 mol) was added gradually. The reaction was stirred at 130 °C for 12 h (Scheme 1) under a nitrogen atmosphere. The obtained mixture was poured into methanol. The light white precipitate was filtered and dried in a vacuum oven at 60 °C for 8 h. The isolated yield is 90%.

**Synthesis of P1-mma.** P1 (5 g, repeat unit 0.07 mol), methacrylic anhydride (1.76 g, 0.17 mol), DMAC (50 mL), and DMAP (0.025g) were added into a 100 mL flask and stirred at 45 °C for 12 h under a nitrogen atmosphere (Scheme 1). The obtained mixture was poured into methanol. The light white precipitate was filtered and dried in a vacuum oven at 60 °C for 8 h. The isolated yield is 85%.

**Synthesis of P1-vbe.** P1 (5 g, 0.07 mol), K$_2$CO$_3$ (1.310 g, 0.08 mol), 4-chloromethyl styrene (1.18 g, 0.08 mol), and DMAC (50 mL) were added into the 100 mL flask and stirred at 80 °C for 12 h under a nitrogen atmosphere (Scheme 1). The obtained mixture was poured into methanol. The off-white precipitate was filtered and dried in a vacuum oven at 60 °C for 8 h. The isolated yield is 90%.

**Curing Procedure of P1-act with Epoxy.** P1-act was thermally cured with DGEBA, HP7200, and CNE, respectively. The molar ratio of acetic moiety to oxirane (epoxy moiety) is 1. P1-act, epoxy resin, and 0.5 wt % of DMAP (based on the weight of epoxy) were dissolved in NMP to make a solution with solid content with 30%. The viscous solution was applied on an automatic film applicator to make a thin film on a glass substrate. The resulting thin films were dried at 80 °C for 1 h. Then, under a nitrogen atmosphere, two curing processes were applied. The first process is 160, 180, 200, and 220 °C for each 1 h, and the second process is 160, 180, 200, and 220 °C for each 2 h. Epoxy thermosets cured by P1-act is generally named P1-act/epoxy. The thermosets cured from the first process are named P1-act/DGEBA-1, P1-act/HP7200-1, and P1-act/CNE-
Curing Procedure of P1-mma with Epoxy. P1-mma was thermally cured with DGEBA, HP7200, and CNE, respectively. The molar ratio of the phenyl methacrylic moiety to oxirane (epoxy moiety) is 1. P1-mma, epoxy resin, 0.5 wt % of DMAP (based on the weight of epoxy), and TBCP (based on the weight of P1-mma) were dissolved in NMP to make a solution with a solid content of 30%. An automatic film applicator was used to cast a thin film on a glass substrate. The resulting thin films were dried at 80 °C for 12 h. Then, under a nitrogen atmosphere, the curing process is 160, 180, 200, and 220 °C for each 2 h. Epoxy thermosets cured by P1-mma is generally named P1-mma/epoxy. The names P1-mma/DGEBA, P1-mma/HP7200, and P1-mma/CNE are applied if the epoxy is specified.

Curing Procedure of P1-vbe. P1-vbe, with reactive vinylbenzyl ether moiety, was self-cured to P1-vbe thermoset. P1-vbe and 1.0 wt % of TBCP (based on the weight of P1-vbe) were dissolved in dioxane to make a solution with a solid content of 30%. The viscous solution was cast by an automatic film applicator to make a thin film on a glass substrate. The resulting thin films were dried at 80 °C for 12 h. Then, cured by the process 160, 180, 200, and 220 °C for each 2 h under a nitrogen atmosphere. The thermoset is named P1-vbe-X, in which X is the final curing temperature. For example, if the final curing temperature is 220 °C, it is named P1-vbe-220. If the final curing temperature is 240 °C, it is named P1-vbe-240.

Characterization. NMR measurements were performed by using a Varian Inova 600 NMR in DMSO-d_6. DMA was performed by using a PerkinElmer Pyris Diamond DMA. The test was performed by a tension mode with an amplitude of 5 mm and with a sample size of 5.0 cm × 1.0 cm × 0.2 cm. The storage modulus and tan δ were recorded with a frequency of 1 Hz at a heating rate of 5 °C/min. The dielectric constant was performed by using an Agilent E5071C network analyzer at 10 GHz. The sample size was 9.0 cm × 9.0 cm × 80 μm. TMA was performed with a SII TMA/SS6100 at a heating rate of 5 °C/min. The CTE was recorded at the temperature range of 50–150 °C. Thermal gravimetric analysis (TGA) was performed with a PerkinElmer Pyris1. The relationship between the temperature and the sample weight was recorded at a heating rate of 20 °C/min in a nitrogen or air atmosphere. The refractive index (n) at various wavelengths was obtained by using an Ellipsometry GES-SE. The dielectric constant (D_n) was calculated from the Maxwell’s equation of D_n = 1.1n^2, in which n is the refractive index at 633 nm.

ASSOCIATED CONTENT

Supporting Information
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IR spectra of P1-act, P1-mma, and P1-vbe (PDF)

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Notes
The authors declare no competing financial interest.

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