# A Novel Benzimidazole Moiety-Containing Benzoxazine: Synthesis, Polymerization, and Thermal Properties

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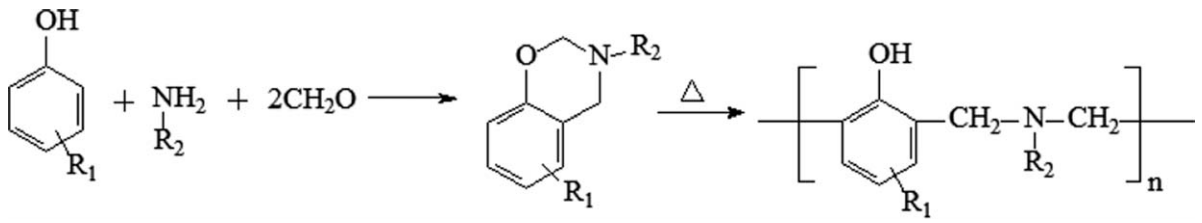
**ABSTRACT**: A novel benzoxazine-containing benzimidazole moiety (P-PABZ) was synthesized from 2-(4-aminophenyl)-1*H*-benzimidazole-5-amine and characterized. With the aid of differential scanning calorimetry and *in situ* Fourier transform infrared, we found the thermal polymerization of P-PABZ in bulk started around 140 °C and its favored polymerization pathway. Compared to the benzoxazine derived from 4,4′-diamine diphenyl methane (P-MDA), P-PABZ exhibited lower processing temperature, and the corresponding polymers had higher glass transition temperature and enhanced thermal stability. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1261–1271, 2012

**KEYWORDS**: benzimidazole; benzoxazine; catalysts; high performance polymers; polybenzoxazine; thermal polymerization

**INTRODUCTION** As shown in Scheme 1, polybenzoxazines are the polymers with —$CH_2$—NR—$CH_2$— (Mannich-type) structure via the thermal polymerization of correspondent benzoxazine monomers synthesized from formaldehyde, phenol or phenol derivatives, and primary amines.[1–7] As an alternative to traditional phenolic resins, polybenzoxazines have been received considerable interest from scientific and industrial community. The major advantages of polybenzoxazines are good thermal stability, good flame retardance, excellent resistance to chemicals and UV light, low-dielectric properties, low-surface energy, low-water absorption, near-zero volumetric shrinkage, and no volatile release during polymerization.[8–17]

Although polybenzoxazines are synthesized very early, they have not been applied widely for a long time because of the high-polymerization temperature.[1] The research for decreasing the polymerization temperature of benzoxazines is therefore receiving a great deal of attention. The target is an approach that can decrease the polymerization temperature and will not have any major adverse effects on their properties. Two approaches have been considered for decreasing the polymerization temperature: (1) by adding catalysts like imidazoles or acidic compounds and (2) by synthesizing novel benzoxazines containing catalytic groups or special molecular structures.[17–28] As for the first approach, imidazoles or acids act as catalysts or initiators, but they are not incorporated into the network, generating residues.[17–20] These free residues can decrease the thermal properties as plasticizers and migrate to the surface to produce fragile materials. For this reason, an approach without using additives is desirable. The benzoxazine contains both special groups and oxazine rings will act as catalysts and comonomer, and will be part of network, which should not interfere with the properties. Hence, synthesis of the benzoxazines-containing catalytic groups or special molecular structures is a considerable approach. As for this approach, a series of benzoxazines containing special groups such as carboxylic acid, side-chain liquid crystal, hydroxyl, diacetylene, and urethane have been synthesized; however, they will release volatile during polymerization or interfere with the polymers' properties, affording polybenzoxazines of poor processability and thermal properties.[21–28]

In this study, we attempt to decrease the polymerization temperature of benzoxazines through synthesis of a benzoxazine-containing special structure. The special structure in this work is benzimidazole. Benzimidazole structure has an active N—H structure and does not release volatile at elevated temperature; moreover, it can restrict the chain mobility as a rigid structure to give the polymers many excellent properties such as good mechanical properties and thermal properties.[29,30] Therefore, if a benzoxazine contains both benzimidazole moiety and oxazine rings, it will act as catalysts and comonomer simultaneously and will be part of network, which will not interfere with or enhance the thermal properties. The aim of this work is synthesis of such benzoxazine (Scheme 5; P-PABZ and $^{iso}$P-PABZ) and



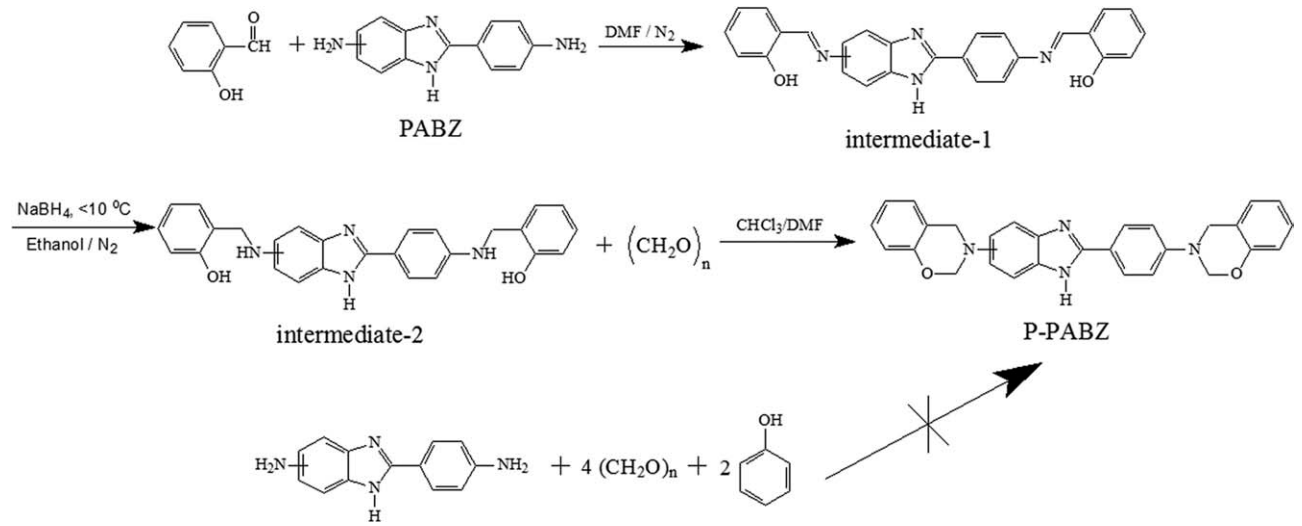
**SCHEME 1** Synthesis of benzoxazines and polybenzoxazines.

determination of its thermal polymerization behavior and thermal properties. Efforts to decrease the polymerization temperature, we also explore the possibility of using this benzoxazine to blend with another benzoxazine derived from 4,4′-diamine diphenyl methane. According to the results, we find that P-PABZ has low-polymerization temperature and can effectively decrease the processing temperature of other benzoxazines, while the thermal properties of their polymers, such as $T_g$s and thermal stability, are not low.

## RESULTS AND DISCUSSION

Because of the poor solubility of PABZ and the formation of gelation between PABZ and paraformaldehyde, P-PABZ was not synthesized by traditional method. Hence, we used a three-step synthetic method to synthesize P-PABZ, according to the procedure presented in Scheme 2.[31–33] In the first step, intermediate-1 was synthesized by *ortho*-hydroxybenzaldehyde and PABZ. Figure 1(b) showed the $^1$H NMR spectra of intermediate-1. The signal at 9.08 ppm for —CH=N— was observed, confirming the formation of imine linkage. Because of intermediate-1's asymmetry structure, the resonances of phenolic OH were observed at 12.97 and 13.10 ppm. Additionally, the signal of benzimidazole unit appeared. After that, the imine linkage of intermediate-1 was reduced by $NaBH_4$ below 10 °C by ice bath, while the benzimidazole structure should be preserved. The $^1$H NMR spectra of intermediate-2 and the assignment were shown in Figure 1(c). The signals at 4.24, 5.67, and 5.90 ppm were assigned to Ar—NH—$CH_2$—, which confirmed the reduction of imine linkage. Because of the isomer of intermediate-2, two signals of benzimidazole unit were observed at 11.86 and 11.97 ppm, and they disappeared after exchanging by deuterium oxide [Fig. 1(d)].

In this study, trial has been made to find the suitable solvents for the synthesis of P-PABZ using intermediate-2 and paraformaldehyde. As shown in Table 1, when toluene, chloroform, and 1,4-dioxane were used as the reaction solvents, no reaction occurred, because intermediate-2 was insoluble in these solvents, even though nonpolar solvents, such as chloroform, toluene and xylene, were regarded as appropriate solvents to synthesize benzoxazines generally.[34,35] Gelation occurred when *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAC) were used. To obtain P-PABZ, so, DMF was added to chloroform as a cosolvent due to the poor solubility of intermediate-2 in nonpolar solvent. The chemical structure of P-PABZ was confirmed by FTIR and $^1$H NMR. The absorption band appeared at 945 $cm^{-1}$ proved the formation of the oxazine ring. The absorption for the benzimidazole unit appeared at 3408 and 1662 $cm^{-1}$. $^1$H NMR was used to further confirm the structure of P-PABZ [Fig. 1(e)]. The characteristic oxazine resonances typically showed downfield singlet for —O—$CH_2$—N— and upfield singlet for Ar—$CH_2$—N—. In this study, because of the asymmetry structure, the —O—$CH_2$—N— resonance split into 5.45 and 5.52 ppm, whereas the Ar—$CH_2$—N—



**SCHEME 2** Synthesis of P-PABZ.

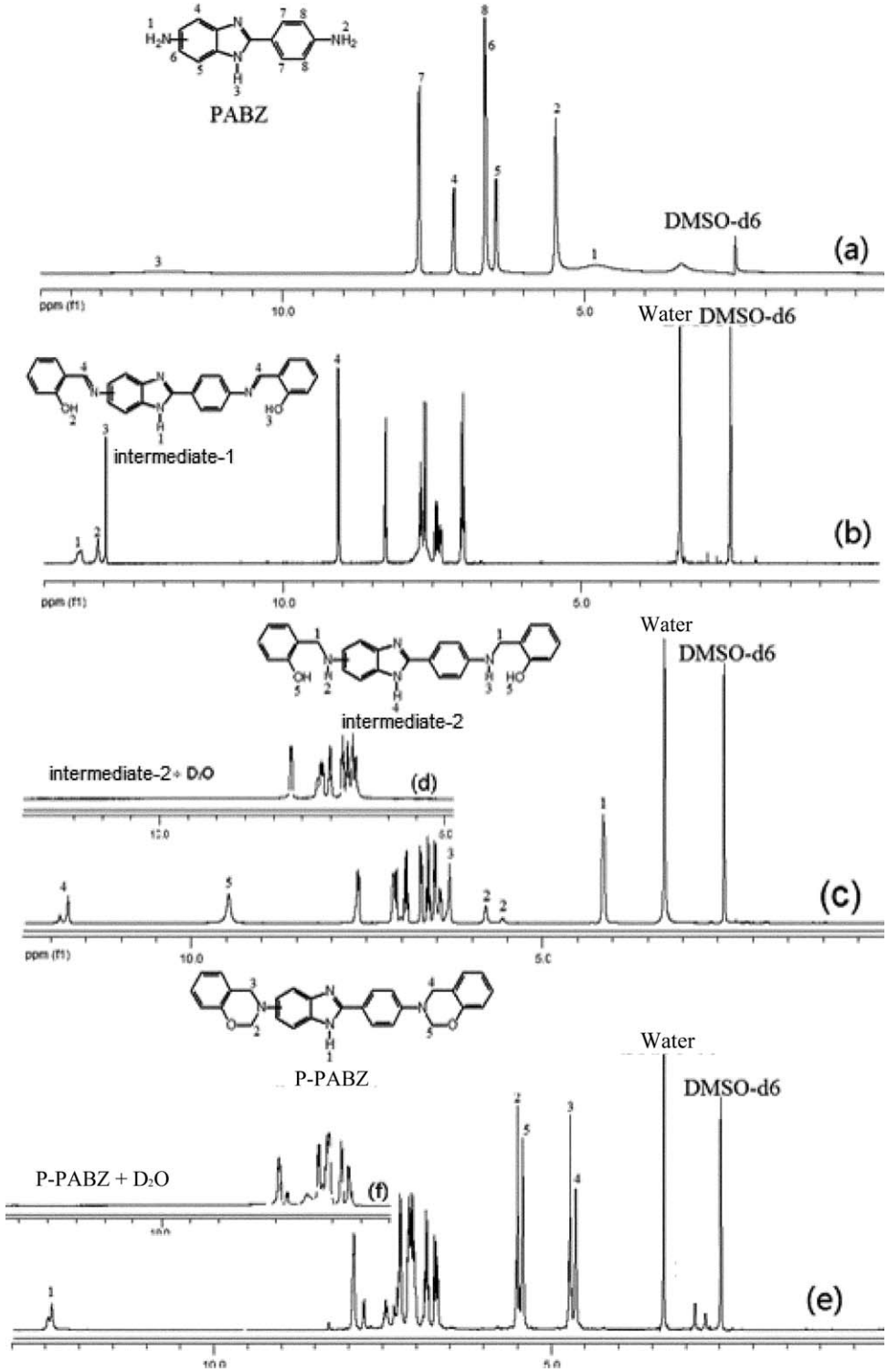



**FIGURE 1** $^1$H NMR spectra (DMSO-$d_6$) of PABZ (a), intermediate-1 (b), intermediate-2 (c) and it exchanged by deuterium oxide ($D_2O$) (d), P-PABZ (e), and it exchanged by $D_2O$ (f).

resonance split into 4.66 and 4.74 ppm. Two signals of benzimidazole moiety were observed at 12.45 and 12.51 ppm and disappeared after exchanging by deuterium oxide [Fig. 1(f)], suggesting that benzimidazole unit was preserved in P-PABZ.

The thermal polymerization behaviors of P-MDA and P-PABZ are investigated by differential scanning calorimetry (DSC) (Fig. 2) at a heating rate of 5 °C/min. As can be seen from Figure 2, the onset of polymerization for P-MDA did not appear until 200 °C, and the exothermic peak centered at

**TABLE 1** The Effect of Reaction Conditions on Synthesis of P-PABZ

| Run[a] | Solvent | Solubility[b] | Reaction temperature (°C) | Reaction time (h) | Result |
|---|---|---|---|---|---|
| 1 | DMF | + | 85 | 5 | Gelation |
| 2 | DMAC | + | 85 | 5 | Gelation |
| 3 | Toluene | − | 85 | 5 | No reaction |
| 4 | Chloroform | ± | 55 | 5 | No reaction |
| 5 | 1,4-Dioxane | ± | 85 | 5 | No reaction |

[a] Intermediate-2 and paraformaldehyde are in a mole ratio of 1:2.
[b] Solubility of intermediate-2 in the solvent, +, soluble; ±, partial soluble; −, insoluble.

222 °C. However, the exotherm of P-PABZ started at around 140 °C and maximized at 181 °C with broad polymerization exotherm peak. The results showed that the thermal polymerization of P-PABZ occurred at a temperature that was nearly 60 °C lower than that of P-MDA, indicating that benzimidazole moiety could decrease the thermal polymerization temperature. Moreover, the sharp melting peak of P-PABZ indicated its high purity.

To further study the polymerization behavior, the relationship of conversion versus temperature obtained from DSC is used and can be expressed as[36,37]

$$\text{Conversion} = \frac{H(T)}{H_R} \times 100\%$$

where $H(T)$ is the enthalpy of reaction up to temperature $T$, and $H_R$ is the total enthalpy of polymerization.

Benzoxazine monomers undergo oxazine ring-opening polymerization to give the corresponding polymers, so that the conversion of oxazine ring consumed can be approximately used as an indicator of the extent of polymerization.[18] In this work, *in situ* FTIR is applied to follow the oxazine ring-opening reaction. As *in situ* FTIR study, polymerization of the benzoxazines from 100 to 300 °C is continuously monitored using a heated transmission cell placed in the spectrometer. The absorbance peak located between ~875 and 1000 $cm^{-1}$ assigning to oxazine ring consumes sustainingly during thermal polymerization (Fig. 3). Because this absorbance band does not have any significant overlapping peaks, the conversion can be calculated from the change in area of oxazine ring absorbance band.[38] The relationship of conversion versus temperature obtained from FTIR is expressed as

$$\text{Conversion} = \left[1 - \frac{A(T)/A'(T)}{A(R)/A'(R)}\right] \times 100\%$$

where $A(T)$ and $A(R)$ are the integrated areas of oxazine ring absorbance band at given temperature ($T$) and 100 °C, respectively, and $A'$ ($T$) and $A'$ ($R$) are the integrated areas of benzene band absorbance around 750 $cm^{-1}$ at given temperature ($T$) and 100 °C, respectively (Fig. 3).

The conversion versus temperature curves of P-MDA and P-PABZ were shown in Figures 4 and 5, respectively. As can be seen from Figure 4, the conversion curve of P-MDA obtained from FTIR was similar to that from DSC. Both the curves showed that the polymerization of P-MDA started at around 200 °C and ended at 250 °C. However, the conversion curves of P-PABZ obtained from FTIR were quite different from that from DSC. The FTIR results showed that P-PABZ reached the conversion of 50% at nearly 170 °C, but, to reach the same conversion, the curves obtained from DSC appeared at ~220 °C. The results probably suggested that different polymerization behaviors took place for P-PABZ and P-MDA, although no additional initiators or catalysts were added. This is probably caused by the benzimidazole moiety of P-PABZ, which acted as the internal catalyst and been part of the benzoxazine molecule.

During the thermal polymerization of benzoxazines, two main structures, Mannich-type structure and *N*,*O*-acetal-type structure (Mannich-type structure and *N*,*O*-acetal-type structure in Scheme 3), will be gained.[17,39–41] For the two structures, phenolic Ar—OH exists in Mannich-type structure but does not exist in *N*,*O*-acetal-type structure, and Mannich-type structure is the thermodynamically more stable structure. Without adding any initiators or catalysts, a benzoxazine monomer relies on the thermal activation of the oxazine ring to produce Mannich-type structure.[39] In this case, Mannich-type structure immediately follows after the oxazine ring opening, the fraction of oxazine ring absorbance band

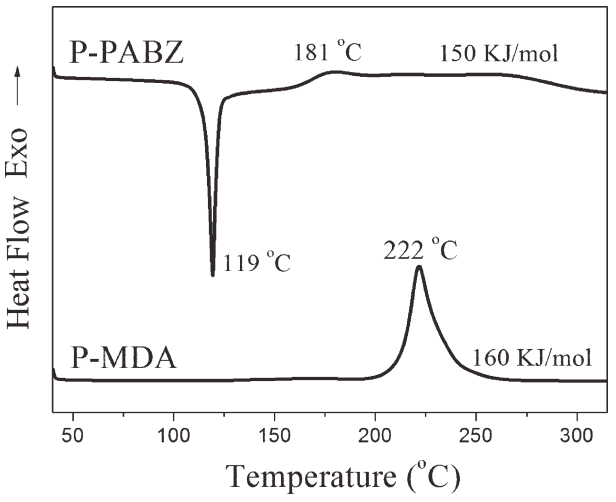



**FIGURE 2** DSC plots of P-PABZ and P-MDA.

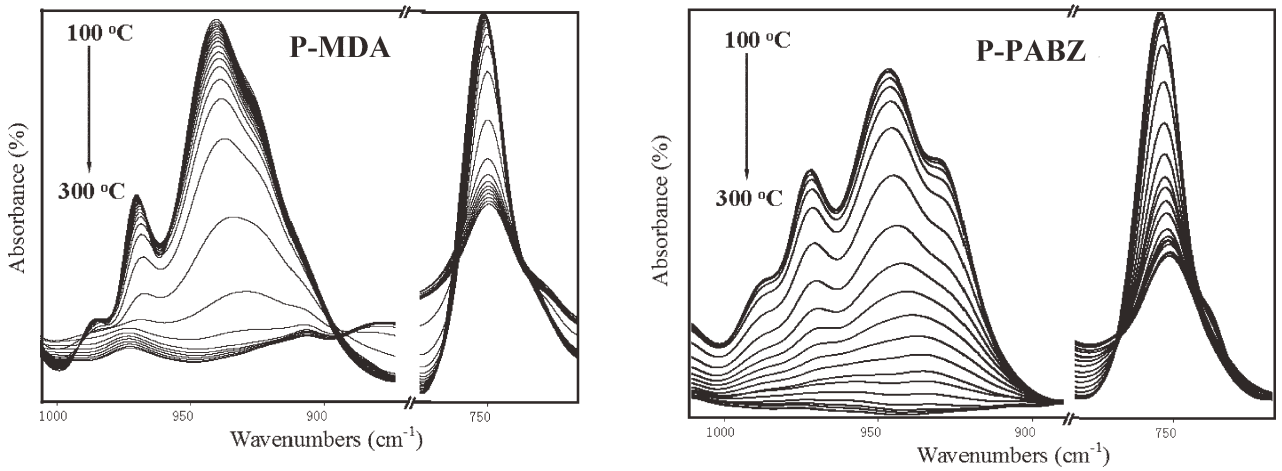



**FIGURE 3** *In situ* FTIR spectra of P-MDA and P-PABZ.

consumed can approximately signify the polymerization process.[18,38] Hence, the conversion curves obtained from FTIR are closer to that from DSC. However, by adding initiators or catalysts, the thermal polymerizations become that corresponding polybenzoxazines via formation of intermediary *N*,*O*-acetal-type structure first and then rearrangement into Mannich-type structures at higher temperature.[17,19,40,41] There is a temperature lag between the oxazine ring opening and polymerization; therefore, the conversion curves obtained from FTIR that is dependent on the oxazine ring opening is different from that from DSC. The polymerization behaviors suggest that the main polymerization of P-MDA is that consumes oxazine ring to produce Mannich-type structure, while P-PABZ is the formation of intermediary *N*,*O*-acetal-type structure first and then rearrangement into Mannich-type structures.

This is also supported by the changes of intensity for phenolic Ar—OH on the FTIR spectra, because Ar—OH just exists in Mannich-type structure. In the case of P-MDA [Fig. 6(b)], Ar—OH-related absorbance peak appeared at near 3500 $cm^{-1}$ when the polymerization started (around 200 °C), indicating the existence of Mannich-type structure. The intensity increases with the rise of conversion, but it increases little above the end temperature (about 250 °C). The results probably suggested that the main polymerization pathway of P-MDA was that consumed oxazine ring to produce Mannich-type structure directly as Scheme 3 Path A shown. For P-PABZ, no obvious bands appeared near 3500 $cm^{-1}$ until at 175 °C indicated little Ar—OH groups existed; however, about 60% of oxazine ring has been consumed according to the conversion curve obtained from FTIR. This probably suggested that *N*,*O*-acetal-type structure was favored at lower temperature. As temperature rises, the bands of Ar—OH groups appeared, and the intensity increased constantly, indicating that produce Mannich-type structure at higher temperature. Hence, the favored polymerization pathway of P-PABZ is probably that formed *N*,*O*-acetal-type structure first (Path B: *Step a* in Scheme 3) and then transformed into Mannich-type structure at elevated temperature (Path B: *Step b* in Scheme 3). This pathway is the same as the benzoxazines with adding initiators or catalysts, but no

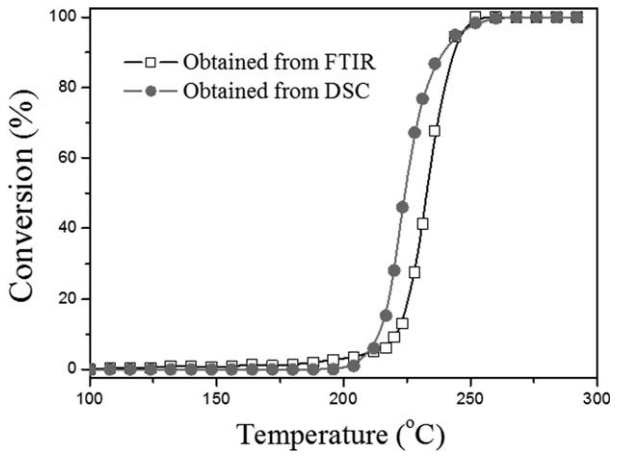



**FIGURE 4** The conversion versus temperature curves of P-MDA.

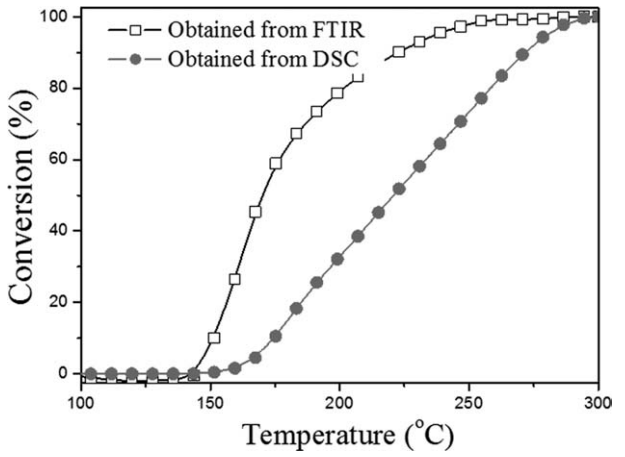
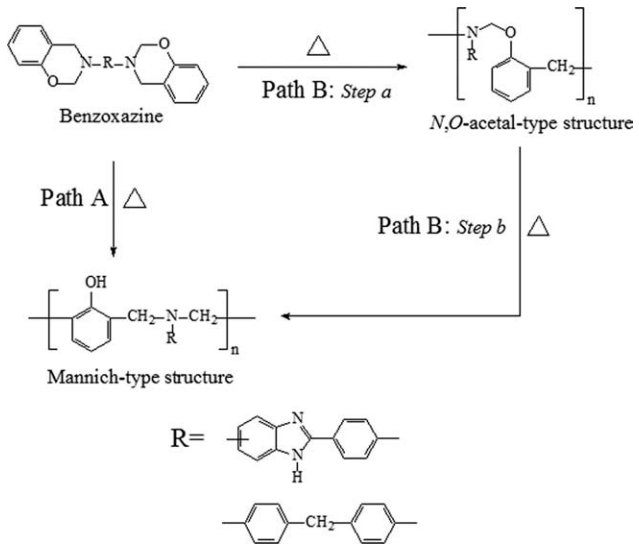



**FIGURE 5** The conversion versus temperature curves of P-PABZ.




**SCHEME 3** Thermal polymerization pathways of P-MDA and P-PABZ.

additional initiators or catalysts are added into P-PABZ.[17] Hence, P-PABZ may have self-catalyzed characteristics ascribed to the benzimidazole moiety. The oxygen atoms of oxazine rings were protonated by the active N—H structure of benzimidazole moiety to form iminium ions, and then these iminium ions were preferred to combine with the corresponding phenoxide into *N*,*O*-acetal-type structure at lower temperature.[18,40]

To the better understanding of the polymeric structure, the region between 2000 and 600 $cm^{-1}$ in FTIR spectra of P-PABZ after different polymerization temperatures is recorded and shown in Figure 7. The oxazine ring absorptions at 945 $cm^{-1}$, the Ar—O—C absorptions at 1056 and 1227 $cm^{-1}$, and the 1,2-disubsituted benzene absorptions at 1484 $cm^{-1}$ disappeared after curing at 200 °C, indicating complete ring-opening reaction of the oxazine ring. However, the absorption band at 1260 and 1478 $cm^{-1}$ revealed the formation of phenolic Ar—OH and 1,2,3-trisubstituted benzene. Additionally, the absorption appeared at 1185 $cm^{-1}$, which corresponded to the C—N—C (Mannich-type) structure, was observed in P(P-PABZ), demonstrating P(P-PABZ) formed Mannich-type polymer. The benzimidazole unit absorption at 1662 shifted to 1657 $cm^{-1}$ after polymerization, illustrating the benzimidazole moiety incorporated into the polymeric network. According to the FTIR analysis, the structure of P(P-PABZ) was proposed and shown in Scheme 4. The benzimidazole moiety was still preserved into the network after thermal polymerization.

In this work, we also explored the possibility of decreasing the thermal polymerization temperature of other benzoxazines by blending with P-PABZ. Imidazoles or acides have been used to decrease the polymerization temperature of benzoxazines.[17–20] In this case, oxazine ring generated the corresponding *N*,*O*-acetal-type structure as an intermediate. Then this intermediate generated the thermodynamically more stable Mannich-type structure through rearrangement upon heating.[17] For example, 3 wt % of imidazole was added as a catalyst to P-MDA produced a decrease of 60 °C in the onset of polymerization temperature as Figure 8 (EMI) shown, whereas it was not incorporated into the network. Thus, some benzoxazines were attempted to use as additives to decrease other monomers' polymerization temperature.[21,38] It was shown previously that the onset temperatures observed to date for the polymerization of P-PABZ were much lower than P-MDA. Significantly, P-PABZ contains both benzimidazole moiety and oxazine ring, so that it will be the catalyst and comonomer and be incorporated into the

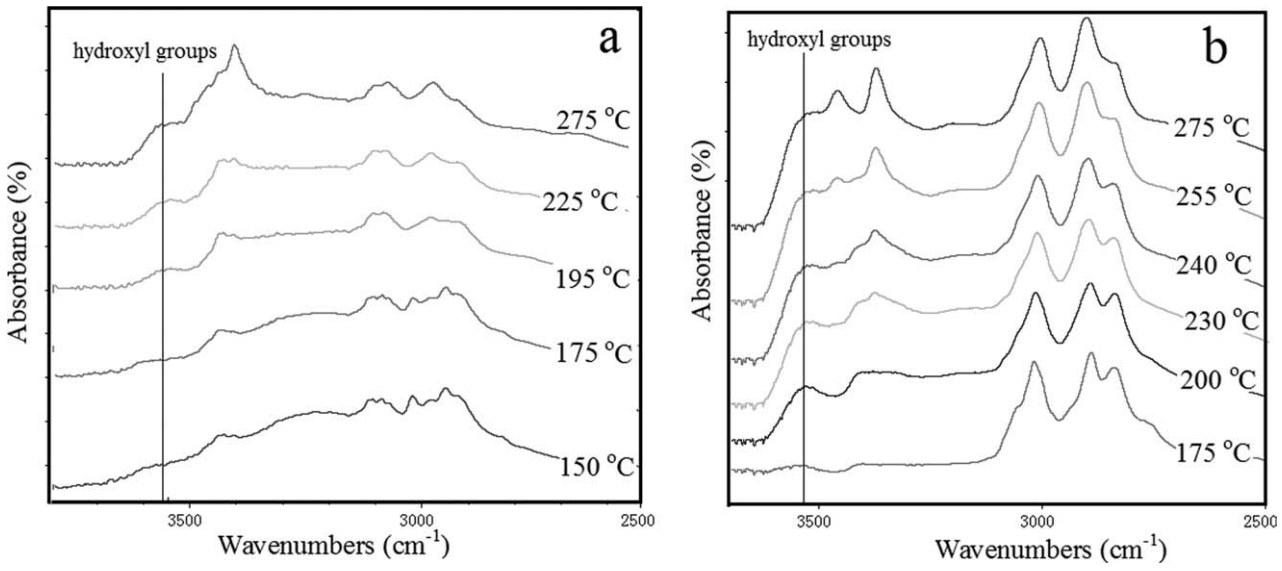



**FIGURE 6** FTIR spectra of P-PABZ (a) and P-MDA (b) at different temperature in the 3800–2500 $cm^{-1}$ region.

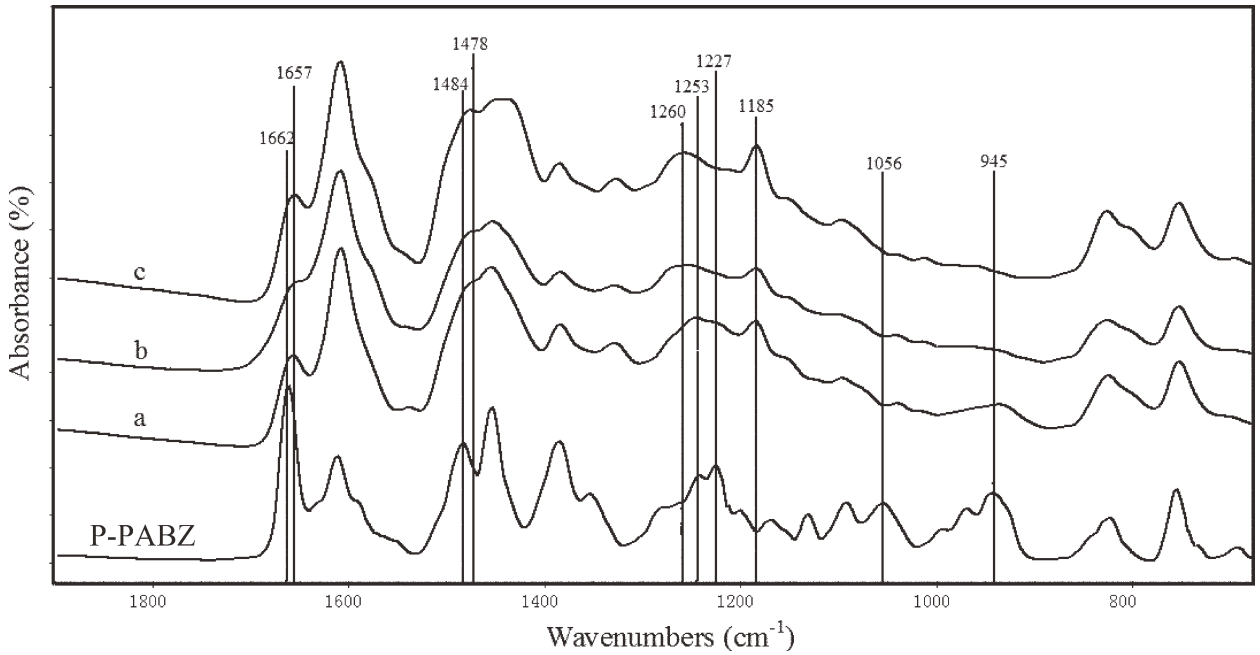


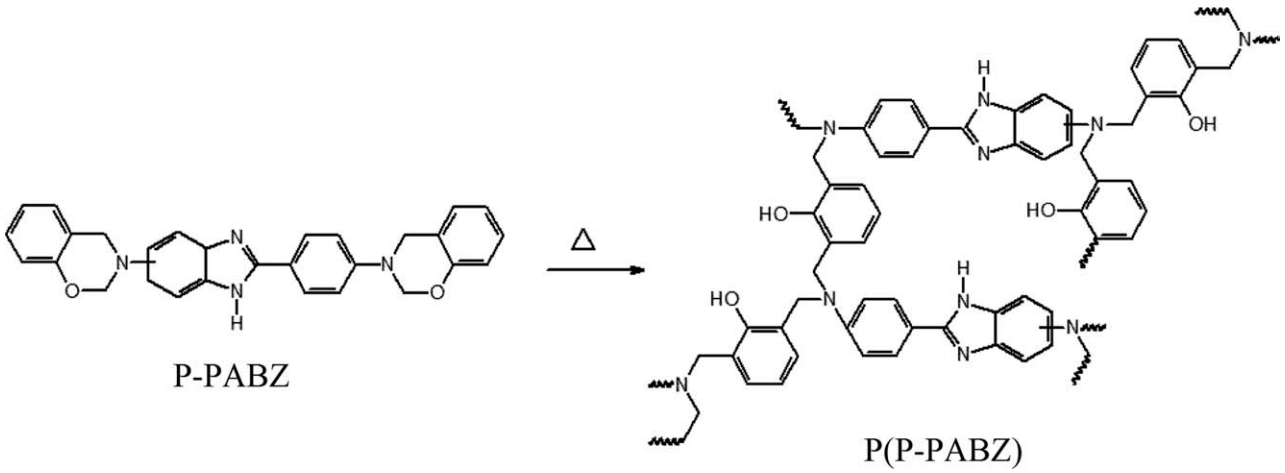

**FIGURE 7** FTIR spectra of P-PABZ between 2000 $cm^{-1}$ to 600 $cm^{-1}$ at room temperature (P-PABZ), cured after 160 °C (a), cured after 180 °C (b), and cured after 200 °C (c).

network structure. This will not give any major adverse effects on the properties.

In an effort to exploit the possibility of decreasing the thermal polymerization temperature of benzoxazines by blending with P-PABZ, several mixtures of P-MDA and 0 (P-MDA), 10 (B10), 30 (B30), and 50 (B50) wt % of P-PABZ were prepared and studied by DSC. The results are collected in Figure 8. As can been seen from Figure 8, the onset of polymerization was shifted almost 45 °C lower, and the exotherm with the peak centered at 220 °C became broad, when 10% P-PABZ (B10) was added. The onset of polymerization temperature decreased nearly 55 °C when the percentage of P-PABZ reached at 30%. As the percentage continued to increase to 50%, the polymerization temperatures became approximately as EMI. Hence, P-PABZ can effectively serve as a catalyst for P-MDA by lowering the temperature for polymerization significantly.

The glass transition temperature is an important property of thermosetting polymer. In this work, dynamic mechanical analyzer (DMA) is applied to probe the polymers. The results are shown in Figure 9 and Table 2.

As can be seen, the measured values of P(P-PABZ) were much higher than that of P(P-MDA), because the rigid benzimidazole moiety restricted the segmental movement effectively. For the blend with P-MDA and imidazole, a decrease of about 15 °C in $T_g$s was detected, probably indicating that imidazole hinders the thermal properties of polybenzoxazines, because it was




**SCHEME 4** Possible structure of P(P-PABZ).

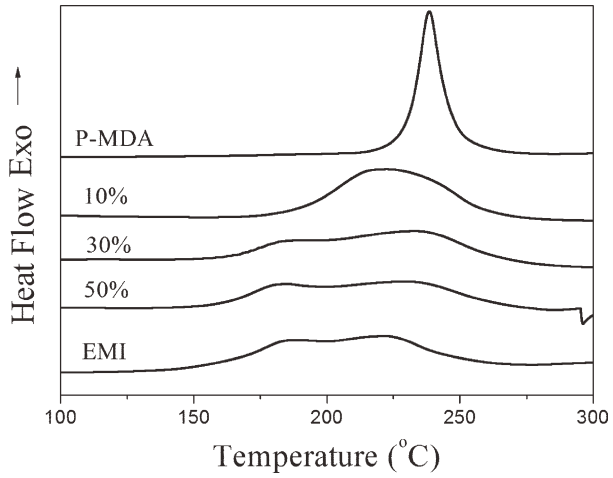



**FIGURE 8** DSC plots of the mixtures of P-MDA and its blends.

not incorporated into the network. For the blends with P-MDA and P-PABZ, scarcely increased in $T_g$s with 10 and 30%, but, an increase of about 10 °C was detected when 50% P-PABZ was used. This is because P-PABZ can incorporate directly into the network, and the rigid benzimidazole units help to reduce the segmental mobility.

Finally, the thermal stability of these polymers is analyzed by thermogravimetric analysis (TGA). The TGA thermograms and the values obtained from TGA are shown in Figure 10 and Table 2, respectively. As can be seen, both the 10% weight loss temperature and the residue of P(P-PABZ) exceed those of P(P-MDA), indicating P(P-PABZ) has better thermal stability than P(P-MDA). Simultaneously, little decrease in 10% weight loss temperature and a slight increase in residue of the polymers by adding P-PABZ, illuminating incorporation of P-PABZ could improve polybenzoxazines' thermal stability. However, the results obtained from TGA also showed that small amounts of imidazole produced a decrease in 10% weight loss temperature (20 °C) and residue, suggesting that imidazole may interfere with the thermal stability of polybenzoxazines.

## EXPERIMENTAL

### Materials

2-(4-Aminophenyl)-1*H*-benzimidazole-5-amine (PABZ) was obtained from ChangZhou Sunlight Medical Raw Material. Co. (China). Paraformaldehyde was supplied by Fydsa (Spain). *Orth*-hydroxybenzaldehyde, sodium borohydride ($NaBH_4$), imidazole, DMF, DMAC, toluene, 1,4-dioxine, chloroform,

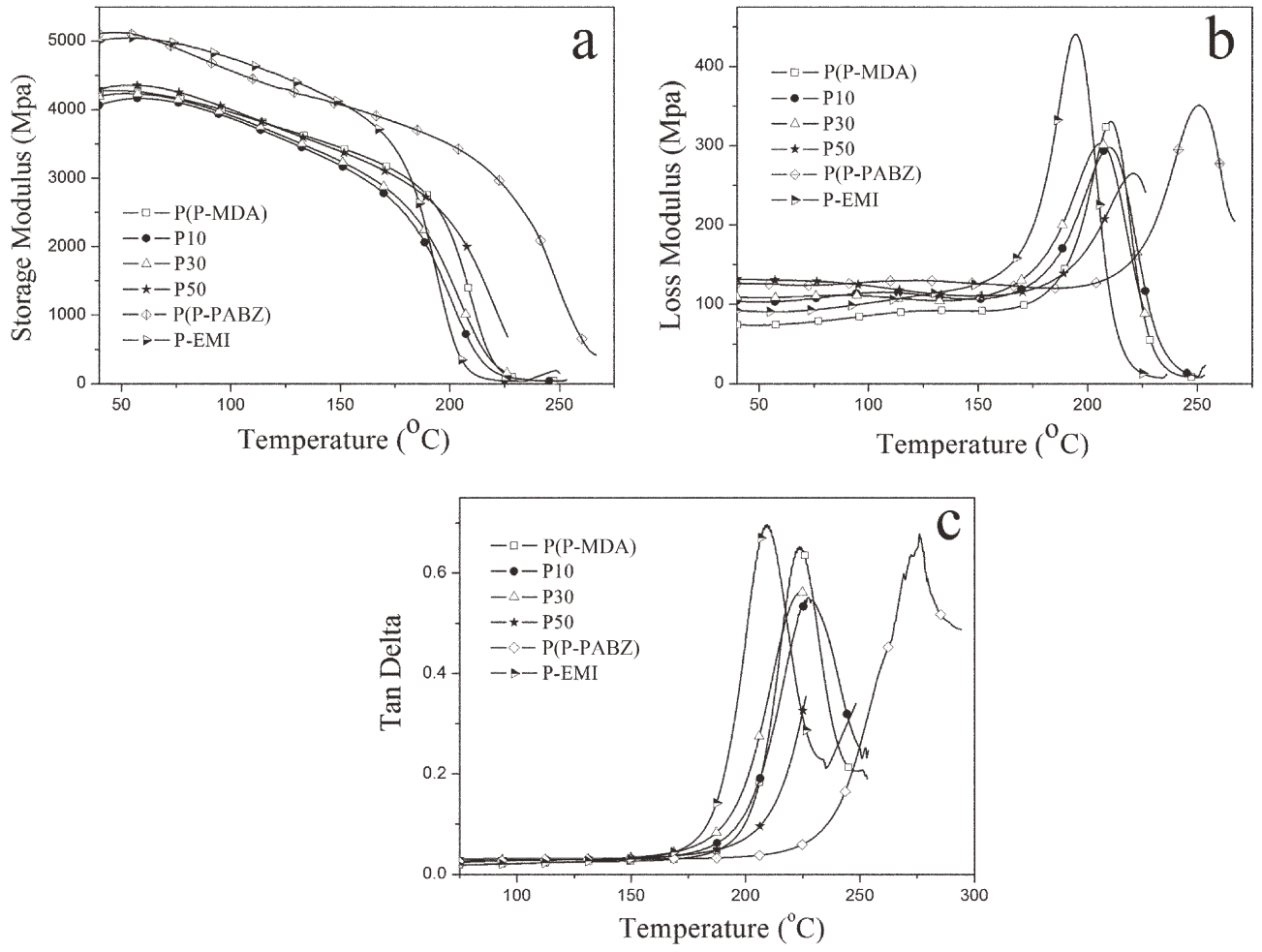



**FIGURE 9** Storage modulus (a), loss modulus (b), and tan $\delta$ (c) of P(P-MDA), P(P-PABZ), and polymers from their blends.

**TABLE 2** DMA and TGA data for P(P-MDA), P(P-PABZ), and polymers from their blends

| Polymer | $T_g$(°C)[a] | $T_g$(°C)[b] | $T_g$(°C)[c] | $T_{10\%}$(°C)[d] | $R$(%)[e] |
|---|---|---|---|---|---|
| P(P-MDA) | 192 | 210 | 223 | 365 | 39 |
| PB10 | 190 | 210 | 228 | 368 | 42 |
| PB30 | 194 | 206 | 224 | 362 | 42 |
| PB50 | 203 | 221 | –[f] | 364 | 41 |
| P(P-PABZ) | 231 | 251 | 276 | 386 | 50 |
| P-EMI | 178 | 194 | 209 | 346 | 37 |

[a] Glass transition temperature obtained from the storage modulus of DMA.
[b] Peak of loss modulus, measured by DMA.
[c] Peak of tan $\delta$, measured by DMA.
[d] Temperature of 10% weight loss in nitrogen measured by TGA.
[e] Residue at 800 °C in nitrogen measured by TGA.
[f] The data cannot be obtained from DMA.

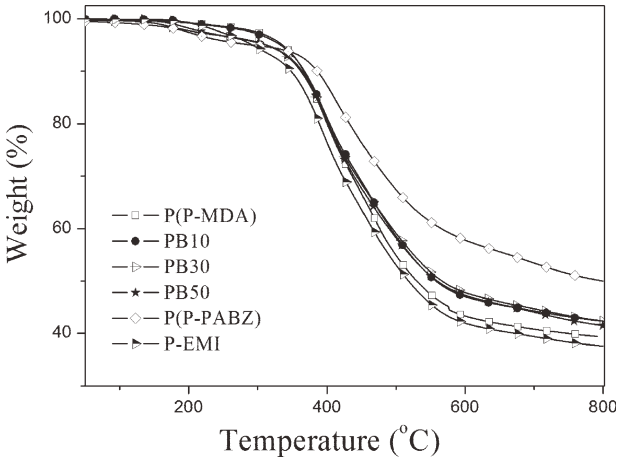



**FIGURE 10** TGA thermograms of P(P-MDA), P(P-PABZ), and polymers from their blends.

butanone, acetone, and ethanol were purchased from ChengDu Kelong Chemical Reagents Corp. (China) and used without further purification. Benzoxazine derived from 4,4′-diamine diphenyl methane (P-MDA) was prepared by our laboratory. The chemical structures of imidazole and P-MDA were shown in Scheme 5.

### Synthesis of Intermediate-1

*Orth*-hydroxybenzaldehyde (24.4 g and 0.2 mol), PABZ (22.4 g and 0.1 mol), and DMF (120 mL) were introduced into a 250-mL three-necked flask under nitrogen atmosphere. The mixture was stirred at 50 °C for 4 h. After the mixture cooling to room temperature, the precipitate was filtered and dried in a vacuum oven to give brown powder intermediate-1 (42.8 g and 99% yields) with a melting point of 243 °C (DSC).

$^1$H NMR (DMSO-$d_6$, ppm): $\delta$ = 6.96–8.30 (15H, Aromatic *H*), 9.08 (2H, Ar—C**H**=N), 12.97 and 13.10 (2H, Ar—O**H**), and 13.38 (1H, N—**H** of benzimidazole). $^{13}$C NMR (DMSO-$d_6$, ppm): $\delta$ = 117–152 (Ar), 160.7 and 160.9 (**C**H=N), 162.3, and 164.3 (—**C**—CH=N). FTIR (KBr, cm$^{-1}$): 1616 (CH=N), 3419 (N—H of benzimidazole), and 3200–3500 (OH). $C_{27}H_{20}N_4O_2$: Calcd. C 75.06 %, H 4.66%, N 12.97%, and O 7.31%. Found C 75.12%, H 4.72%, N 12.74%, and O 7.42%.

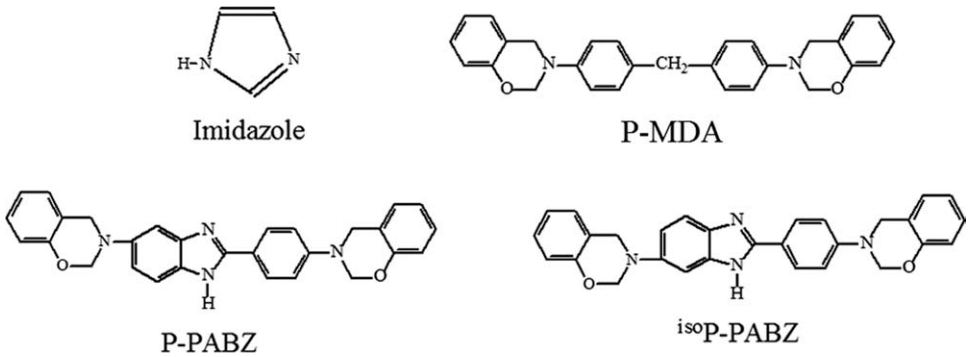
### Synthesis of Intermediate-2

Intermediate-1 (36.75 g and 0.085 mol) and ethanol (150 mL) were introduced into a 250-mL three-necked flask with a nitrogen inlet and a magnetic stirrer. The mixture was cooled by ice bath, followed by adding sodium borohydride ($NaBH_4$) (9.36 g and 0.255 mol) portionwise with stirring for 12 h below 10 °C by ice bath. Finally, the mixture was poured into deionized water (500 mL), and the precipitate was filtered and dried in a vacuum oven at 110 °C for 2 h to obtain 34.1 g (92% yields) of tawny powder intermediate-2 with a melting point of 208 °C (DSC).

$^1$H NMR (DMSO-$d_6$, ppm): $\delta$ = 4.24 (4H, —NH—C**H$_2$**—Ar—), 5.67 and 5.90 (1H, Ar—N**H**—C), 6.42 (1H, Ar—N**H**—C), 9.57 (2H, Ar—O**H**), 11.86 and 11.97 (1H, N—**H** of benzimidazole), and 6.61–7.81 (15H, Aromatic *H*). $^1$H NMR ($D_2O$ + DMSO-$d_6$, ppm): $\delta$ = 4.22 (4H, —N—C**H$_2$**—Ar—), and 6.61–7.81 (15H, Aromatic *H*). $^{13}$C NMR (DMSO-$d_6$, ppm): $\delta$ = 41.7 and 43.0 (NH—**C**H$_2$—Ar), 112–156 (Ar). FTIR (KBr, cm$^{-1}$): 1240 (C—N stretch), 1636 (vibration of benzimidazole), 3424 (N—H of benzimidazole stretch), and 3200–3500 (OH stretch). $C_{27}H_{24}N_4O_2$: Calcd. C 74.31%, H 5.50%, N 12.84%, and O 7.35%. Found C 74.43%, H 5.37%, N 12.94%, and O 7.26%.

### Synthesis of P-PABZ

Intermediate-2 (21.8 g and 0.05 mol), paraformaldehyde (3.3 g and 0.11 mol), chloroform (100 mL), and DMF




**SCHEME 5** Chemical structures of imidazole and the benzoxazines described in the present contribution.

(10 mL) were introduced into a 250-mL three-necked flask. The mixture was stirred at reflux temperature for 4 h. At last, solvents were removed using a rotary evaporator. After recrystallization in butanone/ethanol and drying in a vacuum oven, 14.3 g (63% yields) of white powder (P-PABZ) with a melting peak of 116 °C (DSC) and a curing peak temperature of 187 °C were obtained.

$^1$H NMR (DMSO-$d_6$, ppm): $\delta$ = 4.66 and 4.74 (4H, —NH—C**H$_2$**—Ar—), 5.45 and 5.52 (4H, —N—C**H$_2$**—O—), 12.45 and 12.51 (1H, N—**H** of benzimidazole), and 6.61–7.95 (15H, Aromatic *H*). $^1$H NMR ($D_2O$+DMSO-$d_6$, ppm): $\delta$ = 4.63 and 4.70 (4H, —NH—C**H$_2$**—Ar—), 5.41 and 5.48 (4H, —N—C**H$_2$**—O—), and 6.69–7.96 (15H, Aromatic *H*). $^{13}$C NMR (DMSO-$d_6$, ppm): $\delta$ = 48.9 and 50.7 (—NH—**C**$H_2$—Ar—), 78.3 and 80.9 (—N—**C**$H_2$—O—), and 112–162 (Ar). FTIR (KBr, $cm^{-1}$): 945 (oxazine ring), 1056 (Ar—O—C symmetric stretch), 1227 (Ar—O—C asymmetric stretch), 1662 (vibration of benzimidazole), and 3408 (N—H of benzimidazole stretch). $C_{29}H_{24}N_4O_2$: Calcd. C 75.65 %, H 5.22%, N 12.17%, O 6.96%. Found C 75.54%, H 5.34%, N 12.31%, and O 6.81%.

### Preparation of the Blends of P-PABZ and P-MDA

In the blends of P-PABZ and P-MDA, the weight ratios of P-PABZ to P-MDA were 1/9, 3/7, and 5/5, respectively. The procedure was as follows: in a 50-mL flask equipped with beater, P-PABZ and P-MDA were introduced with the ratios. Then, 5 mL of acetone was added, and the system was stirred at 65 °C until both P-PABZ and P-MDA melted completely. After removing the solvent, transparent light yellow products were obtained, which were named as B10, B30, and B50, respectively.

### Preparation of the Blend of Imidazole and P-MDA

The blend of imidazole and P-MDA was prepared in comparison with the blends of P-PABZ and P-MDA. This blend was prepared as follows: imidazole (0.3 g), P-MDA (10 g), and acetone (5 mL) were introduced into a 50-mL flask. The mixture was stirred at 65 °C until imidazole and P-MDA melt completely. After removing the solvent, we obtained a transparent light yellow product named as EMI.

### Preparation of Polymers from P-PABZ, P-MDA, and the Blends

P-PABZ, P-MDA, B10, B30, B50, and EMI were melted and transferred to an aluminum mold and cured stepwise at 140 °C (3 h), 150 °C (3 h), 160 °C (3 h), 170 °C (3 h), 180 °C (3 h), 190 °C (2 h), and 200 °C (1 h) to obtain polybenzoxazines named as P(P-PABZ), P(P-MDA), PB10, PB30, PB50, and P-EMI, respectively. Then, the samples were cooled to room temperature slowly to prevent cracking.

### Characterizations and Measurements

Fourier transform infrared (FTIR) studies were performed in KBr pellets using a Nicolet Magna 650 spectroscope at a resolution of 4 $cm^{-1}$. The scanned wavenumbers range from 4000 to 400 $cm^{-1}$. $^1$H NMR and $^{13}$C NMR measurements were conducted on a Bruker TD-65536 NMR (400 MHz) in DMSO-$d_6$ as solvent with tetramethylsilane as the internal reference. Elemental analysis was conducted with Elementar vario EL III analyzer. *In situ* Fourier transform infrared (*in situ* FTIR): Nicolet 560 IR spectrometer, which was equipped with a deuterated triglycine sulfate detector. The spectral resolution was 4 $cm^{-1}$, and the number of scans of each spectrum was 40. The sample was protected by dried high-purity nitrogen gas during measurement. The IR spectra were collected from 100 to 300 °C; meanwhile, the temperature increased at a constant rate of 5 °C/min. DSC scans were obtained with a TA Instruments Q20 under nitrogen atmosphere at a heating rate of 10 °C/min without special instructions. DMA was performed with a TA Instruments DMA Q800 at 1 Hz at a heating rate of 5 °C/min in three-point bending model under nitrogen. TGA was performed with a TA Instruments' High Resolution Q600 thermogravimetric analyzer under nitrogen atmosphere from 40 to 800 °C at a heating rate of 10 °C/min.

## CONCLUSIONS

In this work, we synthesized a novel benzoxazine-containing benzimidazole moiety with low-polymerization temperature and good thermal properties. During thermal polymerization, this benzoxazine formed *N*,*O*-acetal-type structure first and then transformed into Mannich-type structure. Adding this benzoxazine into other benzoxazines can effectively decrease the processing temperature, and the polymers have better $T_g$s and enhanced thermal stability. We believe that the benzoxazine-containing benzimidazole moiety can satisfy the demands of decreasing the polymerization temperature of benzoxazines.

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