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Synthesis, characterization, and polymerization of a novel benzoxazine based on diethyltoluenediamine

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ABSTRACT: A novel aromatic diamine-based benzoxazine monomer (PDETDA) was successfully prepared from diethyltoluenediamine (DETDA), phenol, and paraformaldehyde through a simple one-step solvent-less method. The structure of PDETDA was confirmed by FTIR, ^{1}H NMR, and ^{13}C NMR. The curing behavior of PDETDA was studied by DSC, FTIR, and rheological measurement. The results showed that the alkyl substituents on the benzene ring in DETDA not only facilitated the synthesis of PDETDA by effectively hindering the formation of triazine network, but also endowed PDETDA with the advantage of low viscosity (1 Pa s at 90°C). However, steric hindrance of the substituents made PDETDA difficult to form a crosslinked network through ring-opening polymerization, and therefore only oligomers and noncrosslinked polymers were obtained. The curing kinetics of PDETDA was studied by nonisothermal DSC, and the results revealed that the curing of PDETDA displayed autocatalytic characteristic. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41920.

KEYWORDS: crosslinking; differential scanning calorimetry; kinetics; resins; ring-opening polymerization

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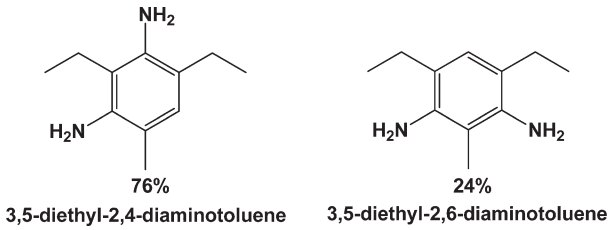
INTRODUCTION

Benzoxazine is a novel thermosetting resin developed in recent years, which is usually prepared from phenols, primary amines, and formaldehyde by Mannich condensation reaction.[1–5] Compared with the conventional thermosetting resins, benzoxazine resin has many unique advantages such as no small molecule byproduct released and near-zero shrinkage during curing, and rich flexibility of molecular design.[6–10] Moreover, the polybenzoxazine exhibits good mechanical properties and thermal stability, low dielectric constant, low water absorption, and high char yield.[4,11–13] As a result, it owns broad application prospects in the aerospace, automotive, electronic packaging, and many other industries.

To date, a large number of benzoxazine monomers and prepolymers have been reported,[14–20] among which most were synthesized by diphenols, primary monoamines, and formaldehyde, namely diphenol-type benzoxazines. However, relatively less attention was paid to the aromatic diamine-based benzoxazines, which were prepared from aromatic diamines, monophenols together with formaldehyde, even though their corresponding polybenzoxazines exhibited higher glass transition temperature (T_g) and better thermal stability than those of the diphenol-type.[21–23] Two reasons account for this discrepancy. On the one hand, aromatic diamines usually have higher melting points and worse solubility than diphenols, plus they are inclined to form insoluble triazines byproduct during the reaction, so the aromatic diamine-type benzoxazines are more difficult to be prepared and the yields are lower. On the other hand, from the processing point of view, benzoxazines with low melting point and melt viscosity are always favorable. For example, in the manufacturing of fiber reinforced composites, resin transfer molding (RTM) is a widely used method that molds large yet precise part with minimum void content, and one of the basic requirements for RTM resins is the sufficiently low viscosity so as to thoroughly permeate the fiber performs.[24–26] However, most of the reported aromatic diamine-type benzoxazines are high melting point solid and thus are difficult to be molded.[21] Therefore, development of low viscosity and easily synthesized aromatic diamine-type benzoxazines are demanded.

Diethyltoluenediamine (DETDA) is a liquid aromatic diamine with very low viscosity (160 mPa s at 25°C), which may produce benzoxazine with low viscosity. It has the structure of *m*-phenylenediamine with two ethyls and one methyl as substituents, and is widely used as chain extender for polyurethane and curing agent for epoxy resin. Commercial product of DETDA is a mixture of two isomers (76% of 3,5-diethyl-2,4-diaminotoluene and 24% 3,5-diethyl-2,6-diaminotoluene). The structures



Scheme 1. The structures of DETDA.

of the two isomers are shown in Scheme 1. To our knowledge, benzoxazine monomer based on DETDA has not been reported. Since there are two ethyls and one methyl substituents in DETDA molecule, the synthesis, properties, and curing behavior of benzoxazine from DETDA would be unique. In this article, we utilized DETDA, phenol and paraformaldehyde to synthesize DETDA-based benzoxazine (PDETDA) through a simple one-step solvent-less method. The structure of PDETDA was characterized, and the curing behavior and curing kinetics of PDETDA were detailed studied.

EXPERIMENTAL

Materials

DETDA (mixture of 76% of 3,5-diethyl-2,4-diaminotoluene and 24% 3,5-diethyl-2,6-diaminotoluene, technical grade), *m*-phenylenediamine (AR, Sinopharm Chemical Reagent, China), paraformaldehyde (95%, Sinopharm Chemical Reagent, China), phenol (AR, Beijing Chemical Works, China), chloroform (AR, Beijing Chemical Works, China), sodium hydroxide (NaOH, AR, Beijing Chemical Works, China), anhydrous sodium sulfate (Na_2SO_4, AR, Beijing Chemical Works, China). All of these reagents were used without further purification.

Synthesis of Diethyltoluenediamine-Based Benzoxazine

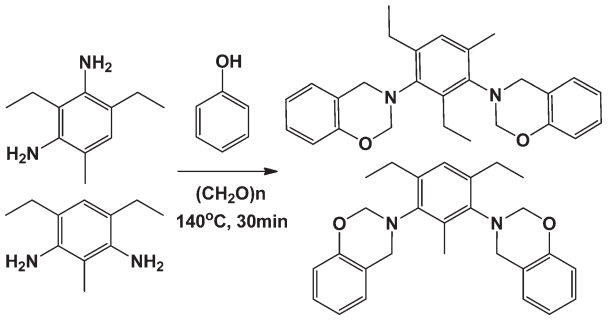
Into a 100 mL round-bottom-flask fitted with a mechanical stirring bar, DETDA 3.56 g (20 mmol), phenol 3.76 g (40 mmol), and paraformaldehyde 2.78 g (88 mmol) were added. The mixture was heated to 140°C and kept stirring for 30 min. After cooling to room temperature, the crude product was dissolved in chloroform and washed first with 1 mol L^{-1} aqueous NaOH solution and then with distilled water. Then the organic phase was separated and dried over anhydrous Na_2SO_4. After removal of Na_2SO_4 by filtration, the resultant solution was evaporated under vacuum to give a reddish brown solid 7.0 g (yield 85%).

Curing of PDETDA

After degassed at 120°C under vacuum, the melt PDETDA was poured into a preheated stainless steel mold treated with a silicone-based mold-release agent, and was cured in accordance with the following conditions: 160°C for 2 h, 180°C for 6 h.

Characterization and Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 400 MHz NMR spectrometer, using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as internal standard.



Scheme 2. Synthetic route for PDETDA.

FTIR measurements were performed on a BRUKER TENSOR-27 FTIR spectrometer at room temperature in the range of 4000–400 cm^{-1}.

DSC measurements were performed on a SII EXSTAR6000-DSC6220 instrument from 30 to 350°C in N_2 flow of 50 mL min^{-1}, and at a heating rate of 5, 10, 15, and 20°C min^{-1}, respectively.

TGA was carried out on a SII EXSTAR6000-TGA6300 instrument at a heating rate of 10°C min^{-1} in N_2 flow of 100 mL min^{-1}.

Rheological behavior was measured using a TA AR-2000 rheometer under air atmosphere with testing temperature range of 50–300°C and at a heating rate of 4°C min^{-1}.

The molecular weight was determined by gel permeation chromatography (GPC) using a Waters 1515 GPC at room temperature with THF as eluent, and the flow rate was 1 mL min^{-1}.

RESULTS AND DISCUSSION

Synthesis of PDETDA

Compared with benzoxazines based on diphenols, aromatic diamines-based benzoxazines produce polymers with higher glass transition temperature (T_g) and better thermal stability.[21–23] However, it is difficult to prepare benzoxazine from aromatic diamines through conventional one-step solvent-less method or solution method. Two reasons account for this problem: (i), aromatic diamines often have poor solubility; (ii), insoluble and infusible crosslinked triazines are prone to generate during the reaction, especially when the two amine groups are connected to the same aromatic ring. In this article, we prepared a novel aromatic diamine-based benzoxazine named PDETDA successfully through the one-step solvent-less method from DETDA, phenol, and paraformaldehyde. The synthetic route of PDETDA is shown in Scheme 2. During the reaction, a transparent homogeneous melt was formed, and the resultant product was completely soluble in chloroform. For comparison, preparation of benzoxazine based on *m*-phenylenediamine was also attempted with the same reaction conditions. Large amounts of insoluble and infusible solids were generated as soon as a few seconds after heating and no target product was obtained. Comparing the structures of DETDA and *m*-phenylenediamine, it was clear that the substituents (ethyls and

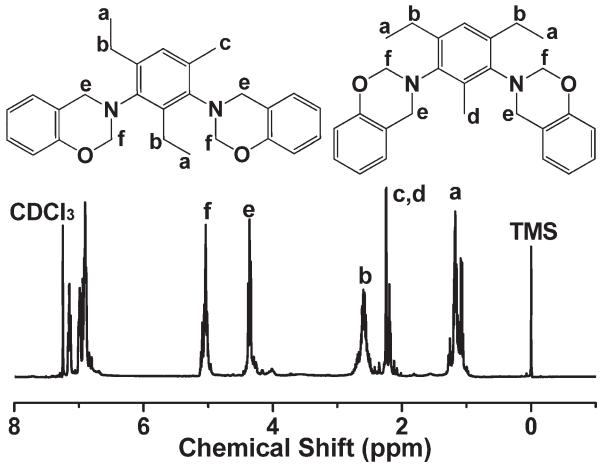


Figure 1. ^{1}H NMR spectrum of PDETDA.

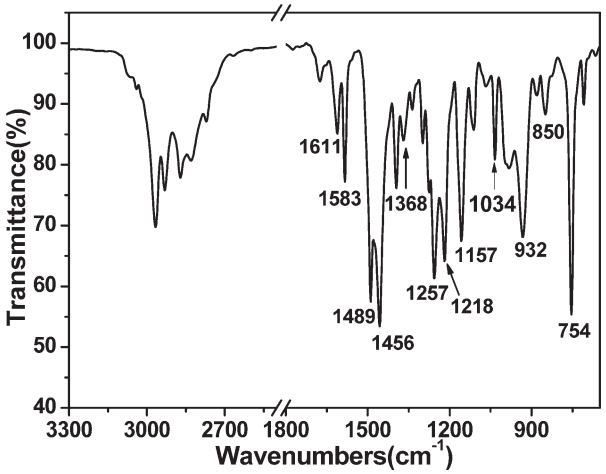


Figure 3. FTIR spectrum of PDETDA.

methyl) in DETDA contributed to the successful synthesis of PDETDA. Because of the steric hindrance of substituents, which inhibited the generation of crosslinked triazine network, the formation of benzoxazine was facilitated.

Characterization of PDETDA

The structure of PDETDA was characterized by ^{1}H NMR, ^{13}C NMR, and FTIR. Figure 1 is the ^{1}H NMR spectrum of PDETDA. The characteristic peaks assignable to methylene (O—CH_2—N) and methylene (Ar—CH_2—N) of oxazine ring were observed at 5.2–4.9 ppm and 4.5–4.2 ppm, respectively. Peaks of aromatic protons appeared at 7.5–6.5 ppm. Peaks at 3.0–2.5 ppm and 2.5–2.0 ppm were attributed to the methylene protons of ethyl and the protons of methyl attached to the benzene ring, respectively. Signals of methyl protons of ethyl appeared at 1.4–0.9 ppm. Since DETDA is a mixture of two isomers, the resulting benzoxazine was actually composed of two different benzoxazine isomers, which made the absorption peaks of methylene in oxazine multiplet.

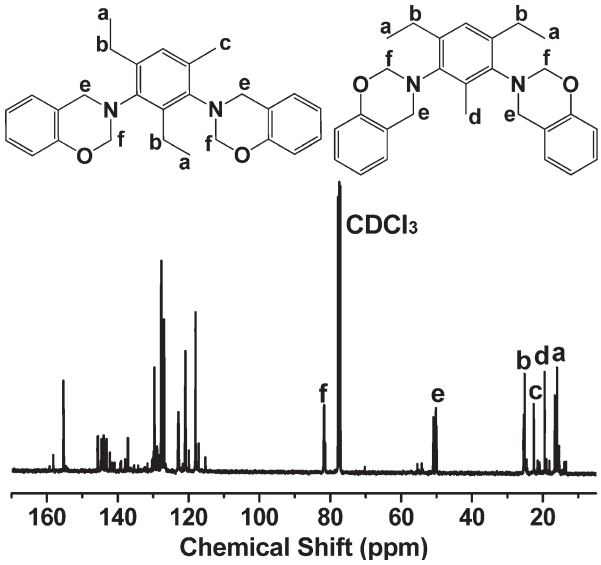


Figure 2. ^{13}C NMR spectrum of PDETDA.

The ^{13}C NMR spectrum of PDETDA is shown in Figure 2. The characteristic peaks around 81.8 and 50.6 ppm were assigned to the methylene carbons of O—CH_2—N and Ar—CH_2—N in oxazine ring, respectively indicating the existence of benzoxazine structure.

FTIR spectrum of PDETDA is shown in Figure 3. Signal at 932 cm^{-1} was attributed to the characteristic vibration absorption of oxazine ring. Absorption peaks at 1034 and 1218 cm^{-1} corresponded to the Ar—O—C symmetric and asymmetric stretching vibration, respectively. 1368 cm^{-1} was the absorption peaks of C—N stretching vibration. The appearance of these peaks proved the existence of the benzoxazine structure.

The results of ^{1}H NMR, ^{13}C NMR, and FTIR indicated that aromatic diamine-based benzoxazine PDETDA was successfully synthesized.

Curing Behavior and Curing Kinetics of PDETDA

Curing Behavior. The curing behavior of PDETDA was studied by DSC, FTIR, and rheological measurement. First, the curing process of PDETDA was monitored by DSC to examine the

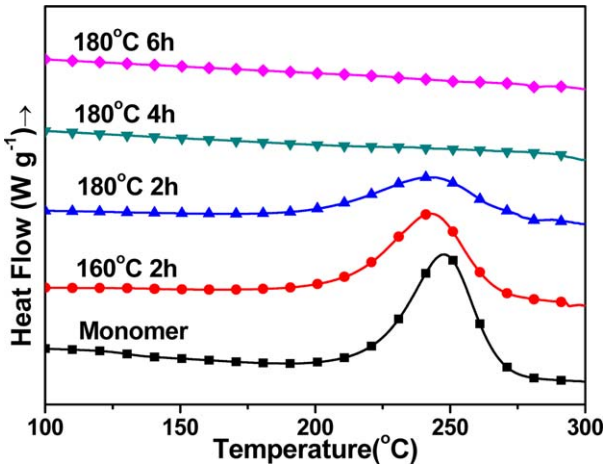


Figure 4. DSC curves of PDETDA at different curing stages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Results of DSC at Different Curing Stages

Curing process	T_p (°C)	ΔH (J g^{-1})	δ (%)
Monomer	245.9	212	0
160°C, 2 h	245.2	196	11.3
180°C, 2 h	244.7	104	52.9
180°C, 4 h	233.6	22	90.2
180°C, 6 h	-	0	100

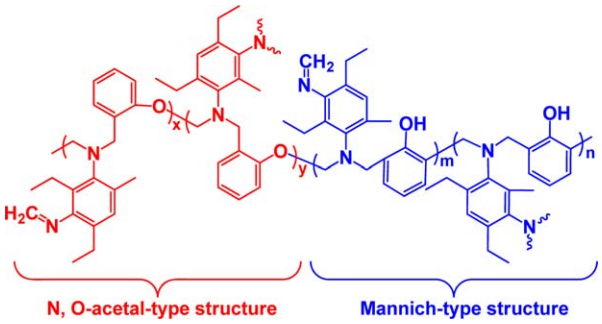
curing curves of PDETDA samples at different curing stages, and the results were shown in Figure 4. It was noted that the amount of exothermic decreased gradually along with the elevation of curing temperature and the extension of curing time, and the exothermic peak disappeared after PDETDA being heated 6 h at 180°C, indicating completely ring-opening polymerization of PDETDA. The conversion rate (δ) of the PDETDA monomer during the polymerization was approximately calculated according to eq. (1) and the data was summarized in Table I,

$$\delta = 1 - \frac{\Delta H}{\Delta H_m} \quad (1)$$

where ΔH and ΔH_m were the reaction enthalpy of PDETDA samples at any curing stage and the reaction enthalpy of PDETDA monomer, respectively.

Generally, due to the fact that the viscosity of the curing system increases drastically as the polymerization proceeds, the curing reaction turns to diffusion-controlled gradually and the peak exothermic temperature (T_p) will shift to higher temperature along with the increase of δ.[27,28] However, as seen in Table I, T_p of PDETDA at different curing stages almost showed no change. This unusual phenomenon was speculated to be related to the substituents on PDETDA.

Figure 5 shows the FTIR spectra of PDETDA at different curing stages. It was seen that the vibration absorption peak corresponding to the oxazine ring at 932 cm^{-1} disappeared after curing 6 h at 180°C, indicating completely ring-opening polymerization of PDETDA. This was consistent with the result of DSC. New signals which arose at 3393 and 1623 cm^{-1} were attributed to the vibrations absorption of phenolic hydroxyl group and the vibration absorption of 1,2,3-trisubstituted benzene, respectively. These changes indicated that ring-opening polymerization of PDETDA happened and the Mannich-type structure was formed. However, symmetric stretching and asymmetric stretching vibration absorption peaks corresponding to Ar—O—C at 1034 and 1218 cm^{-1} were still obvious after curing, suggesting that *N*, *O*-acetal-type structure also existed in the resulting cured product.[29–31] Besides, the new signal at 1675 cm^{-1} indicated that imine groups were formed during the ring-opening polymerization. The possible structure of the cured PDETDA was shown in Scheme 3.



Scheme 3. Possible structure of the cured PDETDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The curing behavior of PDETDA was further examined by the rheological measurement and the viscosity change was recorded in Figure 6. The viscosity of PDETDA was about 200 Pa s at 50°C and decreased to 1 Pa s at 90°C, which was significantly lower than that of the typical bisphenol A-based benzoxazine (26 Pa s at 90°C).[32] The advantage of low viscosity for PDETDA was attributed to the substituents on the benzene ring which decreased the intermolecular forces and thus reduced the viscosity.[33]

Interestingly, it was noted that the viscosity of PDETDA did not exhibit rapid raise before 260°C, which had exceeded the

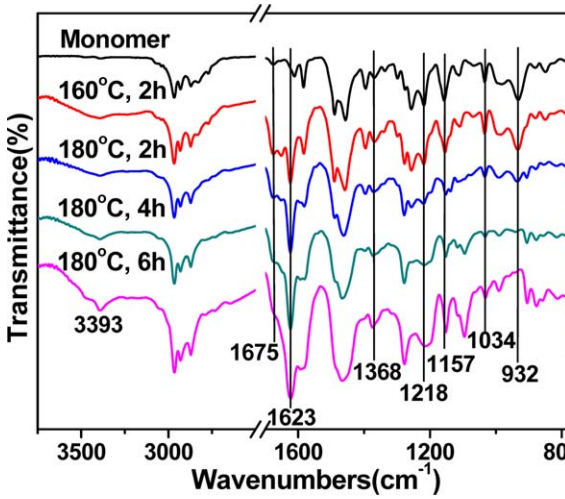


Figure 5. FTIR spectra of PDETDA at different curing stages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

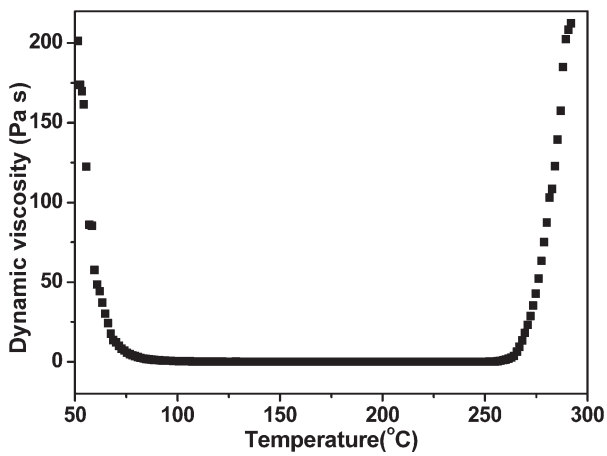


Figure 6. Rheological curve of PDETDA.

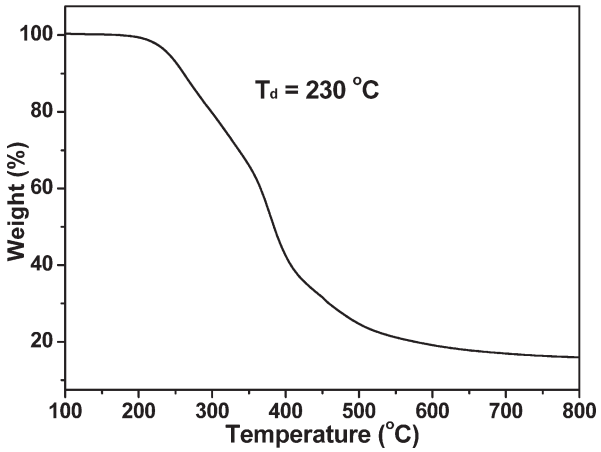


Figure 7. TGA curve of PDETDA.

decomposition temperature (T_d) of PDETDA (TGA curve of PDETDA is shown in Figure 7). In other words, the gelation did not happen until PDETDA began to decompose. Combined with the above DSC and FTIR results, it can be inferred that ring-opening polymerization of PDETDA happened during the curing process while almost no crosslinked network was formed. Therefore, what presented in the cured system were PDETDA oligomers or noncrosslinked polymers, which still showed low viscosity at elevated temperatures. This also explained the result of DSC that the T_p of PDETDA at any cure stage did not increase with the increase of δ. When the temperature rose above 260°C, decomposition and carbonization of PDETDA led to the crosslinking in another way, which resulted in the increase of the viscosity. No gelation before 260°C was ascribed to the steric hindrance of the substitutes in PDETDA, which limited the formation of crosslinked network to some extent.

To further verify the above inference, solubility experiments were conducted for PDETDA at various curing stages. The results showed that the cured product of every stage can be well dissolved in chloroform, and no insoluble residues were observed. Figure 8 shows the ^{1}H NMR spectrum of PDETDA after curing at 180°C for 6 h. It was clear that the signals of methylene in oxazine ring (5.2–4.9 ppm and 4.5–4.2 ppm) disappeared completely after curing, and the new peaks at 3.5–4.3

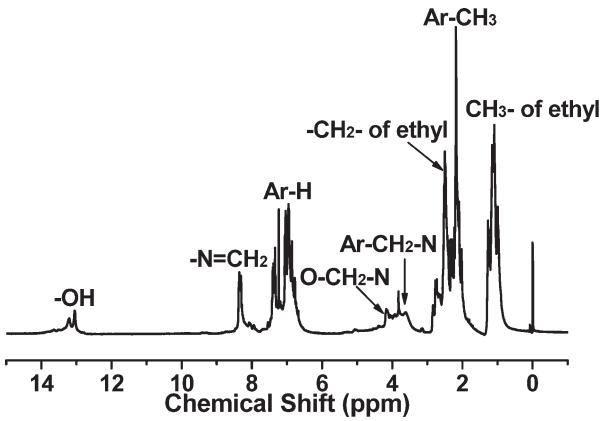


Figure 8. ^{1}H NMR spectrum of PDETDA after curing.

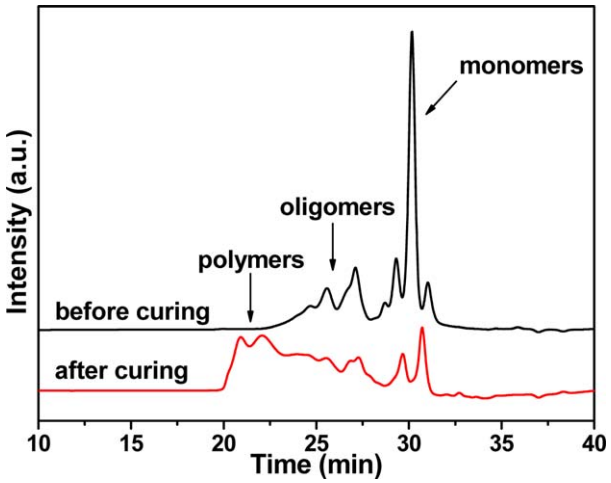


Figure 9. GPC curves of PDETDA before and after curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ppm were assigned to the methylene in Mannich-type structure and *N,O*-acetal-type structure as shown in Scheme 3. Besides, the signals at about 13.2 and 8.3 ppm corresponded to the phenolic hydroxyl groups and the imine groups which were generated from the ring-opening of PDETDA, respectively.

In addition, the molecular weights of PDETDA before and after curing were measured by GPC shown in Figure 9. Before curing, the monomer was the main component in PDETDA, together with a small amount of oligomers. After curing at 180°C for 6 h, the monomer signal completely disappeared and the polymer signals arose. The cured PDETDA showed wide molecular weight distribution with M_w ranging from about 562 to 22,300 g mol^{-1}.

Curing Kinetics. Because of the unusual curing behavior of PDETDA, it is necessary to study its curing kinetics. Nonisothermal DSC, which was carried out at different heating rates, was used here to study the curing kinetic not only because it

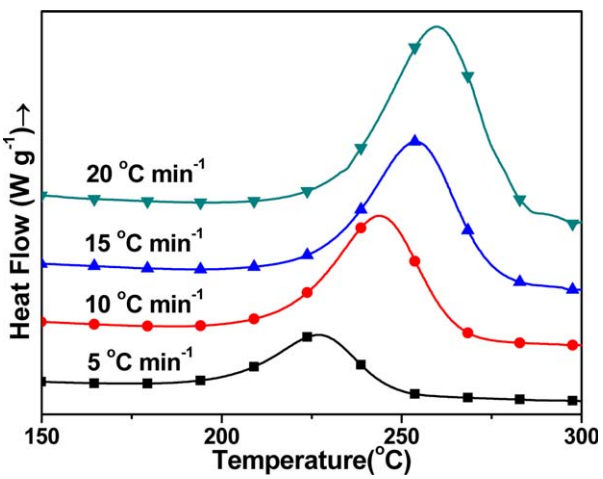


Figure 10. DSC curves of PDETDA at different heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

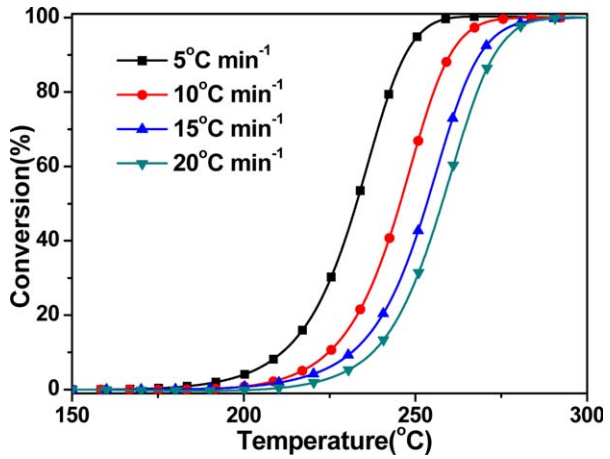


Figure 11. α as a function of temperature for PDETDA at different heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

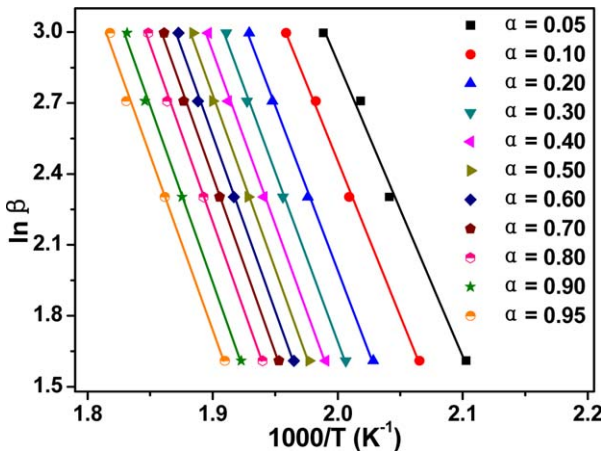


Figure 12. Flynn-Wall-Ozawa plots at different α of PDETDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was more accurate to determine the curing kinetic parameters but also because the kinetic data can be obtained in a relatively short period of time.[34] Figure 10 shows the DSC curves measured at different heating rates. The onset temperature of polymerization (T_o) and the peak exothermic temperature (T_p) moved to higher temperatures when the heating rate increased, which was in accordance with the results reported in the literatures.[34–37]

The DSC curves are analyzed on the basis of the assumption that the exothermic heat evolved during curing is proportional to the conversion of monomer to polymer. The degree of conversion α is thus determined by the following equations:

$$\alpha = \frac{\Delta H_i}{\Delta H_o} \tag{2}$$

$$\Delta H_i = \int_0^t \frac{dH}{dt}\,dt \tag{3}$$

where ΔH_i is the total amount of heat evolved by the reaction from the beginning to time t. ΔH_o is the total heat released in the curing reaction. The variation of α as a function of temperature obtained from the dynamic DSC is shown in Figure 11.

The curing kinetics analysis is based on eq. (4):

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = k(T)f(\alpha) \tag{4}$$

where $k(T)$ is a temperature-dependent reaction rate constant, $f(\alpha)$ is the differential conversion function depending on the reaction mechanism, and $\beta = dT/dt$ is a constant heating rate.

The rate constant $k(T)$ is typically represented through the Arrhenius equation:

$$k(T) = A\exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature.

Combining eq. (4) with eq. (5) results eq. (6):

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = A\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \tag{6}$$

With respect to E_a, an alternative approach to kinetic analysis is to use the model-free methods, which allow evaluating the kinetic parameters regardless of the reaction model. The most known representatives of the model-free approach are the isoconversional methods. In this work, Flynn-Wall-Ozawa method was used to obtain E_a. The method is based on eqs. (7) and (8):

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \tag{7}$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{8}$$

where $g(\alpha)$ is the integral conversion function.

From eq. (7), a plot of ln β vs. $1/T$ at the same α from a series of dynamic DSC experiments at different heating rates would result in a straight line with a slope of $1.052E_a/R$. By repeating this procedure, the E_a values corresponding to different α can

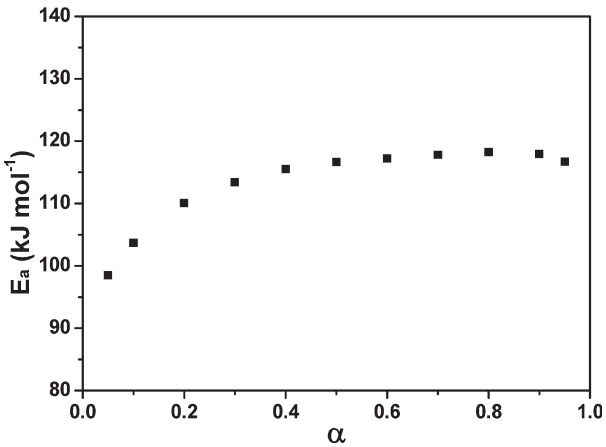


Figure 13. Variation of E_a versus α from Flynn-Wall-Ozawa method.

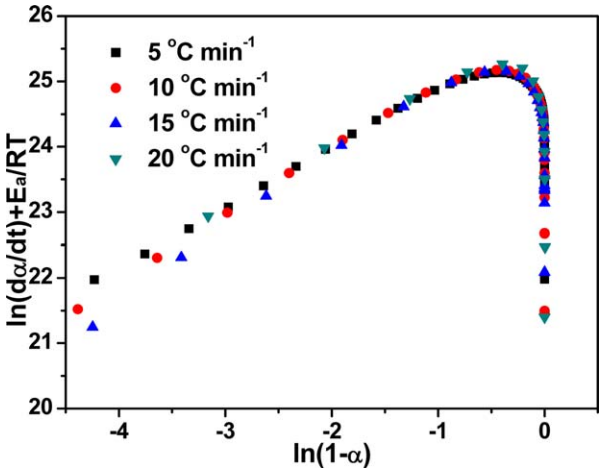


Figure 14. The plots of $\ln(d\alpha/dt) + E_a/RT$ versus $\ln(1-\alpha)$ for different heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

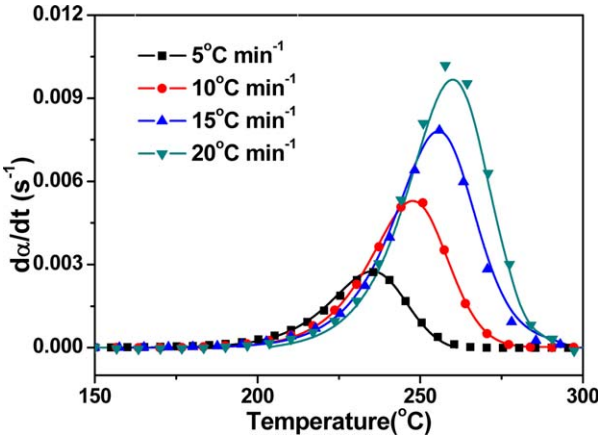


Figure 15. Comparison of experimental values (symbols) and calculated values (lines). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be obtained. Figure 12 shows the Flynn-Wall-Ozawa curves at different α. A good linear relationship between $\ln\beta$ and $1/T$ at any degree of conversion was observed.

The plot of E_a obtained from Flynn-Wall-Ozawa method as a function of α is shown in Figure 13. It was clear that E_a increased with the growth of α and leveled off when α was greater than 0.4. This tendency was different from that of the other reported benzoxazines which showed a continuous increase of E_a with α.[34–38] It was issued that the curing process of benzoxazine followed a reaction mechanism from the kinetic-controlled process to the diffusion-controlled process around the gel point,[39] which led to the continuous increase of E_a.[37,40] However, no crosslinked structure was produced during the curing of PDETDA. As a result, the E_a showed no significant increase in high conversion region. The average value of E_a at different α of PDETDA was 113.2 kJ mol^{-1}.

On the basis of the above average E_a, the other parameters of the curing kinetics can be determined by the Frideman method, which is based on eq. (9):

$$\ln\frac{d\alpha}{dt} = \ln\beta\frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E_a}{RT} \tag{9}$$

In the case of the *n*-order reaction,

$$f(\alpha) = (1-\alpha)^n \tag{10}$$

Combined with eq. (9) results eq. (11):

$$\ln[Af(\alpha)] = \ln\frac{d\alpha}{dt} + \frac{E_a}{RT} = \ln A + n\ln(1-\alpha) \tag{11}$$

According to the experimental data and the average E_a obtained from Flynn-Wall-Ozawa method, the plots of $\ln(d\alpha/dt) + E_a/RT$ vs. $\ln(1-\alpha)$ can be produced as shown in Figure 14. It is known that the *n*-order reaction's rate is the highest at the beginning and decreases as the reaction proceeds, whereas the autocatalytic reaction's rate usually displays a maximum when α ranges between 0.2 and 0.4. Since $\ln(d\alpha/dt) + E_a/RT$ vs. $\ln(1-\alpha)$ was not linearly related and a maximum was evidently shown in the $\ln(1-\alpha)$ range of −0.51 to −0.22, which was corresponding to the α range of 0.2–0.4, the curing reaction of PDETDA was actually autocatalytic in nature. According to other works, the autocatalytic nature of reaction kinetics of PDETDA can be explained by the generation of free phenol groups while the benzoxazine ring starts to open. These phenol groups can further accelerate the ring-opening process.[38,41]

For the autocatalytic reaction,

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{12}$$

Combined with eq. (6) results eq. (13):

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = A\exp\left(\frac{-E_a}{RT}\right)\alpha^m(1-\alpha)^n \tag{13}$$

By taking the logarithm of eq. (13), a linear expression of curing rate can be obtained:

Table II. The Kinetic Parameter Evaluated for the Curing of PDETDA

Heating rate (°C min^{-1})	E_a (kJ mol^{-1})	ln*A* (s^{-1})	Mean	*m*	Mean	*n*	Mean
5	113.2	21.92	22.06	0.43	0.49	0.96	1.04
10		22.04		0.48		1.03	
15		22.12		0.53		1.11	
20		22.15		0.50		1.07	

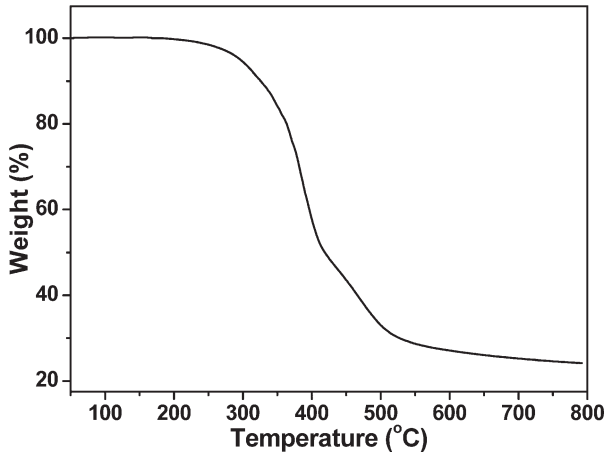


Figure 16. TGA curve of cured PDETDA.

$$\ln\left(\frac{d\alpha}{dt}\right)=\ln\left(\beta\frac{d\alpha}{dT}\right)=\ln A-\left(\frac{E_a}{RT}\right)+m\ln(\alpha)+n\ln(1-\alpha) \quad (14)$$

Equation (14) can be solved by multiple linear regression, in which the dependent variable is $\ln(d\alpha/dt)$, and the independent variables are $\ln\alpha$, $\ln(1-\alpha)$, and $1/T$. Therefore, the values of A, m, and n can be obtained using the average E_a from Flynn-Wall-Ozawa method. The α was chosen between 0.05 and 0.95. The results of the multiple linear regression analysis for all heating rates are listed in Table II. It can be seen that the values of m and n were much smaller than that of the reported benzoxazines.[34–38] It is known that α^m is related to the concentration of the hydroxyl groups that are being generated as polymerization proceeds, and that α^n is related to the concentration of the oxazine rings that are consumed.[42] As a result, small values of m and n meant less relevance of $d\alpha/dt$ to the concentration of the produced hydroxyl groups and the remaining benzoxazines, which indicated that the autocatalytic effect was weakened and the reactivity of PDETDA ring-opening polymerization was low.

According to the above results, the curing kinetic equation of PDETDA can be expressed as:

$$\frac{d\alpha}{dt}=\beta\frac{d\alpha}{dT}=\exp(22.06)\exp\left(\frac{-13616}{T}\right)\alpha^{0.49}(1-\alpha)^{1.04} \quad (15)$$

The experimental curves and predicted curves based on the determined kinetic parameters of curing reaction are shown in Figure 15. It was clearly seen that the calculated data from the model were in good agreement with the experimental results.

TGA of Cured PDETDA

The TGA curve of the cured PDETDA is shown in Figure 16. The cured PDETDA owned good thermal stability. The 5% and 10% mass loss temperatures ($T_{5\%}$ and $T_{10\%}$) were 297 and 326°C, respectively, which was comparable to those of the polybenzoxazine (poly(BA-a)) based on bisphenol-A and aniline ($T_{5\%}$ and $T_{10\%}$ were 310 and 327°C,[5] respectively).

CONCLUSIONS

A novel aromatic diamine-based benzoxazine monomer PDETDA was successfully synthesized through the one-step solvent-less method. The structure of PDETDA was confirmed by ^{1}H NMR, ^{13}C NMR and FTIR. The curing behavior and the polymerization kinetics of PDETDA were studied. The results showed that, the thermal ring-opening polymerization of PDETDA belonged to the autocatalytic reaction, and the curing behavior of PDETDA can be well described by the proposed kinetic model. Steric hindrance effect of substituents had a significant impact on the synthesis and curing of PDETDA. On the one hand, it benefited the synthesis of PDETDA by inhibiting the formation of triazine networks. On the other hand, it limited the formation of a crosslinked polymer during curing of PDETDA, only oligomers and non-crosslinked polymers were obtained. Accordingly, the synthesis and curing of the benzoxazine monomer can be adjusted by introducing suitable substituents on the reactants, which provided useful guidance for the design and synthesis of aromatic diamine-based benzoxazine monomers. What's more, although this low viscosity PDETDA cannot cure to a crosslinked polymer alone, it may co-cure with the epoxy resin to form mechanically sound material and find application as RTM (Resin Transferring Molding) resin, which are currently studied in our lab and will be reported in the near future.

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