Diethylphosphonate-Containing Benzoxazine Compound as a Thermally Latent Catalyst and a Reactive Property Modifier for Polybenzoxazine-Based Resins

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ABSTRACT: A diethylphosphonate-containing benzoxazine compound (DEP-Bz) to be used as a multi-functional reaction agent for preparation of high performance polybenzoxazine thermosetting resins has been reported. The chemical structure of DEP-Bz has been characterized with FTIR, ^{1}H NMR, and elemental analysis. The phosphonate groups of DEP-Bz could convert into phosphonic acid groups which could catalyze the ring-opening addition reaction of benzoxazines, to demonstrate the thermally latent catalytic effect of DEP-Bz on the polymerization of benzoxazine compounds. Moreover, DEP-Bz could also serve as a reactive-type modifier for polybenzoxazines and other thermosets. DEP-Bz modified polybenzoxazine resins have shown relatively low reaction temperature (about 190 °C), high mechanical strength with a storage modulus of about 3.0 GPa, and high flame retardancy with a limit oxygen index of about 32. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3523–3530

KEYWORDS: catalyst; curing of polymers; flame retardance; thermosets

INTRODUCTION Benzoxazine compounds could undergo thermally induced ring-opening polymerization to result in linear and crosslinked polymers.[1] Polybenzoxazine resins are attractive in many fields of applications basing on the simple preparation approaches and convincing properties.[2–4] The thermally induced ring-opening polymerization of benzoxazines does not need addition of catalysts. Nevertheless, the polymerization temperatures for most of the benzoxazine compounds are as high as about 250 °C. The high reaction temperature could be a drawback for fabrication of polybenzoxazines. As a result, reduction of the polymerization temperatures of benzoxazines is highly desired. Studies on the reaction mechanism of benzoxazine[5–9] have provided some practical approaches to lower their polymerization temperatures. The first step of benzoxazine polymerization could be protonation of the oxygen atom of the benzoxazine ring. As a result, acid compounds could promote the protonation reaction so as to catalyze the polymerization reaction of benzoxazines.[10,11] Incorporation of acidic moieties to benzoxazine compounds could effectively reduce their reaction temperatures. This kind of benzoxazine compounds is “reactive type” catalysts for benzoxazines, as they not only promote but also involve in the polymerization reaction. Both hydroxyl[12–14] and carboxylic acid[15–18] moieties have been incorporated to the self-catalytic benzoxazine monomers. Moreover, the acidic groups also provide hydrogen bonding which also contribute to lower the reaction temperature of benzoxazines with stabilization of the reaction intermediates.[12,19] In addition to hydroxyland carboxylic acid groups, *N*-allyl[20] and ferrocene groups[21] have also shown significant effects on stabilization of the zwitterionic intermediates of the benzoxazine polymerization. Benzoxazine compounds possessing these two moieties have shown relatively low polymerization temperatures. Conversely, liquid crystalline benzoxazine compounds have exhibited relatively high polymerization rates.[22] The regular and orderly in molecular arrangement attribute to promote the polymerization reaction of the liquid crystalline benzoxazine compounds. Similar results have been reported to benzoxazine monomers[23] and polymers[24] which possess diacetylene groups, as the diacetylene groups might induce local alignment of benzoxazine groups.

Although uses of catalysts in benzoxazine curing compositions and preparation of benzoxazine compounds with low-polymerization-temperatures are effective to reduce the requested temperatures for benzoxazine fabrication, these

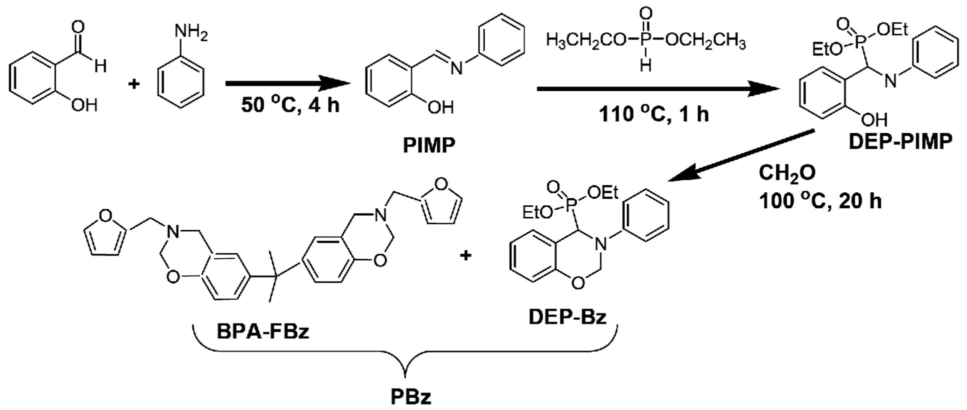

FIGURE 1 Preparation of DEP-containing benzoxazine compound and its cured resins PBz.

approaches still encounter some problems in storages of the curing compositions. With the presence of catalytic agents, benzoxazines might polymerize in the period of storage. To overcome this problem, thermally latent catalysts for benzoxazine compounds have received research attention.[25–31] The thermally latent catalysts do not perform the catalytic effect at ambient or storage temperatures and could promote the polymerization reaction at high or processing temperatures. Kimura et al.[25–27] reported the uses of complexes of amine and sulfonic acid compounds as latent curing agents for benzoxazines. The mixture of the catalyst agent and benzoxazine monomer was stable below 100 °C and proceeded rapid polymerization at temperatures above 170 °C. Endo et al.[28] reported a similar approach using *p*-toluenesulfonates as the thermally latent initiators for benzoxazine polymerization. The initiators undergo thermally induced dissociation reaction to generate alkyl cations and/or *p*-toluenesulfonic acid, which are capable to initiate benzoxazine polymerization.[28] The mechanism has also been applied for the preparation of thermally latent catalysts possessing oligomeric silsequioxane groups.[29] Another compounds showing thermally latent effect on benzoxazine polymerization are resorcinol-based aromatic urethanes. This kind of urethanes could undergo thermal dissociation to generate resorcinol and phenyl isocyanate. The isocyanate groups are active species for promotion of the benzoxazine polymerization.[30]

From the molecular design viewpoint, incorporation of the thermally latent groups to benzoxazine structure results in reactive type catalysts.[31] This kind of agent is not only a catalyst but also a co-monomer for the curing compositions of benzoxazines. As a result, in this work a diethylphosphonate (DEP)-containing benzoxazine compound (DEP-Bz, Fig. 1) has been prepared and used as a reactive type thermally latent catalyst for benzoxazine resins. The thermally induced dissociation reaction of the diethylphosphonate group of DEP-Bz generates phosphonic acid group, which is capable of promotion of the benzoxazine polymerization. Conversely, DEP-Bz is an efficient reactive-type flame retardant for polybenzoxazine and other polymers, as it has a high phosphorus content of about 9 wt %.[32,33] Addition of 20 wt % of DEP-Bz to the benzoxazine curing composition is able to significantly improves the flame retardancy of the resulting polybenzoxazine by an increase in the limited oxygen index (LOI) from 25 to 33. The results demonstrate that DEP-Bz is a multifunctional agent for preparation of polybenzoxazine resins.

EXPERIMENTAL

Materials

2-Hydroxybenzaldehyde (Aldrich, 99.99% in purity), aniline (Acros Chemical Co.), paraformaldehyde (Acros Chemical Co.), and diethylphosphite (DEP, > 95%, Strem Chemical Co.) were used as received. Bis(3-furfuryl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (BPA-FBz) was prepared in our laboratory according to the reported method.[34] Reagent-grade solvents, 1,4-dioxane, *n*-hexane, chloroform, and tetrahydrofuran (THF) were all purchased from TEDIA Chem. Co. and purified with the standard methods prior to use.

Characterization

FTIR spectra were measured with a Perkin–Elmer Spectrum One FTIR. ^{1}H and ^{31}P NMR spectra were recorded with a Varian Unityinova-500 (500 MHz) NMR spectrometer. Solid-state ^{31}P NMR spectra were recorded with a Brüker Avance III 400 NMR spectrometer (400 MHz). Differential scanning calorimetry (DSC) was performed with a Thermal Analysis (TA) DSC-Q100 instrument under nitrogen atmosphere. The gas flow rate was 40 mL min^{-1}. The measurements on the anhydrous and moistured samples were carried out at a heating rate of 1 and 10 °C min^{-1}, respectively. The moistured DEP-Bz sample was obtained by wetting the sample in small amount of water and the excess water was blotted with tissue paper. Thermogravimetric analysis (TGA) was performed with a TA TGA-Q500 thermo gravimetric analyzer at a heating rate of 10 °C min^{-1} under nitrogen and air atmosphere. Dynamic mechanical analysis (DMA) was measured with a TA DMA-Q800 instrument, using the three-point bending method with an amplitude of 10 μm, a force of 0.1 N, and a frequency of 1 Hz. The samples for DMA analysis were in the dimension of $3 \times 7 \times 0.5$ mm^3. Elemental analysis (EA) was conducted with a Heraeus CHN—O rapid elemental analyzer using acetanilide as a standard. Limited oxygen index (LOI) values were measured on a Stanton

Redcraft flame meter. The percentage in the O_2-N_2 mixture deemed sufficient to sustain the flame was taken as the LOI. Powder samples (0.5 g) of PBz resins in sizes of about 500 μm have been used for the measurements.

Preparation of 2-(Phenylimino)methylphenol[35]

2-Hydroxybenzaldehyde (9.98 g, 82 mmol) and aniline (7.6 g, 82 mmol) were charged into a 25 mL round-bottom flask. The mixture was reacted at 50 °C for 4 h under stirring and cooled to room temperature. The product in yellow solid was obtained with a yield of 100%.

Preparation of DEP-Functionalized Benzoxazine

DEP (10.0 g, 72.4 mmol) and PIMP (14.3 g, 72.4 mmol) were charged into a 100 mL round-bottom flask. After reaction at 110 °C for 1 h, paraformaldehyde (3.25 g, 10 mmol) and 1,4-dioxane (40 mL) were added into the reaction flask. The solution was then reacted at 100 °C for 20 h under nitrogen atmosphere. The solvent was removed with a rotary evaporator. The residue was dissolved in chloroform (100 mL) and washed with 2 M NaOH aqueous solution twice. The organic layer was collected and dried over anhydrous $MgSO_4$. After removal of the solvent with a rotary evaporator, the residual was precipitated from *n*-hexane. The product was collected with filtration and dried under vacuum at room temperature (yield: 80%). FTIR (KBr): 2967 cm^{-1} ($-CH_3$), 1245 cm^{-1} (P=O), 1013 cm^{-1} (symmetric stretching of C—O—C), 1235 cm^{-1} (asymmetric stretching of C—O—C), 1335 cm^{-1} (CH_2 wagging).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.28$ ppm (3H), $\delta = 1.36$ ppm (3H), $\delta = 4.14$–4.28 ppm (4H), $\delta = 4.84$ ppm and $\delta = 4.89$ ppm (1H), $\delta = 5.35$ ppm and $\delta = 5.37$ ppm (1H), $\delta = 5.7$ ppm and $\delta = 5.76$ ppm (1H), $\delta = 6.82$–7.27 ppm (9H); ^{31}P NMR ($CDCl_3$, ppm): $\delta = 21.35$ ppm; $C_{18}H_{22}NO_4P$: Calcd. C 62.24, H 6.34, N 4.03; Found C 61.84, H 6.63, N 3.96.

Preparation of Crosslinked Polybenzoxazine Resin

DEP-Bz and BPA-FBz in different ratios were dissolved in THF (0.5 g in 2 mL). As the THF solvent was not dried prior to use, no additional water was added to the solution. The solution was poured into an aluminum mold. The samples were then thermally cured in a vacuum oven at 160 °C for 1 h, 200 °C for 1 h, and 220 °C for another 2 h. The curing condition was determined with the results of DSC measurements. The obtained crosslinked polybenzoxazine resins were coded as PBz-X, where X denotes to the weight percentages of DEP-Bz in the curing composition.

RESULTS AND DISCUSSION

Preparation and Characterization of DEP-Functionalized Benzoxazine DEP-Bz

Preparation of DEP-functionalized benzoxazine (DEP-Bz) has been carried out with a one-pot synthesis using PIMP and DEP as precursors (Fig. 1). The precursor PIMP has been prepared in our laboratory according to the reported method.[35] The —C=N— group of PIMP is reactive toward the P—H group of DEP through a nucleophile addition reaction.[36] The intermediate product DEP-PIMP then react with paraformaldehyde to result in DEP-Bz through the cyclization reaction. As isolation of DEP-PIMP is not necessary in the synthetic procedure, DEP-Bz is obtained with an one-pot synthesis. For experimental supports to the reaction scheme, DEP-PIMP has been obtained and characterized with ^{1}H and ^{31}P NMR. The NMR spectra of the isolated DEP-PIMP compounds are included in Figure 2 for comparison. The chemical structure of DEP-Bz is first characterized with an FTIR. The FTIR spectrum [Fig. 2(a)] shows the characteristic peaks associating to the functional groups of the compound. The

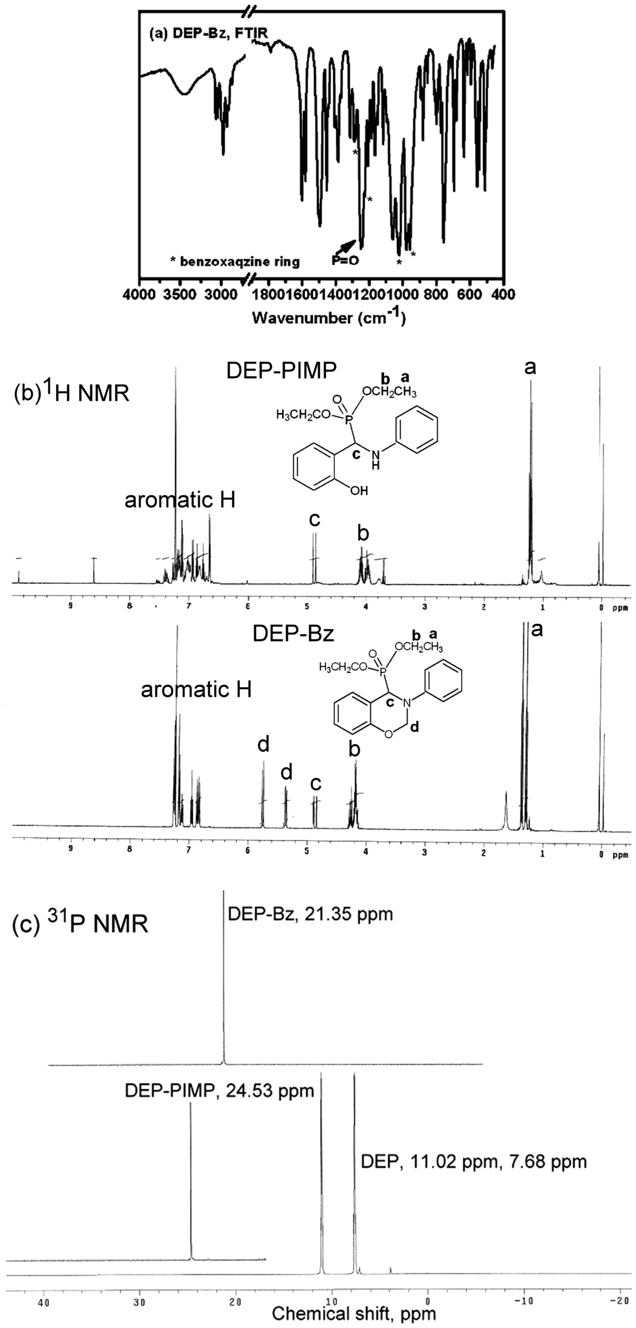

FIGURE 2 Characterization of DEP-Bz with (a) Fourier transform infrared, (b) ^{1}H NMR, and (c) ^{31}P NMR.

characteristic absorptions of the P=O group and —CH_3 group are at 1245 and 2967 cm^{-1}, respectively. The characteristic absorptions of benzoxazine structure for DEP-Bz are at 1013 cm^{-1} (symmetric stretching of C—O—C), 1235 cm^{-1} (asymmetric stretching of C—O—C), 1335 cm^{-1} (CH_2 wagging), and 950 cm^{-1} (out-of-plane C—H vibration).[37] The benzene rings of DEP-Bz also exhibit absorptions at about 1500–1600 cm^{-1}. The absorptions of P—H group at 2400 cm^{-1} and C=N group at 1700 cm^{-1} disappear, demonstrating the performance of the addition reaction between these two groups. Further characterization of DEP-Bz has been carried out with ^{1}H NMR. The spectrum shown in Figure 2(b) provides sufficient support to the chemical structure of DEP-Bz. The peaks at δ = 4.86 and δ = 4.90 ppm (1H) correspond to the P-coupled P—C—H proton of the six-membered ring of DEP-Bz. The protons of the methylene group of the ring raise the resonance peaks at δ = 5.40 ppm (1H) and δ = 5.79 ppm (1H). These two protons which have the same chemical environment exhibit peaks at different chemical shift in the ^{1}H NMR spectrum, indicating that they could be sterically distinguished each other due to the bulky substituent of DEP on the benzoxazine ring. The ethyl groups have been characterized with the resonance peaks at δ = 1.28 ppm (3H), δ = 1.36 ppm (3H), and δ = 4.14–4.28 ppm (4H). The peaks associating to the aromatic protons appear at δ = 6.82–7.27 ppm (9H). The reaction route for preparation of DEP-Bz has also been monitored with ^{31}P NMR. As shown in Figure 2(c), DEP exhibits two peaks at δ = 7.68 ppm (6H) and at δ = 11.02 ppm in the ^{31}P NMR spectrum, as the P nuclei of P—H group is coupled with the proton. After reaction with PIMP, the resonance peak shifts to δ = 24.53 ppm and the spin–spin splitting disappears. Cyclization of DEP-PIMP to DEP-Bz further result in a peak shift to δ = 21.35 ppm. No other peaks appear in the ^{31}P NMR spectra of DEP-PIMP and DEP-Bz, indicating that these two compounds were obtained in high purity. Hydrolysis of the phosphonate groups of these two compounds did not occur in the preparation and purification process.

The Thermally Latent Characteristics of DEP-Bz for Benzoxazine Polymerization

The thermal behavior of DEP-Bz has been characterized with a DSC. A broad exothermic peak centered at about 260 °C appears in the DSC thermogram of DEP-Bz recorded at a heating rate of 10 °C min^{-1}. This exothermic peak corresponds to the ring-opening addition reaction of benzoxazine groups. The decomposition behavior of the P-OEt groups of DEP-Bz is not observed in the DSC heating scan, as it might overlap with the exothermic peak of benzoxazine polymerization. To improve the resolution of DSC analysis, the DSC thermogram of DEP-Bz recorded at a heating rate of 1 °C min^{-1} has been obtained. As shown in Figure 3(a), the sharp endothermic peak at about 71 °C corresponds to the melting behavior of DEP-Bz. The sharp exothermic peak centered at about 210 °C is contributed from the ring-opening polymerization of benzoxazine group of DEP-Bz. The activation energy of the ring-opening polymerization of DEP-Bz which is determined with the dynamic Kissinger's method[38] is 82.6 kJ mol^{-1}. This value is much lower than the activation energies recorded with some conventional benzoxazine compounds,[11,39–41] indicating a catalytic effect might involve in the polymerization reaction.[11] It is noteworthy that the exothermic peak exhibits a clear left shoulder at about 206 °C.

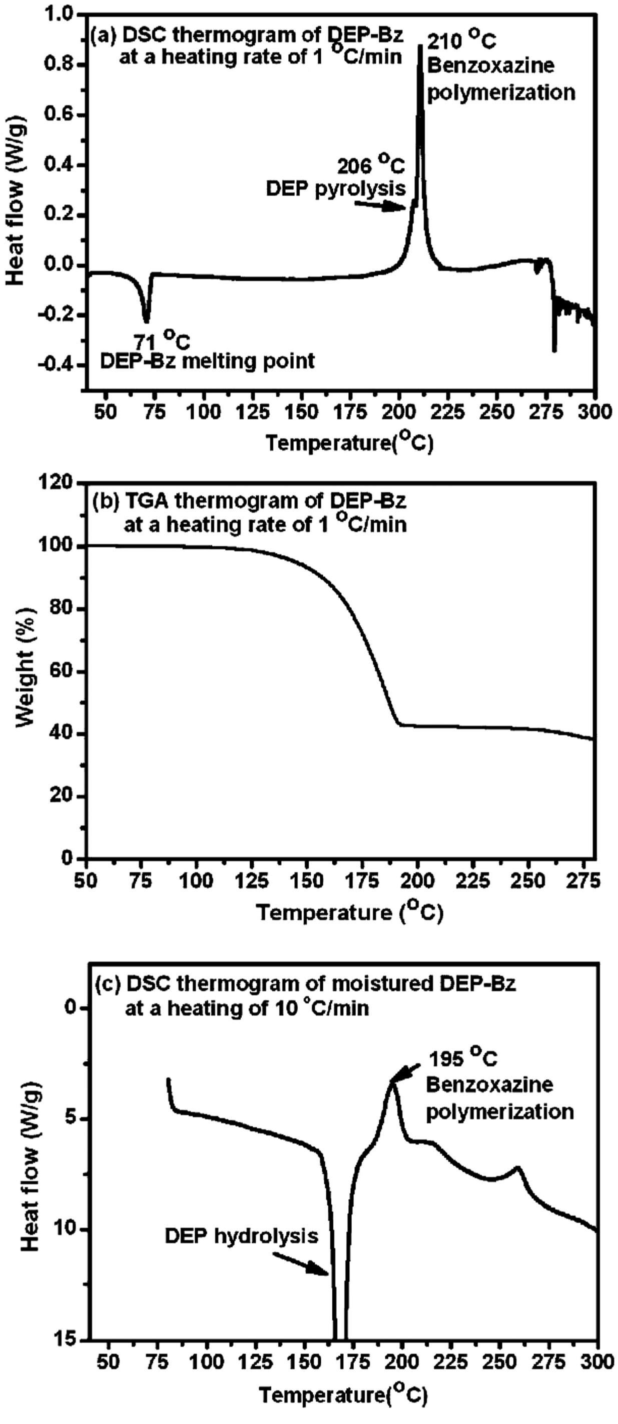

FIGURE 3 Thermal analysis on DEP-Bz: (a) DSC thermograms of dry DEP-Bz at a heating rate of 1 °C min^{-1}, (b) TGA thermogram of dry DEP-Bz at a heating rate of 1 °C min^{-1}, and (c) DSC thermogram of the moistured DEP-Bz at a heating rate of 10 °C min^{-1}.

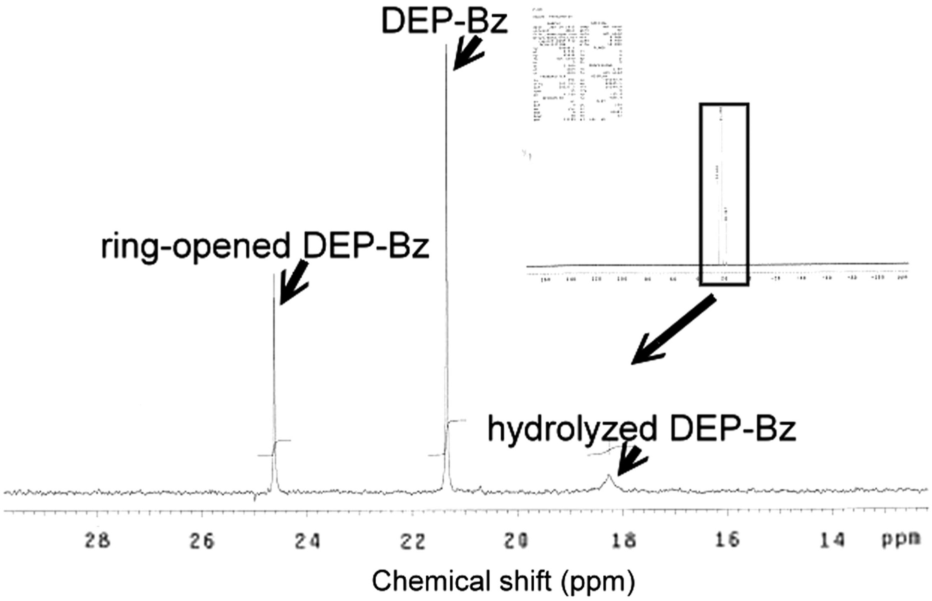

FIGURE 4 ^{31}P NMR spectrum of DEP-Bz (with water in DMSO-d_6) after heating at 130 °C for 3 h in DMSO for monitoring on the hydrolysis reaction of DEP-Bz.

This result indicates that the exothermic behavior could be composed of at least two exothermic reactions. DEP could undergoes thermally induced dissociation reaction with formation of phosphite (O=P(OH)$_2$—H).[42] The generated acidic phosphite group could promote the polymerization of benzoxazines. As a result, it is reasonable to assign the first exothermic reaction to the dissociation reaction of the DEP group of DEP-Bz and the following peak to the benzoxazine polymerization. The dissociation reaction of the DEP group results in a weight loss in the heating process of DEP-Bz, which has been observed in the TGA thermogram of DEP-Bz at a heating rate of 1 °C min^{-1} [Fig. 3(b)]. Nevertheless, the weight loss percentage is higher than the weight fraction of the ethoxy groups of DEP-Bz, indicating the molecules might decompose under the experimental condition. With the dissociation reaction, the generated acidic phosphite group catalyzes the polymerization of benzoxazine groups, so as to reduce the activation energy of the benzoxazine polymerization reaction. It is noteworthy that the dissociation of DEP group of the anhydrous DEP-Bz compound performs at a high temperature region. As a result, the effect of DEP-Bz dissociation on lowering the polymerization temperature of DEP-Bz is not as significant as other agents.

Figure 3(C) shows the DSC thermogram (at a heating rate of 10 °C min^{-1}) of moisturized DEP-Bz sample, to demonstrate the thermally latent catalytic effect of the DEP group on benzoxazine polymerization. The endothermic peak at about 167 °C associates to the hydrolysis reaction of the ethoxy groups of DEP-Bz. Once the hydrolysis reaction occurs, the formed P—OH groups catalyze the ring-opening addition reaction of the benzoxazine group, so as to exhibit the exothermic peak at about 195 °C in the DSC thermogram. The temperature is much lower than the reaction temperature recorded with the anhydrous DEP-Bz sample, which shows a reaction temperature at 260 °C at a heating rate of 10 °C min^{-1}. The catalytic effect of the formed P—OH groups on the polymerization reaction of benzoxazine groups has been demonstrated. Moreover, the hydrolysis reaction of DEP-Bz and the corresponding catalytic effect on benzoxazine ring-opening reaction has been monitored with a ^{31}P NMR. DEP-Bz and water (in molar ratio of 1:8) were dissolved in DMSO-d_6 solvent. The solution was heated at 130 °C for 3 h and then applied to ^{31}P NMR measurement. As shown in Figure 4, the resonance peak at about $\delta = 21.35$ ppm corresponds to DEP-Bz. The hydrolyzed of DEP-Bz shows a resonance peak at about $\delta = 18.26$ ppm. The P—OH groups formed with hydrolysis reaction catalyze the ring-opening reaction of benzoxazine groups, and the reaction products result in the resonance peak at about $\delta = 24.63$ ppm. As the conventional benzoxazine compound BPA-FBz does not show hydrolysis behavior under the same condition, the resonance signal at $\delta = 24.63$ ppm could be contributed from the P—OH-catalyzed ring-opened benzoxazine groups rather than from the hydrolyzed benzoxazine. The results supports to the proposed reaction mechanism for DEP-Bz self-catalytic reaction.

Properties of Polybenzoxazines Prepared with DEP-Bz

The above results indicate that DEP-Bz could serve as a thermally latent catalyst for benzoxazine compounds. Not like other additive-type catalysts which do not involve in the polymerization reaction of benzoxazines, DEP-Bz is a reactive-type agent as it possesses a benzoxazine group in the structure. As a result, DEP-Bz is not only a catalyst but also a reactive modifier for polybenzoxazine resins. Polybenzoxazine resins could be obtained with the mixtures of DEP-Bz and other benzoxazine compounds in a wide range of mixing fractions. Moreover, DEP-Bz is also effective to improve the flame retardant property of polybenzoxazine

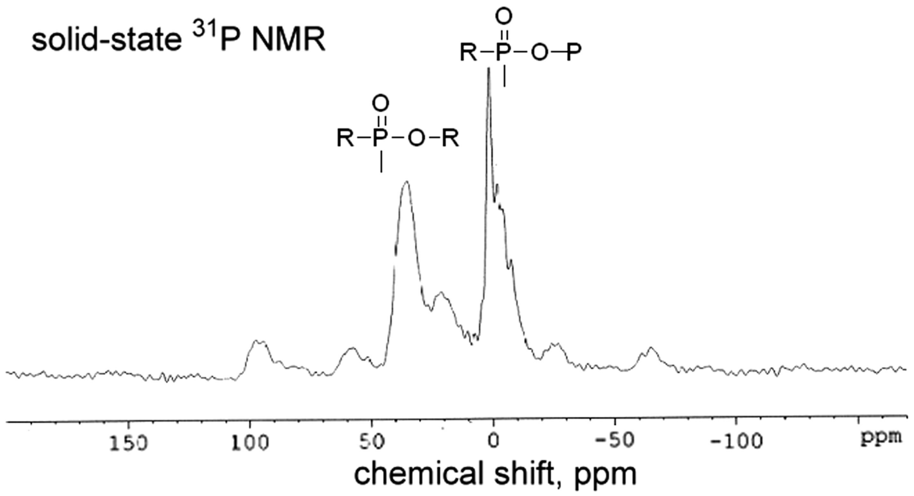

FIGURE 5 Solid-state ^{31}P NMR spectrum of PBz-20 showing the presence of phosphorus-containing groups in the DEP-Bz-modified resin.

resins,[32,33] as DEP-Bz has a high phosphorus content of about 9 wt %.

Polybenzoxazine resins of DEP-Bz and BPA-FBz (PBz-*X*, where *X* denotes to the DEP-Bz weight fraction in the resin composition) have been obtained with thermally curing their mixtures in different fractions. DEP-Bz plays as both a reactive modifier and a thermally latent catalyst for the polybenzoxazine resins. After copolymerization, the PBz-*X* resins still possess phosphorus-containing groups in the structures. As shown in Figure 5, PBz-20 exhibits two groups of resonance peaks in the solid-state ^{31}P NMR spectrum. The peaks at about $\delta = 21$–35 ppm corresponds to the phosphonate ester groups which might form with the condensation reaction between $-\mathrm{P}(=\mathrm{O})\ -\mathrm{OH}$ group and phenol (formed with the ring-opening reaction of benzoxazines) group. The peaks at $\delta = -7$–1 ppm indicates the presence of $-(\mathrm{O}=)\mathrm{P}-\mathrm{O}-\mathrm{P}(=\mathrm{O})$ groups which form with the dehydration condensation reaction between $-\mathrm{P}(=\mathrm{O})-\mathrm{OH}$ groups. As discussed later, the phosphorous groups would contribute to improve the flame retardancy of the polybenzoxazine resins.

Figure 6 shows the typical DMA thermograms of PBz-*X* samples, and the data is collected in Table 1. Under the curing condition, PBz-0 (pure poly(BPA-FBz) resin) show a high storage modulus of 3285 MPa at 50 °C and a glass transition temperature (T_g) at 328 °C (determined with the peak of tan δ). Addition of DEP-Bz in the curing composition alters the storage modulus and T_g's of the resulting PBz samples. Nevertheless, the values of the storage modulus and T_g's do not exhibit a positive relationship with respective to the DEP-Bz contents. Addition of DEP-Bz to the curing composition might reduce the crosslinking density and the T_g's of PBz resins, as DEP-Bz is a mono-functional benzoxazine monomer. Conversely, the P═O group of DEP-Bz might provide more sites for formation of intermolecular hydrogen bonds, so as to increase the chain interaction of PBz resins. The interchain H-bonds result in the relatively higher T_g's of PBz-15 and PBz-20 compared to PBz-10. Similar results have been reported for other modified polybenzoxazine resins.[43] The storage modulus at glassy state of PBz resins is lower than that of the pure poly(BPA-FBz) resin, as DEP-Bz is a monofunctional benzoxazine compound. Nevertheless, the differences in the storage modulus are not large, as the strong chain interaction of the DEP-Bz-modified resins contributes to increase their storage modulus. Moreover, addition of DEP-Bz to the curing composition results in an increase in the values of tanδ of the polybenzoxazine resins, indicating that DEP-Bz is also effective on the improvement of the damping character of PBz resins.

The thermal stability of PBz resins has been examined with a TGA (Fig. 7). All PBz samples show high thermal stability with T_{d5} above 375 °C (the temperatures at 5 wt % loss). Compared to PBz-0, the rapid weight loss (determined with the peak of the derivative thermogravimetric curves) of PBz-15 and PBz-20 appears at the relatively low temperature region. This result is reasonable as the phosphonate groups

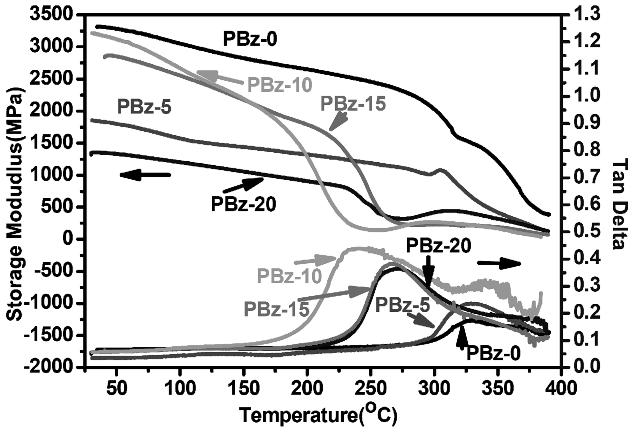

FIGURE 6 DMA thermograms of PBz resins containing various contents of DEP-Bz.

TABLE 1 Thermal Property and Flame Retardancy of DEP-Bz Modified Polybenzoxazine Resins

	DMA Analysis		TGA Analysis in N_2 Atmosphere			
Sample	Storage Modulus at 50 °C (MPa)	Glass Transition Temperature at peak of tan δ (°C)	Temperature at 5 wt % Loss (°C)	Rapid Degradation Temperature[a] (°C)	Char Yield at 800 (°C)	LOI
PBz-0	3,285	328	386	445	54	25
PBz-5	1,800	328	397	450	55	26
PBz-10	3,120	232	390	450	57	28
PBz-15	2,810	256	376	405	65	32
PBz-20	1,350	248	380	405	64	33

[a] The temperatures at the peak of the derivative thermogravimetric curves

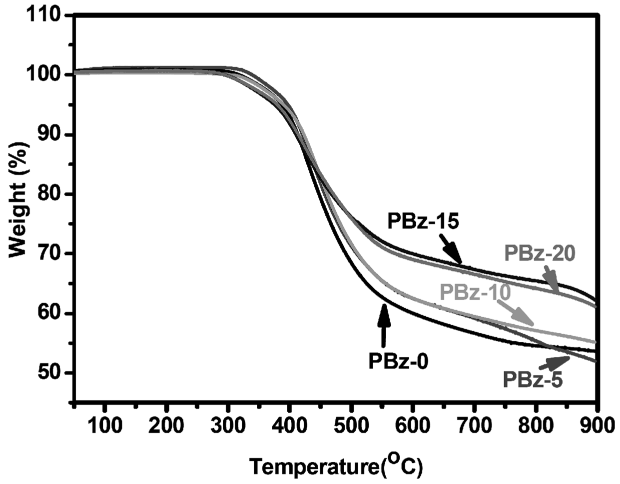

FIGURE 7 TGA thermograms of PBz resins containing various contents of DEP-Bz (under a nitrogen atmosphere).

of the PBz samples are relatively thermally instable. Similar results have been widely observed for other phosphorylated resins.[32,33,42,44] Degradation of the phosphonate groups generate phosphonic acid groups which could induce the dehydration and carbonization of the residuals of PBz resins. The reactions promote the formation of thermally stable char. As a result, PBz-15 and PBz-20 exhibit a retarded weight loss behavior at temperatures above 500 °C and high char yields of about 65 wt % at 800 °C. Moreover, the high char yields of the PBz resins mean less combustible degradation products being evolved to the gaseous phase, so as to increase the flame retardancy of the resins. The flame retardancy of PBz resins has been evaluated with measurement of their LOI values. As shown in Table 1, PBz-0 shows an LOI value of about 25. Addition of DEP-Bz to the curing composition increases the LOI values of the obtained resins. The higher DEP-Bz contents that the resins have, the higher LOI values are demonstrated. It is noteworthy that only 15 wt % of DEP-Bz is enough to increase the LOI value of PBz resins to 32. The efficiency of DEP-Bz as a reactive-type flame retardant for polybenzoxazines has been demonstrated. DEP-Bz could be applied for other kinds of thermosets, such as phenolic resin, epoxy resin, polyurethanes, and polyester resins for further studies.

CONCLUSIONS

The phosphonate-containing benzoxazine compound DEP-Bz shows thermally latent catalytic effect on benzoxaizne curing reaction in the presence of water and property-enhancing characteristics for polybenzoxazine resins. DEP-Bz is a reactive-type catalyst, which could be added to the curing compositions in a wide range of fractions. This feature is attractive for the formulation of benzoxazine curing compositions. DEP-Bz is also an effective property modifier for polybenzoxazines to increase their T_g's, thermal stability, and flame retardancy.

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REFERENCES AND NOTES

1 N. N. Ghosh, B. Kiskan, Y. Yagci, *Prog. Polym. Sci.* **2007**, *32*, 1344–1391.

2 S. K. Kim, S. W. Choi,, W. S. Jeon, J. O. Park, T. Ko, H. Xhang, J. C. Lee, *Macromolecules* **2012**, *45*, 1438–1446.

3 T. Agag, J. Liu, R. Graf, H. W. Spiess, H. Ishida, *Macromolecules* **2012**, *45*, 8991–8997.

4 H. Y. Li, Y. L. Liu, *J. Mater. Chem. A* **2013**, *1*, 1171–1178.

5 A. F. McDonagh, H. Smith, *J. Org. Chem.* **1968**, *33*, 8–12.

6 T. Hayakawa, Y. Osanai, K. Niizeki, O. Haba, M. Ueda, *High Perform. Polym.* **2000**, *12*, 237–246.

7 A. Sudo, R. Kudoh, H. Nakayama, K. Arima, T. Endo, *Macromolecules* **2008**, *41*, 9030–9034.

8 P. Chutayothin, H. Ishida, *Macromolecules* **2010**, *43*, 4562–4572.

9 C. Liu, D. Shen, R. M. Sebastián, J. Marquet, R. Schönfeld, *Macromolecules* **2011**, *44*, 4616–4622.

10 J. Dunkers, H. Ishida, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 1913–1921.

11 Y. L. Liu, J. M. Yu, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 1890–1899.

12 R. Kudoh, A. Sudo, T. Endo, *Macromolecules* **2010**, *43*, 1185–1187.

13 B. S. Rao, A. Palanisamy, *Prog. Org. Coat.* **2012**, *74*, 427–434.

14 M. Baqar, T. Agag, R. Huang, J. Maia, S. Qutubuddin, H. Ishida, *Macromolecules* **2012**, *45*, 8119–8125.

15 R. Andreu, J. A. Reina, J. C. Ronda, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 6091–6101.

16 C. Zúñiga, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, *Polymer* **2012**, *53*, 3089–3095.

17 C. Zúñiga, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, *Polymer* **2012**, *53*, 1617–1623.

18 S. Li, T. Zou, *J. Appl. Polym. Sci.* **2012**, *123*, 922–928.

19 Y. C. Yen, C. C. Cheng, Y. L. Chu, F. C. Chang, *Polym. Chem.* **2011**, *2*, 1648–1653.

20 H. Oie, A. Sudo, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5357–5363.

21 W. Li, T. Wei, Y. Gao, K. Xi, X. Jia, *Polymer* **2012**, *53*, 1236–1244.

22 P. Velez-Herera, H. Ishida, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 5871–5881.

23 A. Chernykh, T. Agag, H. Ishida, *Polymer* **2009**, *50*, 3153–3157.

24 A. Chernykh, T. Agag, H. Ishida, *Macromolecules* **2009**, *42*, 5121–5127.

25 H. Kimura, Matsumoto, K. Ohtsuka, *J. Appl. Polym. Sci.* **2008**, *109*, 1248–1256.

26 H. Kimura, Matsumoto, K. Ohtsuka, *J. Appl. Polym. Sci.* **2008**, *107*, 710–718.

27 H. Kimura, Matsumoto, K. Ohtsuka, *J. Appl. Polym. Sci.* **2009**, *112*, 1762–1770.

28 A. Sudo, H. Yamashita, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3631–3636.

29 L. Wang, W. Du, Y. Wu, R. Xu, D. Yu, *J. Appl. Polym. Sci.* **2012**, *126*, 150–155.

30 A. Sudo, A. Mori, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2183–2190.

31 A. Sudo, R. Kudoh, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1724–1729.

32 M. Spontón, M. S. Larrechi, J. C. Ronda, M. Galià, V. Cádiz, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 7162–7172.

33 H. C. Chang, H. T. Lin, C. H. Lin, *Polym. Chem.* **2012**, *3*, 970–978.

34 Y. L. Liu, C. I. Chou, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 5267–5282.

35 C. H. Lin, S. L. Chang, C. W. Hsieh, H. H. Lee, *Polymer* **2008**, *49*, 1220–1229.

36 C. H. Lin, H. T. Lin, J. W. Sie, K. Y. Hwang, A. P. Tu, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4555–4566.

37 Y. Cheng, J. Yang, Y. Jin, D. Deng, F. Xiao, *Macromolecules* **2012**, *45*, 4085–4091.

38 H. E. Kissinger, *Anal. Chem.* **1957**, *29*, 1702–1706.

39 T. Agag, T. Takeichi, *Polymer* **2000**, *41*, 7083–7090.

40 H. Ishida, Y. Rodriguez, *Polymer* **1995**, *36*, 3151–3158.

41 Y. L. Liu, C. M. Yu, C. I. Chou, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 5954–5963.

42 Y. S. Chiu, Y. L. Liu, W. L. Wei, W. Y. Chen, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 432–440.

43 Y. L. Liu, C. W. Hsu, C. I. Chou, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 1007–1015.

44 Q. Tai, Y. Hu, R. K. K. Yuen, L. Song, H. Lu, *J. Mater. Chem.* **2011**, *21*, 6621–6627.