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PAPER

A facile method to introduce phosphoester groups into polybenzoxazines backbone as multifunctional modifiers

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Phosphoester groups were introduced conveniently into benzoxazine monomers by chemical bonding through nucleophilic reaction of benzoxazine ring with diethyl phosphite (DEP). The reaction process was monitored by ^{31}P NMR. The ^{31}P NMR characteristic peaks corresponding to DEP disappeared entirely when the reaction was run at 90 °C for 24 h, which implied the completion of the nucleophilic reaction. The obtained products directly underwent ring-opening polymerization to produce DEP-modified polybenzoxazines. The introduction of DEP into polybenzoxazines led to a reduction of the onset polymerization temperature. The adsorption ability for Cd(II) was improved due to the phosphoester group providing an efficient chelating sites for heavy metal ions.

Introduction

As ideal alternatives of traditional phenol-formaldehyde (PF) thermosets, polybenzoxazines have attracted an increasing interest due to their superior properties. Polybenzoxazines conquer some defects of conventional PF thermosets and exhibit excellent properties, such as high thermal stability, low water absorption, resistance against flame and chemical, limited volume-shrinkage during curing process.[1,2] Besides these advantages, the ring-opening polymerization of benzoxazine monomers is a thermally induced curing reaction which can be accomplished without any initiator or curing agent.[3-5] However, polybenzoxazines still have a few shortcomings and limitations, e.g., unsatisfactory processability, brittleness and high polymerization temperatures, which hinder their widely practical applications.[6-8]

The most important characteristic of polybenzoxazines is the variability of structure and function benefiting from the molecular design flexibility of monomer.[9-21] For example, to reduce brittleness and improve toughness of polybenzoxazine, the concept of side-, main-, and end-chain polymeric benzoxazine precursors was suggested by various research groups, and these precursor polymers showed excellent film-forming properties both before and after curing reaction.[22-25] Introducing phosphoester groups into polymer chain as “inherent plasticizer” by chemical bonding could overcome the “transportation problem”.[26-29] Moreover， difunctional benzoxazine monomers with second polymerizable sites exhibited high thermal and mechanic stability, high resistance of solvent, moisture and chemical had been designed and prepared, which could induce further cross-linking reactions to generate three-dimensional networks. These second curing groups included allyl,[13, 30] acetylenyl,[31-34] propargyl,[35, 36] and nitrile groups.[37]In order to improve the curing process, active hydrogen containing groups such as carboxylic[38] and phenolic groups[39] were incorporated into benzoxazine monomers, which could effectively decrease curing temperature due to their catalytic effect on ring-opening polymerization. Recently, Gorodisher and coworkers reported that benzoxazines could undergo catalytic ring-opening reaction initiated by thiols at ambient conditions.[40] The process was named as COLBERT reaction (Catalytic Opening of the Lateral Benzoxazine Rings by Thiols) which proceeded via a two-step acid catalyzed nucleophilic addition.[41] Subsequently, Yagci[42] demonstrated that crosslinked but additionally curable soft benzoxazine films could be prepared by simultaneously photo-induced thiol-ene and COLBERT reactions using difunctional thiol and diallyl benzoxazines. The obtained polybenzoxazine precursors still contained benzoxazine and allyl groups, which were readily available for the subsequent curing.

In this paper, we prepared phosphoester-modified polybenzoxazines based on the molecular design flexibility of benzoxazine monomer. Phosphoester-containing benzoxazine monomers were prepared firstly by nucleophilic addition reaction of tri-functional benzoxazine (TBOZ) with calculated amount of diethyl phosphite. Then DEP-modified polybenzoxazine were obtained by cationic ring-opening polymerization. Comprehensive properties of the DEP-modified polybenzoxazine were investigated for evaluating the influence of the introduction of DEP. At last, the Cd(II) adsorption ability of this DEP-modified polybenzoxazine was researched because the phosphoester group could act as efficient chelating sites for many heavy metal ions.

2. Experimental

2.1. Chemicals

1,1,1-tris(4-hydroxyphenyl)ethane (98%) was purchased from TCI (Shanghai) Development Co., Ltd. Paraformaldehyde (95%), aniline (99%), diethyl phosphite (DEP, 99%), sodium hydroxide (99%) and Cadmium sulfate (99%) were purchased from

Sinopharm Chemical Reagent Co., Ltd., China. 1,4-dioxane (99%) was also purchased from Sinopharm and purified by distillation over calcium hydride (from Sinopharm) and stored over molecular sieves. Standard stock solutions of Cd(II) was prepared by dissolving Cadmium sulfate in deionized water.[43]

Synthesis of tri-functional benzoxazine monomer TBOZ

TBOZ was prepared according to reported method[44] with a few modifications. The typical procedure was as follows: Aniline (8.21 g, 0.09 mol) and paraformaldehyde (5.94 g, 0.198 mol) were mixed in 250 mL three-neck flask and stirred in ice bath for 1 h. Then 150 mL toluene, 1,1,1-Tris(4-hydroxyphenyl)ethane (9.19 g, 0.03 mol) were added into the mixture under stirring. The mixture was gently heated to 110 °C and refluxed for 10 h. Water produced during reaction was separated out by azeotropic distillation with toluene. At the end of reaction, toluene was removed by rotary evaporation and the residues were extracted with chloroform. The chloroform solution was washed with 0.5 M NaOH and distilled water successively, then dried with anhydrous Na_2SO_4 over night. After filtration the filtrate was concentrated and dropped into petroleum ether under stirring. White powder was collected and dried in vacuum at 50 °C for 48 h. (Scheme 1)

Yield: 91.6%. MP. 57-59 °C. ^1H NMR ($CDCl_3$, TMS, ppm): 6.64-6.93(24H, Ar-H), 4.52 (6H, Ar-CH_2-N), 5.34 (6H, O-CH_2-N), 2.04(3H, -CH_3)。 ^{13}C NMR (DMSO-d_6, TMS, ppm):152.4 (C-O), 148.3 (C-N), 141.7 (C-O), 129.6 (CH), 128.3 (CH), 126.9 (C), 120.8 (CH), 117.6 (CH), 115.9 (CH), 50.8 (Ar-CH_2-N), 78.9 (O-CH_2-N), 49.6(C). [Fig. S1]

Nucleophilic reaction of TBOZ with DEP (Example for synthesis of (1/1)TBOZ/DEP ((1/1)TBOZ/DEP means molar ratio of TBOZ to DEP equals 1/1)

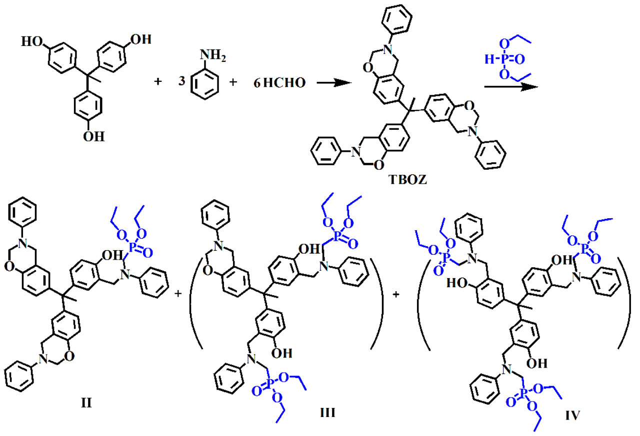
TBOZ (3.29 g, 5 mmol) and diethyl phosphite (0.64 mL, 5 mmol) were added into a 500 mL three-necked flask containing 200 mL of dried dioxane. The reaction mixture was gently heated to 90 °C and refluxed at this temperature for 24 h. The reaction was monitored by ^{31}P NMR and was stopped after the chemical shift corresponding to diethyl phosphite disappeared. Then all volatiles was removed out under reduced pressure and the residual yellow precipitate was dried under vacuum at 40 °C for 48 h to get the desired product with quantitative yield. The compound was utilized directly for next studies without further purification.

^1HNMR (DMSO-d_6, TMS, ppm): 6.70-7.21 (Ar-H, m), 5.38 (O-CH_2-N, s), 4.53 (C-CH_2-N, s), 4.18 (N-CH_2-P, s), 3.75 (N-CH_2, s), 4.01-4.07 (O-CH_2, q), 1.21-1.24 (CH_3, t), 2.00 (C-CH_3, s), 9.36 (Ar-OH, s). [Fig. 2]

The synthetic procedures for (1/0.5)TBOZ/DEP and (1/2)TBOZ/DEP were the same as the model compound II. (Scheme 1)

Preparation of polybenzoxazines

Samples for dynamic mechanic analysis, impact resistance test, dielectric measurement and humidity absorption test were prepared as follows: TBOZ or DEP-modified TBOZ was added to the tinfoil mold and gently melted at 160 °C and 180 °C under vacuum each for 1 h. Later, the samples were heated stepwise and cured in a temperature-controlled oven at 180 °C and 200 °C each for 8 h, then post-cured at 220 °C and 240 °C each for 2 h. Thereafter, samples were slowly cooled down to room temperature to prevent cracking. Samples for batch adsorption experiments of Cd(II) were prepared by wet-milling process at the ratio of polybenzoxazines: Alumina ball: ethyl alcohol equal to 2:50:10 for 8 h,[45] followed by sieving with 80 mesh sieve.



Scheme. 1 Synthesis of TBOZ and its nucleophilic reaction with diethyl phosphite

2.2. Characterization

The structure of TBOZ and other compounds were verified by solution-state proton (^1H) and phosphorus (^{31}P) nuclear magnetic resonance spectroscopy (NMR) using Bruker AV400NMR spectrometer at proton frequency of 400 MHz as well as the corresponding phosphorus frequency at room temperature. Chemical shifts were reported in ppm downfield from $SiMe_4$. Thermal transitions were monitored with a differential scanning calorimeter (DSC), Model 204F1 from NETZSCH Instruments, and scan rate of 10 °C/min over a temperature range of 30~300 °C and nitrogen flow rate of 20 mL/min were used in DSC experiments. Thermogravimetric analysis (TGA) was performed with a NETZSCH Instruments' High Resolution STA 409PC thermogravimetric analyzer that was purged with nitrogen at a flow rate of 70mL/min. A heating rate of 20 °C/min was used and scanning range was from RT to 1000 °C. Infrared spectra were recorded using a Bruker VERTEX 70 Fourier transform infrared spectrometer (FT-IR) under ambient condition. And the potassium bromide disks were prepared by compressing the powder. Mechanic properties were measured using a dynamic mechanic thermal analysis (DMA) apparatus (PerkinElmer, Diamond DMA). Specimens (50×10×1.0 mm) were tested in 3 point bending mode. The thermal transitions were studied in the scope of 20~200 °C at a heating rate of 4°C/min and at a fixed frequency of 1 Hz.

2.3. Gel content

The gel fraction was determined by standard extraction method[46] using chloroform. The process involved in continuous extraction with chloroform in a 500 mL round bottom flask for 72 h until constant weight obtained. After the extraction, the samples were dried and the gel content was calculated according to the formula (1) as follows, where m_t and m_0 represented the sample weights after and before extraction, respectively.

$$\text{Gel content (\%)} = \frac{m_t}{m_0} \times 100\%, \quad (1)$$

Impact resistance test

The impact strength of the cured specimens (80 mm×10 mm×4 mm) was measured with a Pendulum Impact Testing Machine (Model ZBC from SHENZHENG SANS TESTING MACHINE Co.LTD) at 25 °C according to Chinese standard of GB/T 1043-1993. The material's response (maximum stress or fracture) to the applied load was measured for 5 samples of each material group and the average values recorded.[47]

Dielectric measurements

Dielectric constant and dielectric loss were measured at room temperature in an air atmosphere by the two parallel plate modes at 125 Hz ~ 18 MHz using Agilent 4294A Precision Impedance Analyzer.[14] A sample (about 20 mm×10 mm×2 mm) was placed between the two copper electrodes to form a parallel plate capacitor. Prior to each measurement, the sample was dried under vacuum at 100 °C for 3 h.

Humidity absorption

The cured samples were conditioned under vacuum at 90 °C for 20 h before placed in air (75% and 33% RH). All these experiments were conducted at room temperature. Then, the weight percentages of humidity absorption of the cured samples were calculated according to the formula (2) as follows, where the W_t and W_0 represented the sample weights after and before (dry sample) humidity absorption, respectively.[48]

$$\text{Humidity absorption content (\%)} = \frac{\left(W_t - W_0\right)}{W_0} \times 100\%, \quad (2)$$

Batch adsorption experiments

A batchwise process was employed to study the adsorption of Cd (II) from aqueous solutions onto the PTBOZ, I (P(1/0.5)TBOZ/DEP), II (P(1/1)TBOZ/DEP) and III (P(1/2)TBOZ/DEP) adsorbents.[43] All the adsorption batch experiments were performed at 25 °C and the initial Cd(II) concentration was 100 mg L^{-1}. The mixtures were then centrifuged at 18000 rev/min. for 30 mins, and the residual concentration of Cd(II) was determined by atomic adsorption spectrometer (AAS, Varian Spectra AA 55). The effects of contact time and pH on adsorption ability were determined. All the adsorption experiments were performed in triplicate, and the means were used in the data analysis. The amount of adsorbed Cd (II) q_t (mg/g) at any time t was calculated by using the general equation (3):

$$q_t = \frac{\left(C_0 - C_t\right)V}{m}, \quad (3)$$

Where C_0 was the initial concentration of Cd(II) (mg/L), C_t was the Cd(II) solution concentration at any time t (mg/L), V was the solution volume (L), and m was the adsorbent mass (g).

3. Results and Discussion

3.1. Nucleophilic reaction of TBOZ with DEP

The NMR results of TBOZ were shown in Fig. S1. The proton resonance signals at 4.52 and 5.34 were assigned to the methylene protons of Ar-CH_2-N (6H) and O-CH_2-N (6H) of the benzoxazine ring, respectively. The proton resonance signal at 2.04 was assigned to the methyl proton (3H). The integral area ratio of the methylene protons (6H) and the methyl protons (3H) combined with ^{13}C NMR spectra of TBOZ indicated that the synthesis of TBOZ was succesful.

The nucleophilic addition reaction of TBOZ with DEP was monitored by ^{31}P NMR and the results are presented in Fig. 1 and Fig. 2. From Fig. 1, it could be estimated that at low temperature (70 °C) the addition reaction rate between TBOZ and DEP was slow. After 24 h, the unreacted DEP still existed, which was verified by the two peaks at 6.14 and 10.47 ppm corresponding to DEP. The reaction rate was speeded up by increasing the reaction temperature. At 90 °C, the addition reaction was completed within 24 h. But further raising the temperature (110 °C) would cause some side reaction because some small peaks appeared (Fig. 1C) around 0 ppm, which might be due to phosphite groups resulting from the hydrolysis of DEP at such condition.

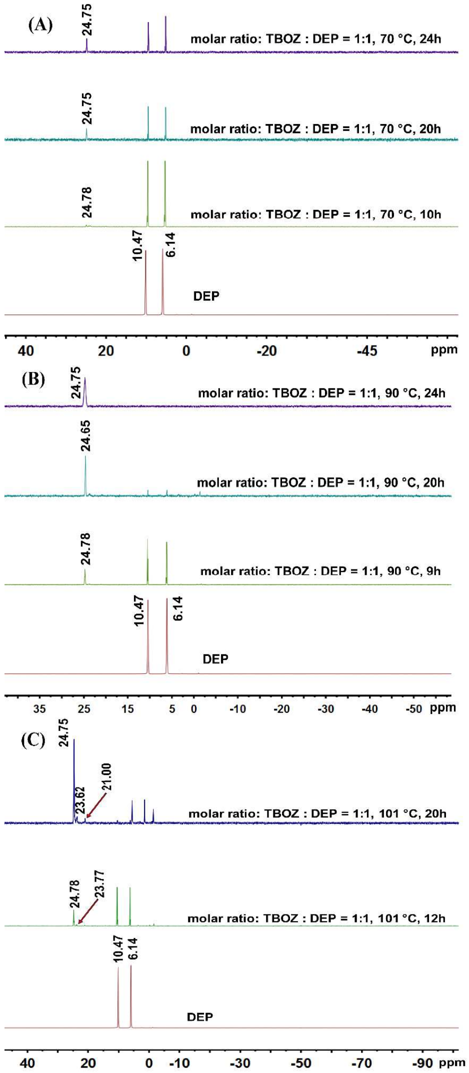


Fig. 1 ^{31}P NMR spectra of products from reaction of TBOZ with DEP at (A)

70 °C; (B) 90 °C; (C) 101 °C for different time.

But we should point out here that when TBOZ reacted with DEP at equal molar ratio, compound II was not the only product. At this condition, the product consisted of TBOZ, compound II, III and IV, certainly the compound II was the main product. In order to simplify the preparation procedure, we didn't give any further purification to the final product and it was used directly for next studies. Thus, according to the molar ratio of TBOZ and DEP used in the reaction, the corresponding DEP-modified product was named as (1/0.5)TBOZ/DEP, (1/1)TBOZ/DEP and (1/2)TBOZ/DEP. The synthetic procedures for (1/0.5)TBOZ/DEP and (1/2)TBOZ/DEP were the same as the model compound II.

^{1}H NMR spectrum of (1/1)TBOZ/DEP was shown in Fig. 2. Peaks at 4.01-4.07 ppm (O-CH$_2$) and 1.21-1.24 ppm (-CH$_3$) verified the successful introduction of DEP to TBOZ structure. Signals at 4.53 ppm (C-CH$_2$-N) and 5.38 ppm (O-CH$_2$-N) for benzoxazine ring were also observed, confirming that benzoxazine groups were still present which could undergo ring-opening polymerization during curing. After nucleophilic reaction the phenolic groups appeared and the signal for phenolic OH located at 9.36 ppm. The rest signals in Fig. 2 were attributed to P-CH$_2$-N (4.18 ppm), N-CH$_2$-Ar (3.75 ppm), aryl (6.70-7.21 ppm), P-O-CH$_2$ (4.01-4.07 ppm), CH$_3$ (1.21-1.24) and Ar$_3$-C-CH$_3$ (2.00 ppm).

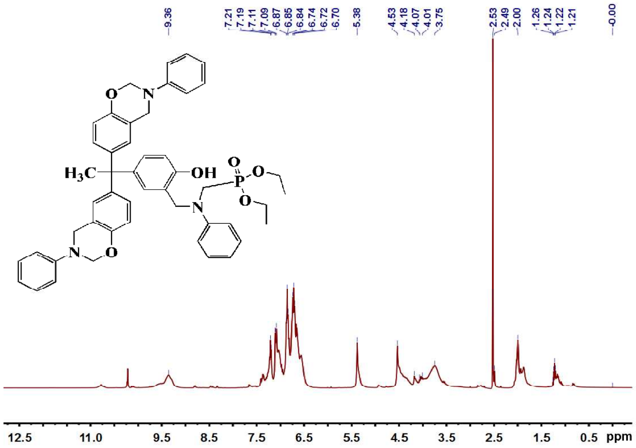


Fig. 2 ^{1}H NMR spectrum of model compound (1/1)TBOZ/DEP.

IR spectra of all cured samples were shown in Fig. 3. The wide peaks around 3418 cm^{-1} were attributed to the phenolic groups resulting from ring-opening polymerization. The peaks at 1250 cm^{-1}, 1061 cm^{-1} and 1380 cm^{-1} were due to P=O, P-O-C and P-C absorption, these facts further certified that the DEP groups had been successfully introduced into the cured polymer after polymerization.

DSC studying the curing behavior and thermal properties of cured polymers

The polymerization behavior of TBOZ, (1/0.5)TBOZ/DEP, (1/1)TBOZ/DEP and (1/2)TBOZ/DEP was monitored by DSC as shown in Fig. 4(A) and Table 1. In order to see the melting endothermic transition (57.5 °C) more clearly, the separately displayed DSC plot was shown in Fig. S2. It was obvious in Fig. 4(A) that DEP-modification caused dramatically changes to the polymerization characters of TBOZ. It showed a sharp exothermic transition with an onset temperature around 215.8 °C and a peak maximum at 238.1 °C. After nucleophilic addition reaction with DEP, both the onset and peak temperatures of resulting products ((1/0.5)TBOZ/DEP, (1/1)TBOZ/DEP and (1/2)TBOZ/DEP) shifted to lower temperature (Seeing table 1 for details). These results were attributed to two factors. First，it was known that phenolic group could lower the polymerization temperature of benzoxazine monomer due to its activated hydrogen.[38] From Scheme 1, it could be figured out that after modification by DEP, phenolic group appeared and it would catalyze the curing reaction of newly obtained TBOZ derivatives. With the increase of the molar ratio of TBOZ/DEP, the amount of phenolic groups increased simultaneously. For example, the onset and peak temperature of (1/2)TBOZ/DEP were 98.1 °C and 195.3 °C, respectively. Secondly, Liu and coworkers proved that phosphoester groups could also act as thermally latent catalyst for the curing reaction of benzoxazine monomers.[49] As we expected, higher DEP dosage would result in lower polymerization temperature.

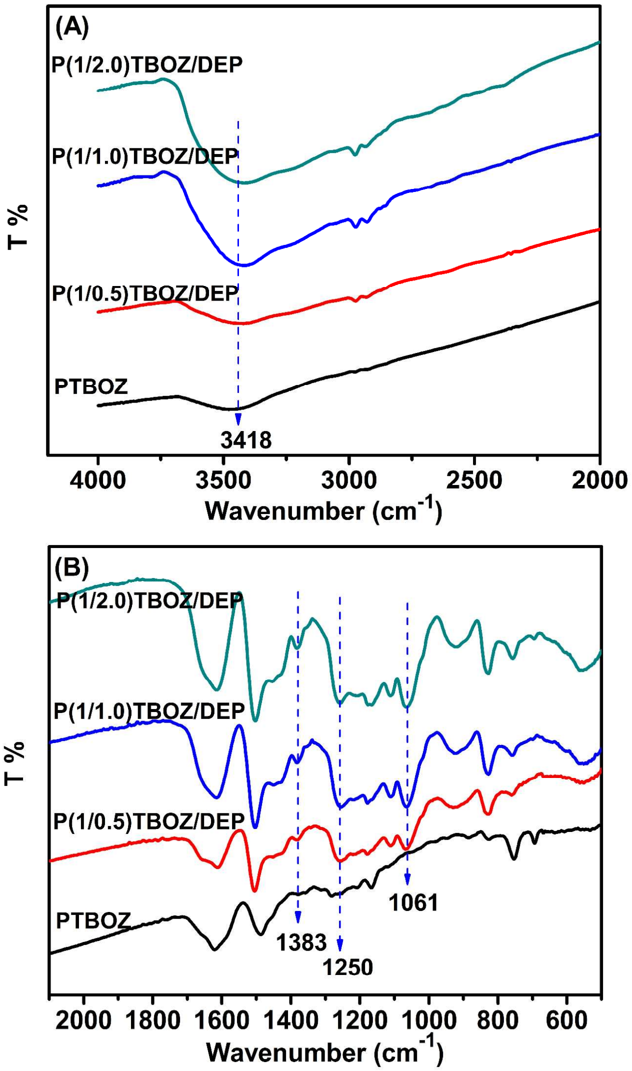
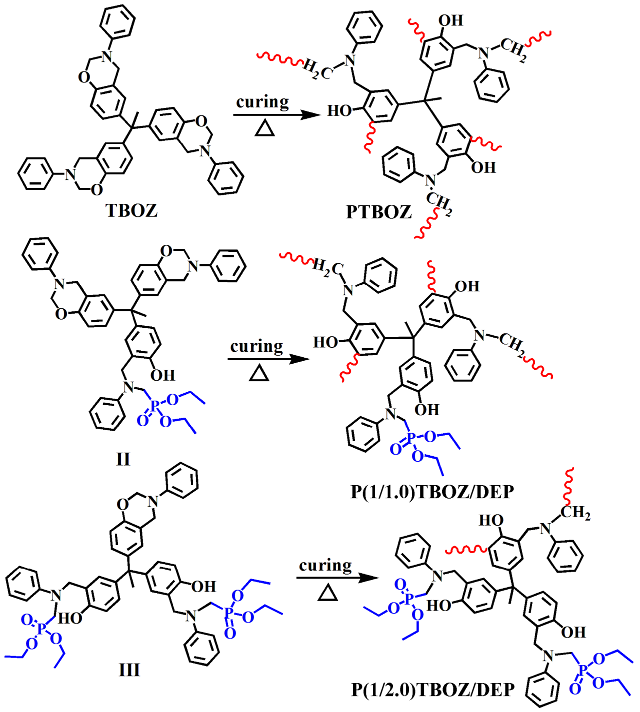


Fig. 3 FT-IR spectra of polybenzoxazines in the region between (A) 4200 and 2000 cm^{-1}; (B) 2100 and 500 cm^{-1}.



Scheme. 2 Polymerization of TBOZ, (1/1)TBOZ/DEP and (1/2)TBOZ/DEP under heating.

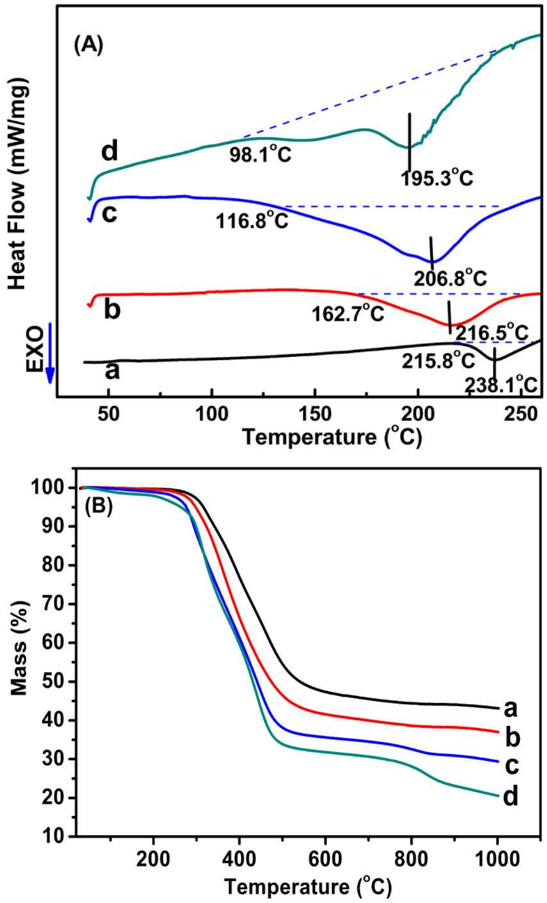


Fig. 4 DSC plots (A) of the four monomers (a: TBOZ; b: (1/0.5)TBOZ/DEP; c: (1/1)TBOZ/DEP; d: (1/2)TBOZ/DEP) and TG curves (B) of corresponding cured polymers.

In order to estimate the effect of DEP dosage on crosslinking density of cured polymer, the gel contents of cured TBOZ, (1/0.5)TBOZ/DEP, (1/1)TBOZ/DEP and (1/2)TBOZ/DEP was measured by solvent-extraction and the results were given in Fig. 5. After curing at the same condition, the gel content of PTBOZ, P(1/0.5)TBOZ/DEP, P(1/1)TBOZ/DEP and P(1/2)TBOZ/DEP was 99.79%, 99.63%, 98.35% and 97.06%, respectively. Though the gel content of cured polymer decreases with the addition of DEP, but all samples showed higher gel content above 97%, it meant that highly crosslinked polymer were obtained after curing reaction. This fact was consistent with the proposal that the reaction product between TBOZ and DEP is a mixture of TBOZ and DEP-modified TBOZ. According to theoretical calculation, when TBOZ/DEP underwent nucleophilic reaction at molar ratio 1/2, only compound III was with one benzoxazine ring left. In this case, the compound III would give a low gel content after curing reaction. But the experiment data showed the opposite result. Thus, we presumed the reaction product was a mixture and the residual TBOZ and compound II could act as crosslinker during curing reaction (see in Scheme 2).

The thermal stability of cured polymer was studied by TGA and the results were listed in Fig. 4 (B) and Table 1. Below 250 °C, all cured polymer showed similar thermal stability and weight loss could be neglected. The onset degradation temperature ($T_{5\%}$) of cured polymer decrease with addition of DEP, for PTBOZ the onset temperature is 315 °C, for P(1/2)TBOZ/DEP dropped down to 263 °C. $T_{10\%}$ and T_{max} showed similar trends. Between 300 °C and 500 °C, all cured polymer showed rapid thermal degradation. The char yields of cured polymer reduced with the increase of the DEP dosage, the value for PTBOZ was 44.0% at 850 °C, whereas the value for P(1/2)TBOZ/DEP reduced to 24.7%. It was obvious that the thermal stability of the polymer decreased with introducing the DEP groups into its structure. As we known, except the chemical structure, crosslinking density was one of the most important factors to determine the thermal stability of thermosetting polymer. Normally higher crosslinking density of polymer resulted in higher thermal stability. For PTBOZ originated from tri-functional monomer, it possessed the highest crosslinking density among the studied polymers, so it showed the best thermal stability. By introducing the DEP group into TBOZ, some of benzoxazine rings underwent ring-opening reaction with DEP and the average functionality of final products declined gradually, which would decrease the crosslinking density of cured polymers. Meanwhile, DEP would undergo thermal degradation at lower temperature range compared with polybenzoxazine itself. So it was another fact to deteriorate the thermal stability of cured polymers. Accordingly, the LOI[50] (limited oxygen index) changed from 35.1 for PTBOZ to 27.4 for P(1/2)TBOZ/DEP. But all cured polymer showed good fire retardancy.

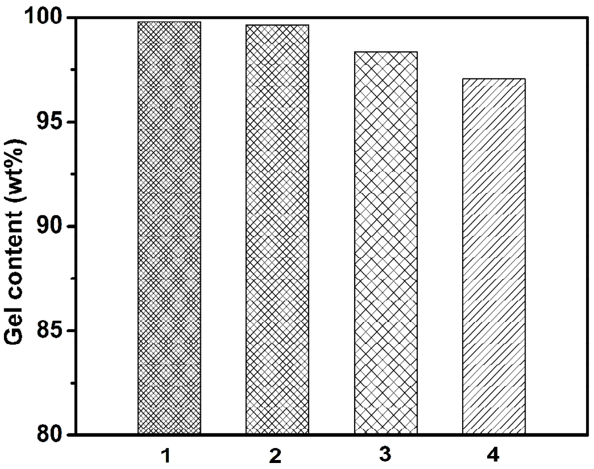


Fig. 5 Gel contents of the polybenzoxazines (1: PTBOZ; 2: P(1/0.5)TBOZ/DEP; 3: P(1/1)TBOZ/DEP; 4: P(1/2)TBOZ/DEP).

Mechanic properties of polybenzoxazine

Fig. 6 showed the typical DMA thermograms of all cured samples. Though all samples showed a high storage modulus at room temperature, the storage modulus decreased after addition of DEP, for PTBOZ the value was 5.36 GPa，the value gradually declined to 5.29 GPa for P(1/0.5)TBOZ/DEP, 4.28 GPa for P(1/1)TBOZ/DEP and 2.69 GPa for P(1/2)TBOZ/DEP. The glass transition temperature was determined by the peak of tan δ, it showed the similar trend as storage modulus. For example, the T_g of PTBOZ was 199 °C. With the introduction of DEP, the T_g of modified PTBOZ shifted down to 178 °C for P(1/0.5)TBOZ/DEP, 176 °C for P(1/1)TBOZ/DEP and 160 °C for P(1/2)TBOZ/DEP. The above results proved that the introduction of DEP into benzoxazinbe monomers would dramatically altered the storage modulus and T_g of the cured polybenzoxazines. The changes were attributed to the fact that the storage modulus and T_g of cured polymers mainly depended on crosslinking density of cured polymers. By introduction the DEP through nucleophilic reaction, the average functionality of monomers dropped down from three to one, which resulted in low crosslinking-density.

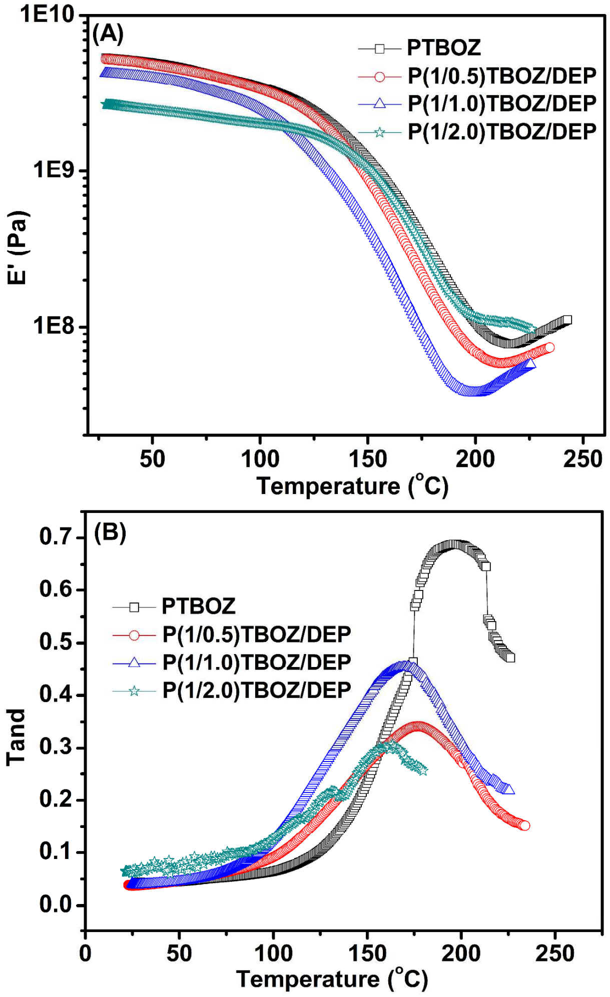


Fig. 6 Storage moduli (A) and Tan δ curves (B) of polybenzoxazines with different DEP content.

Impact properties

The dependence of the impact strength of cured polymers on DEP content was exhibited in Fig. 7. As expected, the impact strength at RT was appreciably enhanced by the introduction of DEP in polybenzoxazines. The impact strength of neat PTBOZ was about 2.2 kJ/m^2, the value for P(1/2)TBOZ/DEP increased to 6.2 kJ/m^2. The increase in the impact strength of the DEP-modified PTBOZ was due to the fact that the decrease in crosslinking density of cured resins by introduction of DEP would increase the flexibility of thermosets. Meanwhile, the DEP groups suspending to the polymer network were easy to move and could act as inherent plasticizer for cured polybenzoxazines.

Table 1 Thermal stability of polybenzoxazines modified with different content of DEP

Samples	T_o [a] (°C)	T_{max} [b] (°C)	$T_{5\%}$ [c] (°C)	$T_{10\%}$ [d] (°C)	T_{max} [e] (°C)	Y_c [f] (%)	LOI[g]
TBOZ	229.7	250.3	315	343	393	44.0	35.1
(1/0.5)TBOZ/DEP	162.7	216.5	298	324	366	38.4	32.9
(1/1.0)TBOZ/DEP	116.8	206.8	276	296	294	31.3	30.0
(1/2.0)TBOZ/DEP	98.1	195.3	263	290	311	24.7	27.4

[a] Onset temperature of exothermic peak.

[b] Maximum of the polymerization exotherm.

[c] The temperature for 5% weight loss

[d] The temperature for 10% weight loss.

[e] Maximum weight loss temperature.

[f] Char yields at 850 °C.

[g] calculated according to literature.[50]

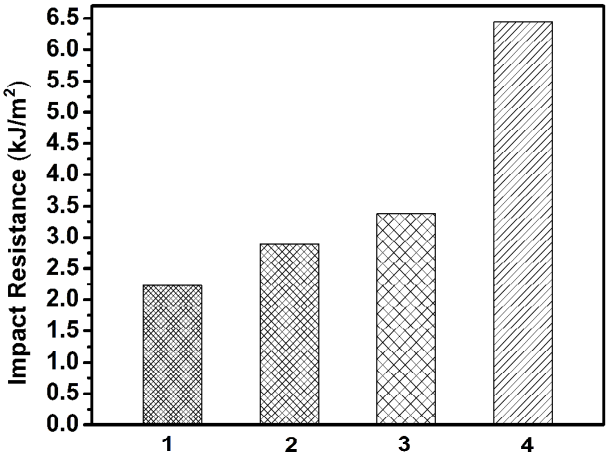


Fig. 7 Impact resistance of the polybenzoxazines (1: PTBOZ; 2: P(1/0.5)TBOZ/DEP; 3: P(1/1)TBOZ/DEP; 4: P(1/2)TBOZ/DEP).

Dielectric Analysis of Polybenzoxazines

Dielectric property of polymers is one of the key characters for its application in microelectronic devices.[14] The dependence of the dielectric constant and dielectric loss of all samples on the frequency range of 125 Hz ~ 18 MHz was studied at room temperature. Fig. 8 showed that both the dielectric constant (ε) and the dielectric loss (tan δ) of samples depended largely on the amount of DEP. Because the dielectric constant and dielectric loss were directly related to the polarizability of materials and could be increased by increasing the polarizability. Therefore, the dielectric constant and dielectric loss was strongly dependent on its chemical structure.[10] In theory, pure PTBOZ was uniform cross-linked polymer and all its components linked together by chemical bonds, so it showed lowest polarizability. By introducing DEP into polymer network, the DEP acted as polar pendant groups linked to the network by chemical bond and would increase the polarizability of modified polymers. Meanwhile，increasing the amount of DEP meant lower the cross-linking density of cure polymers, which would also result in the increase of polarizability for cured polymers. The experimental results were consistent very well with theoretical analysis. The dielectric constant of PTBOZ at 125 Hz was about 5.14, for P(1/0.5)TBOZ/DEP, P(1/1.0)TBOZ/DEP and P(1/2.0)TBOZ/DEP were 5.21，5.65 and 6.46, respectively. In the frequency range of 125 Hz to 0.1 MHz, the dielectric constant for each sample showed a little decrease. When the frequency of applied field exceeded to 1 MHz, the dielectric constants of all samples declined rapidly due to the suppression of orientation polarization of dipolar. The dielectric loss of PTBOZ, P(1/0.5)TBOZ/DEP, P(1/1.0)TBOZ/DEP and P(1/2.0)TBOZ/DEP at 125 Hz were 0.027, 0.038, 0.039 and 0.062, respectively. These values showed slightly decrease in the frequency range of 125 Hz ~ 0.1 MHz, and dropped remarkably when the frequency of applied field surpassed 1 MHz. The reason for such changes was the same as that of the dielectric constant.

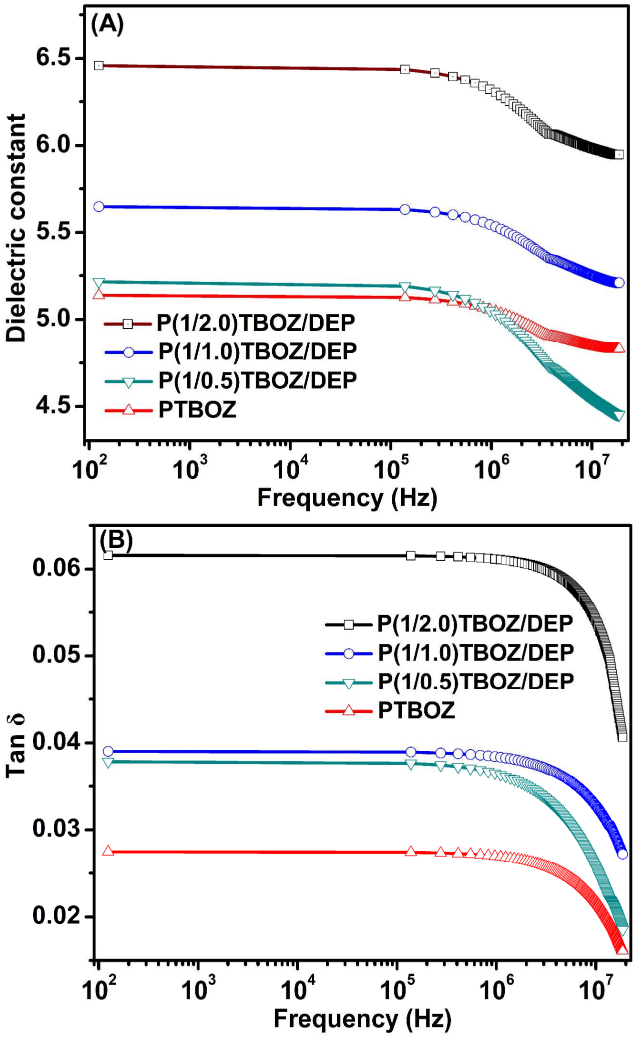


Fig. 8 Frequency dependence of the dielectric constant and dielectric loss of DEP-modified polybenzoxazines.

Humidity absorption of the polybenzoxazines

Many results[18,51] showed that polybenzoxazines possessed low water uptake ability under humid environment. This advantage was duo to the complete hydrogen-bond network formed between phenolic OH and nitrogen atoms which hindered the water absorption and transportation. As shown in Fig. 9, all the polybenzoxazine samples exhibited low water uptake value (<1.0 wt%) at room temperature after 9 days regardless of the RH value of the air was high or low. As expected the water uptake ability of the four samples changed regularly with introduction of DEP. The final water absorption values of the four polybenzoxazines increased in the order of PTBOZ, P(1/0.5)TBOZ/DEP, P(1/1.0)TBOZ/DEP, P(1/2.0)TBOZ/DEP. The value of PTBOZ was about 0.46 wt%, which was very close to other reports,[18,51] and the value increased to about 0.93 wt% for P(1/2.0)TBOZ/DEP. The higher water uptake ability of DEP-modified PTBOZ was attributed to polar phosphoester groups in the network and low crosslinking density.

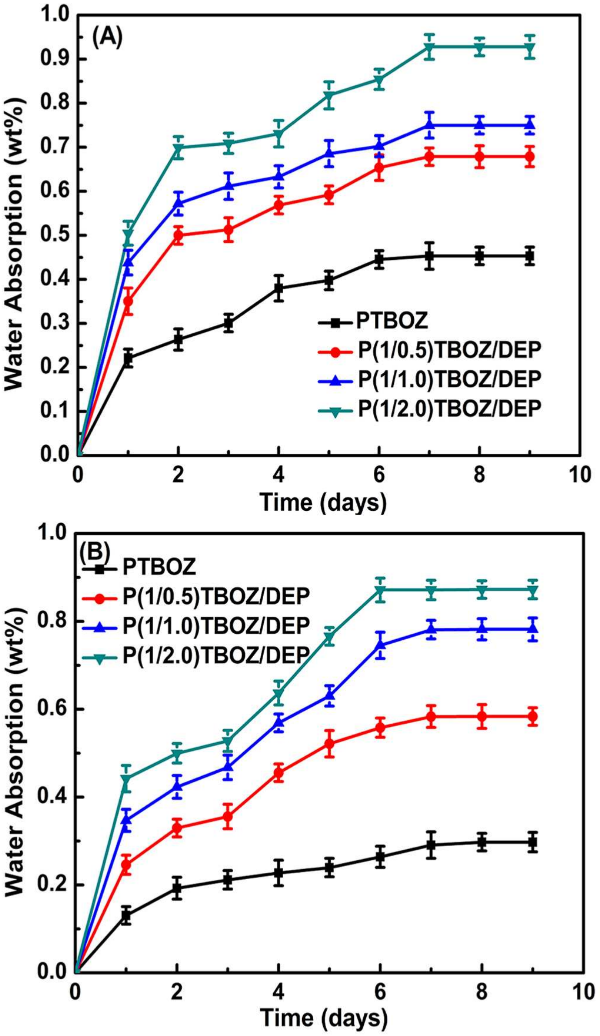


Fig. 9 Humidity adsorption of the polybenzoxazines with different DEP content at different relative humidity (RH) at room temperature. A. RH= 75%; B. RH= 33%.

Absorption ability of polybenzoxazine for Cd(II) in water

Heavy metals being discharged into water can cause serious environmental damage for its toxicity and non-biodegradablity. Various methods have been proposed for this mandatory work, such as chemical precipitation, neutralization, membrane filtration, and adsorption. Among these techniques, adsorption by using chelating polymers has gained considerable attention because of its high efficiency, recyclability of the adsorbents, and ease of handling.[52–54] The chelating polymeric ligands are characterized by the reactive functional groups containing O, N, S, or P as donor atoms, and they are capable of forming a coordination complex with different metal ions. A few reports have proven that polybenzoxazine aerogel can act as a chelating polymer to remove metals from water.[55] The powder-like DEP-modified polybenzoxazines contained O, N and P atoms and could possibly act as a new chelating material to remove Cd(II) from waste water. As shown in Fig. 10, the equilibrium adsorption capacity (q_e) increased with the introduction of DEP due to the fact that the phosphoester group was an efficient chelating site for many metal ions. For all four samples, the most suitable pH value for Cd(II) adsorption was about 5. At low pH range, the H^+ ion would compete for the chelating sites with Cd(II) and decrease the equilibrium adsorption capacity for Cd(II). At high pH value range, the Cd(II) would precipitate from water in the form of Cd(OH)$_2$. The critical pH value for Cd(OH)$_2$ formation was about 8.1 calculated from its solubility product constant ($K_{sp} = 5.27\times10^{-15}$). Meanwhile, the adsorption rates of the four polymers were also studied at pH = 5. The q_e of neat PTBOZ was about 82 mg/g after adsorption for 6 h, the value for P(1/2)TBOZ/DEP increased to over 100 mg/g in the same absorption condition. The results showed that the introduction of DEP into polybenzoxazines by chemical bonding was an efficient and practical method to improve the adsorption ability of polybenzoxazines for Cd(II) and other heavy metal ions even in its powder form.

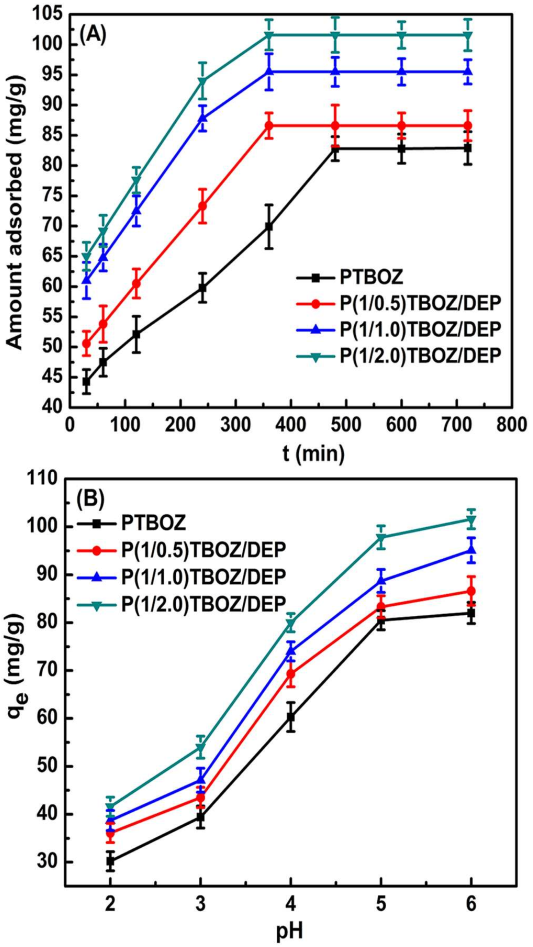


Fig. 10 Effect of time (A) and pH value (B) on the adsorption of Cd(II) from aqueous solution at 25 °C.

4. Conclusions

In this work, we have revealed a facile method to introduce phosphoester groups into polybenzoxazines backbone by chemical bonding through nucleophilic reaction of benzoxazine ring with diethyl phosphite (DEP). The novel products directly underwent ring-opening polymerization. A comprehensive research was carried out on the properties of the prepared DEP-modified polybenzoxazines. With the introduction of DEP, the onset polymerization temperature greatly decreased and the weight loss at 850 °C increased. All cured polymers showed excellent mechanic properties, higher impact strengths and high gel content after the addition of DEP. Meanwhile, all polymer powders showed high absorption ability for Cd(II). We believe this thought can help researchers design and explore novel polybenzoxazines resins and apply them in a wide range of areas.

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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