

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Effect of Iron acetylacetonate on the crosslink structure, thermal and flammability properties of novel aromatic diamine-based benzoxazines containing cyano group

Hongqiang Yan^a, Huaqing Wang^b, Jie Cheng^a, Zhengping Fang^{a*}, Hao Wang^c

^a Lab of Polymer Material and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China;

^b Zhejiang Textile & Fashion Technology Collage, Ningbo 315211, China

^c Centre of Excellence in Engineered Fibre Composites (CEEFC), University of Southern Queensland, Toowoomba, Queensland 4350, Australia

Abstract:

Iron acetylacetonate ($\text{Fe}(\text{AcAc})_3$) was chosen as catalyst for a novel aromatic diamine-based benzoxazine containing cyano group (BAPBACP). Its effect on the curing process, thermal and flammability properties of BAPBACP were investigated. The results indicated that without $\text{Fe}(\text{AcAc})_3$ the ring-opening polymerization of the BAPBACP monomer occurred and an arylamine Mannich bridge structure was formed at the low curing temperature stage; and then cyclotrimerization of cyano group followed at the high curing temperature stage, but the cyano group was not fully cyclotrimerized even after curing at 350 °C for 0.5 h. Addition of 3.5% $\text{Fe}(\text{AcAc})_3$ speeded up the curing reaction and the cyano group was fully cyclotrimerized at 350 °C. Thermogravimetric analysis and microscale combustion calorimetry results showed that the poly(BAPBACP) resins possess excellent thermal

* Corresponding author: Tel(Fax):+86 574 88220132. E-mail address: zpfang@zju.edu.cn (Z Fang).

and flammability properties due to the existence of the arylamine Mannich bridge structure and triazine ring in their crosslinked structure.

Keyword: benzoxazine; Iron acetylacetonate; thermal property; flammability property.

1. Introduction

Benzoxazine resins have attracted increasing attention in the past decade due to their excellent high temperature stability, low water absorption, good dielectric properties and structure design flexibility, in addition to their zero shrinkage or a slight expansion upon curing.¹⁻⁴ These good properties give them a huge potential in industrial applications, such as high speed printed circuit boards, aerospace structural composites, *etc.*^{5,6} With the rapid development of aerospace, microelectronics and energy industries, there is an urgent requirement to further improve the properties of benzoxazine resins, such as heat resistance, flame retardance, toughness, low dielectric constant, *etc.* Therefore, further enhancing thermal stability and flame retardancy of polybenzoxazines has become one of the research focuses.

In general, introduction of additional functional groups into monomers to prepare copolymers and polymer alloys is widely used to achieve high performance in polybenzoxazines.^{2,4} For example, benzoxazines, which are usually derived from phenols/biphenols, monoamines and formaldehyde, have been prepared by introducing allyl, acetylene, nitrile, maleimide and aldehyde groups to the main chain or terminal position.^{4,7-10} Copolymerization of benzoxazine with another reactive comonomer has been developed, such as urethane-benzoxazine, benzoxazine-epoxy,

benzoxazine-cyanate and benzoxazine-cyanate-epoxy copolymers,¹¹⁻¹⁴ but the resulted systems often exhibit higher curing temperature and viscosity than the neat polybenzoxazines.^{7,15}

Due to structure design flexibility of benzoxazine resins, another simple and attractive approach is to synthesize aromatic diamine-based benzoxazines, which are derived from aromatic diamines, monophenols and formaldehyde. Recently, a series of novel monomers have been successfully synthesized by using high boiling point nonpolar solvent or a three-step synthetic method, with increased thermal stability compared to the conventional polybenzoxazines due to the nitrogen linkage to other repeating units.^{16,17} However, up to date, very limited success in preparing this kind of benzoxazine has been achieved mainly because of the difficulty of this benzoxazine ring-forming reaction and the unknown structure-property relationship. In our recent study,¹⁸ three kinds of novel aromatic diamine-based benzoxazines containing cyano group have been designed and synthesized by the reaction of 4-hydroxybenzotrile, paraformaldehyde, and pre-synthesized diamine compounds. These novel benzoxazine resins show good thermal stability, especially high char residue. However it seems the cyano group does not cure under the normal curing conditions because the cyclotrimerization of the cyano group is very difficult. To fully understand and control the curing process of this new thermoset, it is necessary to study the curing kinetics of the thermoset in detail and the effect of catalyzers on the curing reaction of the cyano group and benzoxazine resin properties.

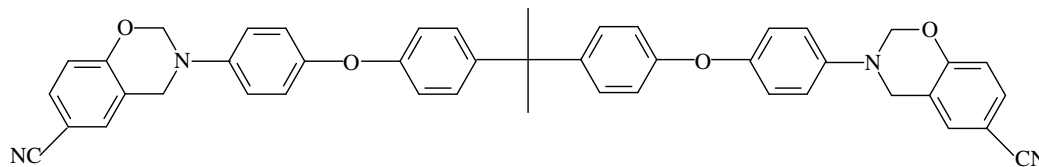
The purpose of this research is to study the curing process of 3,3'-((propane

-2,2-diylbis(4,1-phenylene))bis(oxy))bis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carbonitrile) (BAPBACP) with and without catalysts. For the choice of catalyst, many types of catalysts have been studied for the curing reaction of benzoxazine resins.¹⁹⁻²¹ Gu et al²¹ found that benzoxazine resins could partially undergo the ring-opening polymerization at a low temperature in the presence of FeCl₃ and generate some oligomers containing N, O-acetal-type bridge structures which can delay the degradation of benzoxazine resins; but the inorganic metal catalyst of FeCl₃ cannot dissolved in benzoxazine resins easily, resulting in very low catalytic efficiency. In order to improve the efficiency of catalysts, metal organic compounds are added to dissolve in benzoxazine monomer to effectively catalyze the resin curing. Meanwhile, metal organic compounds are also high efficiency catalysts for cyano group.²²⁻²⁴ In this study, iron acetylacetonate (Fe(AcAc)₃) is chosen as the catalyst for the BAPBACP monomer system; and the effects of Fe(AcAc)₃ on the complex curing process, thermal and flammability properties of BAPBACP resin are determined by using DSC, FTIR, TG and MCC.

2. Experimental

2.1. Materials

Synthesis of BAPBACP monomer has been described elsewhere.¹⁸ The structure of BAPBACP is shown as Scheme 1. Iron acetylacetonate (Fe(AcAc)₃ (99%) was used as received from J&K Chemical Co. Ltd. (Shanghai, China). All solvents used were of reagent grade.



Scheme 1 The structure of BAPBACP monomer

2.2. Sample preparation

The required amount of iron acetylacetonate ($\text{Fe}(\text{AcAc})_3$) was added to the preselected weight of BAPBACP dissolved in chloroform, stirred for 5 min, and evaporated the solvent in vacuum at room temperature. The mixture was pulverized to obtain a homogeneous mixture. BAPBACP monomer and its mixture containing 3.5% $\text{Fe}(\text{AcAc})_3$ were cured in an air oven by stagewise heating process: 170 °C for 2 h, 190 °C for 2 h and 210 °C for 2 h. The sample obtained is denoted as poly(BAPBACP)-210. Poly(BAPBACP)-210 resin was further cured in a muffle furnace at 280 °C for 0.5 h (denoted as poly(BAPBACP)-280), then at 350°C for 0.5 h (denoted as poly(BAPBACP)-350). The cured resins were measured by thermogravimetric analysis (TG) and Microscale Combustion Calorimeter (MCC).

2.3. Measurement

DSC measurements were performed with a Netzscn 200 P C supported with a Netzscn TASC 414-5 computer for data acquisition. DSC was calibrated with high purity indium, and measurements were conducted under a nitrogen flow of 20 cm^3/min . In DSC experiments, all the samples were subjected to a dynamic DSC scan from 50 to 400 °C at heating rate of 10 °C/min. *In-situ* FTIR studies were performed using a Thermo Nicolet iS10 FTIR Spectrophotometer (Nicolet) equipped with a temperature-controlled sample holder that allows for *in-situ* analysis of curing

reaction. Thin resin film was prepared by the resin being dissolved in solvent and cast on NaCl cells. The samples were then seared in the preheated sample holder for the designed stagewise heating process (170 °C for 2 h, 190 °C for 2 h, 210 °C for 2 h, 280 °C for 0.5 h and 350 °C for 0.5 h). The spectra were obtained at the end of the every isothermal stage. The C-H vibration of 1, 2, 4-trisubstituted benzene ring at 1500 cm⁻¹ was used as the reference peak, which should not be changed during the curing reaction. Because the area of peak is directly proportional to the concentration, the normalized concentration of cyano vibrations at any temperature can be calculated from

$$C(T) = \frac{A(T)/A(T)_{1500}}{A(0)/A(0)_{1500}}$$

where $A(T)$ is the absorbance of cyano vibrations at temperature T ; $A(T)_{1500}$ is the absorbance of 1, 2, 4-trisubstituted benzene ring at temperature T ; $A(0)$ is the initial absorbance of cyano vibrations and $A(0)_{1500}$ is the initial absorbance of 1, 2, 4-trisubstituted benzene ring; and $C(T)$ is the fraction of unreacted cyano group. TG analysis was carried out using a TGA 209 F1 Thermal Analyzer (Netzsch, Germany) to study the thermal degradation behavior of the cured resins. Samples were heated from room temperature to 950 °C at a heating rate of 20 °C/min in nitrogen with a flow rate of 40 cm³/min. Microscale combustibility experiments were conducted using an MCC-2 MCC (Govmark, USA). 5 mg sample was heated to 750 °C at a heating rate of 1 °C/s in a mixed stream of oxygen and nitrogen flowing at 20 and 80 cm³/min respectively.

3. Result and discussion

3.1. DSC measurements of BAPBACP resin systems

DSC was carried out to study curing behavior of the BAPBACP monomer systems.

Fig. 1 shows the typical nonisothermal DSC thermograms; and the results summarized in Table 1.

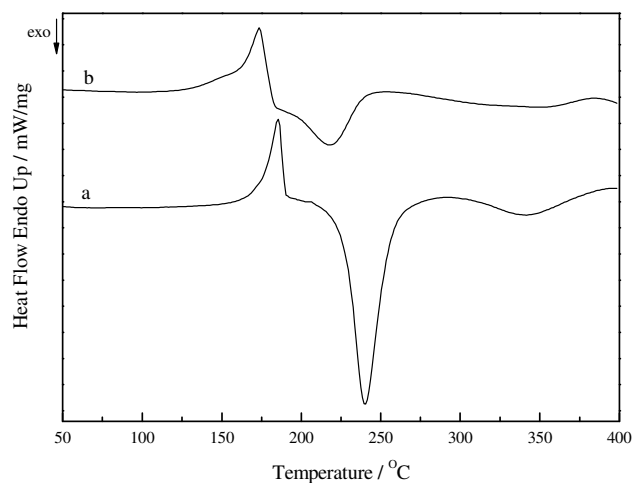


Fig.1 The DSC curves of the BAPBACP monomers

(a) neat BAPBACP) monomer; (b) BAPBACP monomer with 3.5% Fe(AcAc)₃;

Table1 Thermal cure characteristics of the BAPBACP monomers

	$T_m/^\circ\text{C}$	$T_{p1}/^\circ\text{C}$	$\Delta H_1/\text{J/g}$	$T_{p2}/^\circ\text{C}$	$\Delta H_2/\text{J/g}$
Neat BAPBACP monomer	185.4	240.1	246.4	341.4	61.6
BAPBACP monomer including of 3.5% Fe(AcAc) ₃	173.7	218.1	72.3	350.6	46.0

The DSC curves given in Fig. 1 show a clear two-stage curing for the two BAPBACP monomer systems. The first stage was the endothermic melting of the BAPBACP monomer. Adding 3.5% Fe(AcAc)₃ lowered the melting temperature from 185.4 °C to 173.7 °C. The second stage was the exothermic curing reactions, with a sharp exothermic peak in a temperature range of 210~290 °C with a maximum at 240.1 °C (T_{p1}) and a small exothermic peak in a temperature range of 290~390 °C

with a maximum at 341.4 °C (T_{p2}), which were attributed to the ring-opening polymerization of benzoxazine and homo-polymerization of cyano group respectively. When 3.5% Fe(AcAc)₃ was added as catalyst, the first curing exotherm shifted to a lower temperature as observed from a systematic drift in the curing characteristics, such as peak temperature (T_{p1}) from 240.1 °C to 218.1 °C, and its ΔH_1 value also decreased from 246.4 J/g to 72.3 J/g. However the second curing exotherm was little altered, and the ΔH_2 value only decreased from 61.6 J/g to 46.0 J/g. The first curing reaction of BAPBACP monomer at low temperature stage was significantly catalyzed by Fe(AcAc)₃, but the second curing reaction of BAPBACP monomer was almost not affected. As a transition metal salt, Fe(AcAc)₃ is an effective catalyst for polymerization of BAPBACP monomer even at small quantity.

3.2. FTIR Analysis of BAPBACP monomer systems

The different curing behaviors probably caused by different curing mechanisms. To further study the curing behavior of BAPBACP monomer systems with and without Fe(AcAc)₃ and their crosslinked structures, the FTIR spectra of BAPBACP monomer systems cured at various temperatures were conducted.

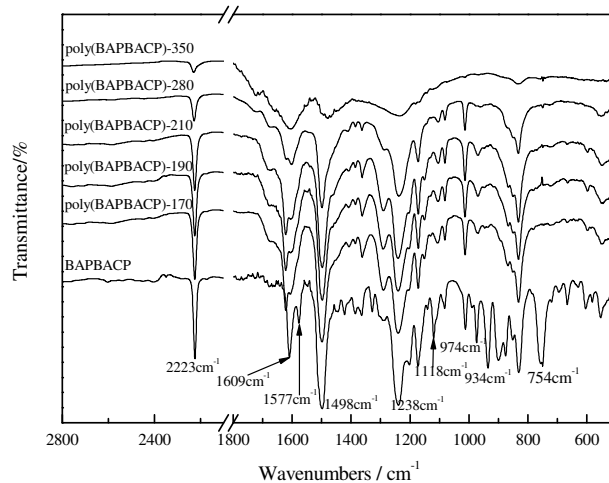


Fig. 2 FTIR spectra of different cured temperature of the neat BAPBACP monomer system

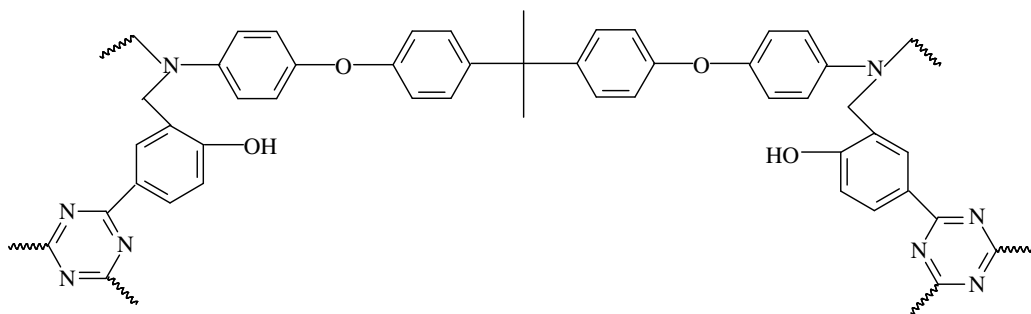
Table 2 The characteristic absorption wavenumbers in IR spectra for the neat BAPBACP monomer system

Chemical group	Absorption wavenumbers/cm ⁻¹
Out-of-plane C-H	934
C-N-C bond	1118
C-O-C bond	1238
1,2,4-trisubstituted benzene	1500
Triazine ring	1604
C=N bond	1680
Cyano group	2223

Fig. 2 shows the FTIR spectra of the neat BAPBACP monomer at different cured temperatures. The characteristic absorption wavenumbers in FTIR spectra are listed in Table 2. At the initial reaction stage (BAPBACP curve in Fig. 2), there were obvious characteristic peaks of cyano group (2223 cm^{-1}) and out-of-plane C-H of oxazine ring (934 cm^{-1}). After curing at $170\text{ }^{\circ}\text{C}$ for 2h, The 934 cm^{-1} out-of-plane C-H of oxazine ring peak disappeared completely, confirming the ring-opening polymerization of oxazine ring. However, the absorption band at approximately 1238 cm^{-1} did not disappear completely, which was probably due to the asymmetric stretching vibration

of aryl ether linkages which was overlapped with that of C-O-C for oxazine ring.²⁵ Furthermore, intensity of the absorption band at 1500 cm^{-1} , assigned to 1, 2, 4-trisubstituted benzene, had little change during the curing, indicating the benzene ring in the structure of BAPBACP monomer did not alter during the ring-opening process. The band at 1480 cm^{-1} , assigned to 1, 2, 4, 6-tetrasubstituted benzene, could not be observed. Meanwhile, the intensity of the band at 1118 cm^{-1} assigned to C-N-C bond weakened gradually. These results indicated that the main crosslinked structure was arylamine Mannich bridge rather than phenolic Mannich bridge. At curing temperatures below $210\text{ }^{\circ}\text{C}$, the intensity of the band at 2223 cm^{-1} assigned to cyano group weakened slowly and the band at 1604 cm^{-1} assigned to the triazine groups (C=N-C) could be observed, indicating that some cyano groups of BAPBACP monomer had been cyclotrimerized to form triazine structure. This result demonstrated that the cyclotrimerization of cyano group was slower than the ring-opening polymerization of oxazine ring. At the same time, new absorption was observed at 1680 cm^{-1} assigned to 1,2-bisquinone compound, which might be attributed to the C-N stretching of Schiff base byproduct formed in ring-opening reaction.^{13,26,27} When the curing temperatures were above $210\text{ }^{\circ}\text{C}$, the intensity of the band of cyano group decreased obviously, meaning the cyclotrimerization of cyano group was prompted at the high curing temperature stage. The band at 2223 cm^{-1} did not disappear completely after curing at $350\text{ }^{\circ}\text{C}$ for 0.5h. This indicated that the formation of triazine structure was very difficult and the cyano group was not cyclotrimerized completely. The crosslinked structure of poly(BAPBACP) resin is

shown in Scheme 2.



Scheme 2 The structure of poly(BAPBACP) resin

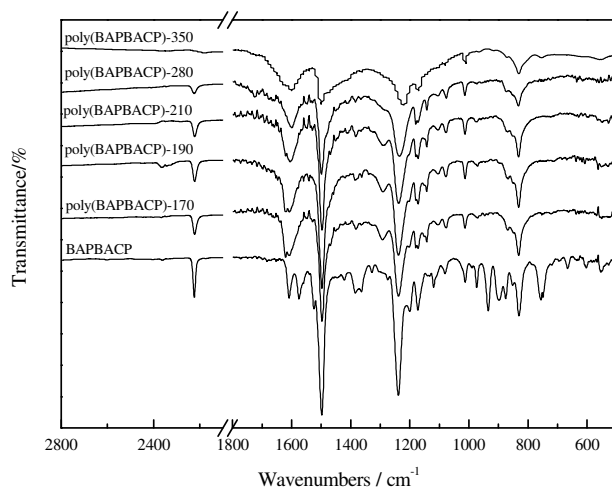


Fig. 3 FTIR spectra of poly(BAPBACP) resin with 3.5% $\text{Fe}(\text{AcAc})_3$ at different curing temperatures

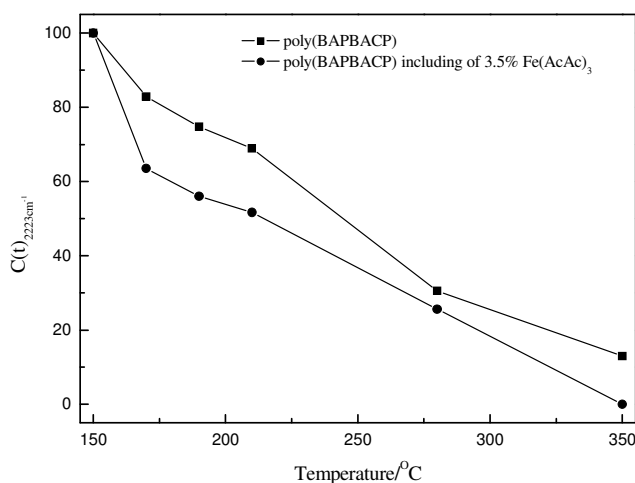
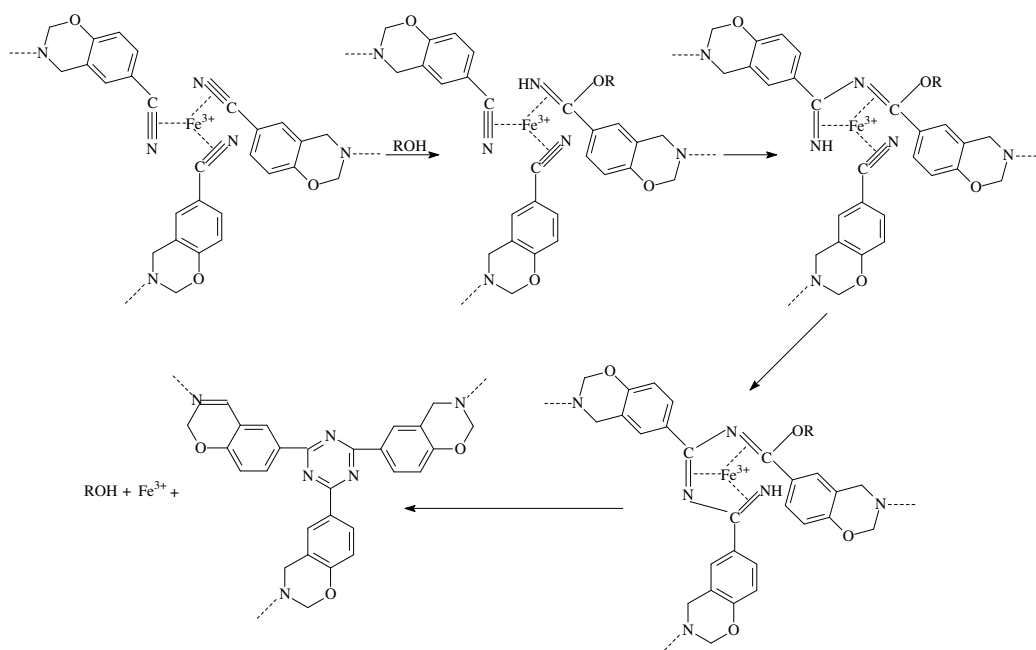


Fig. 4 The C(T) variation of cyano group at 2223 cm⁻¹ for the BAPBACP monomer systems at different curing temperatures

Fig. 3 shows the FTIR spectra of for the BAPBACP monomer system with 3.5% Fe(AcAc)₃ at different curing temperatures. Compared with Fig.2, they are similar. The C(T)s of the cyano group for the BAPBACP monomer systems are shown in Fig. 4. The change of C(T) of the cyano group in the catalyzed system beyond 210 °C was quicker than that in the neat system, indicating that the cure reaction of the cyano group was speeded up evidently as a result of the existence of Fe(AcAc)₃. After curing at 350 °C for 0.5h, the band at 2223 cm⁻¹ was disappear completely, indicating that with the addition of 3.5% Fe(AcAc)₃, the formation of triazine structure became easier and more triazine groups were formed in the crosslinked structure of poly(BAPBACP) resin. With the existence of phenol hydroxyl, which was generated during the ring-opening polymerization of benzoxazine, the cyano groups had a high tendency for catalysis by metal ions (Fe³⁺) through coordination with the cyano groups, as shown in Scheme 3. The mechanism involved the formation of a metal

complex intermediate with reduced electron density at the carbon atom, which could react with the nucleophilic nitrogen of other cyano group to form triazine and regenerate the catalyst.^{22,22,28} Additionally the band at 1680 cm^{-1} disappeared, meaning that the C-N stretching of Schiff base was not oxidized in the BAPBACP monomer system with 3.5% $\text{Fe}(\text{AcAc})_3$.



Scheme 3 Mechanism of catalysis of cure reaction for the BAPBACP monomer system with 3.5% $\text{Fe}(\text{AcAc})_3$

3.3. Thermal properties of poly(BAPBACP) resin

The thermal behavior (thermal stability) of poly(BAPBACP) resins was evaluated by using TG under nitrogen atmosphere. The TG curves of poly(BAPBACP) resins and their derivatives (DTG) are shown in Figs. 5 and 6, with the results summarized in Tables 3 and 4. The extensional onset temperature (T_e) is defined as the onset temperature of the degradation of different poly(BAPBACP) resins. T_{max} is the temperature with the maximum mass loss rate, Mass is the mass loss of every

decomposition stage, Peak value was the maximum mass loss rate of every decomposition stage in DTG curve, and Char is the percentage of the char yielded at 800 °C under nitrogen atmosphere.

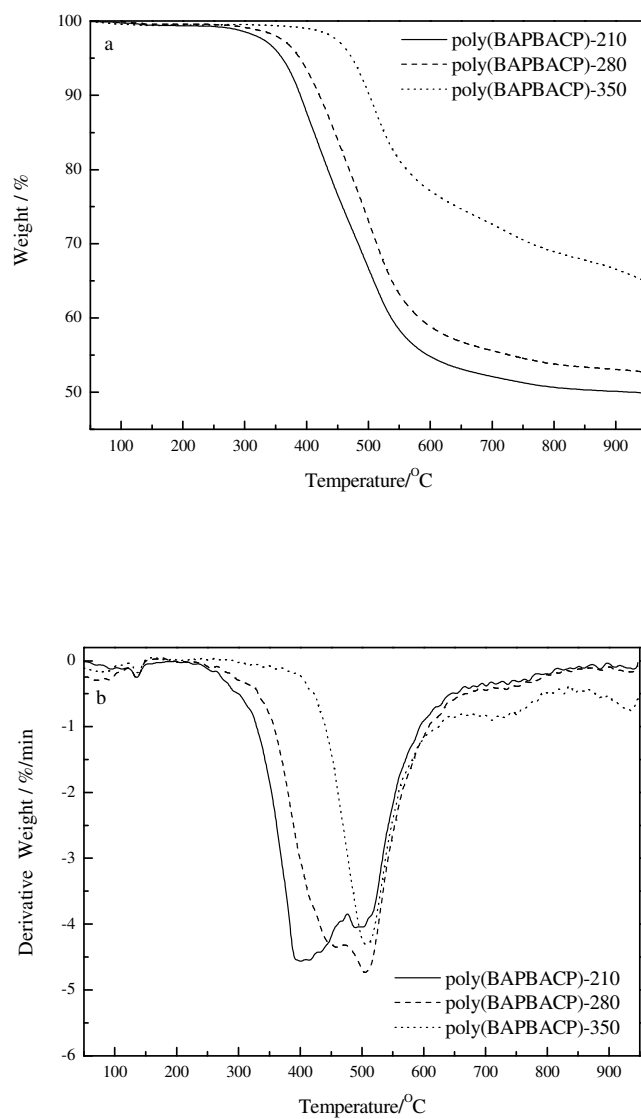


Fig.5 TG curves (a) and DTG curves (b) for poly(BAPBACP) resins under nitrogen atmosphere.

Table 3 TGA results of poly(BAPBACP) resin under nitrogen atmosphere.

Sample ID.	T_c (°C)	T_{max1} (°C)	Mass ₁ (%)	Peak ₁	T_{max2} (°C)	Mass ₂ (%)	Peak ₂	Char
				value			value	
				(wt%/°C)			(wt%/°C)	(%)

Poly(BAPBACP)-210	337.6	400.9	28.7	4.56	489.4	20.6	4.05	50.7
Poly(BAPBACP)-280	374.3	459.3	21.2	4.35	504.8	24.6	4.73	54.2
Poly(BAPBACP)-350	457.1	-	-	-	507.0	25.3	4.31	68.1

As shown in Fig.5 and Table 3, T_e , T_{max1} and T_{max2} of poly(BAPBACP)-210 resin are 337.6, 400.9 and 489.4 °C respectively, and the char residue at 800 °C is 50.7%. As expected, the poly(BAPBACP) resin showed good thermal stability, especially high char residue. In its DTG curve, poly(BAPBACP) resin showed a two-stage weight loss process, which was different from the classic three-stage weight loss process in benzoxazine resin.^{29,30} As seen from Fig. 2, the main crosslinked structure of poly(BAPBACP) resin was the arylamine Mannich bridge structure rather than the phenolic Mannich bridge structure. Compared with the classic three-stage weight loss process, the first major weight loss event of the aniline moieties of the arylamine Mannich bridge structure was retarded to a higher temperature and overlapped with the second event to form one weight loss event, meaning that the arylamine Mannich bridge structure was more stable than the phenolic Mannich bridge structure. With the increase of curing temperature, the characteristic temperature and char residue of poly(BAPBACP) resin had been improved, especially the poly(BAPBACP)-350 resin. This was mainly because more cyano groups of BAPBACP monomer had been cyclotrimerized to form more triazine structure with the increase of curing temperature. Because the curing reaction of the cyano group was more quicker at higher temperatures, T_e , and T_{max2} of poly(BAPBACP)-350 resin had been improved to 457.4 and 507.0 °C, and its char residue at 800 °C also increased to 68.1%. The DTG curve of poly(BAPBACP)-350 resin only gave a one-stage weight loss process,

centered at near 510 °C, and its peak value of DTG curve also decreased from 4.73 to 4.31 wt%/°C. Thus it could conclude that the poly(BAPBACP) resins possessed good thermal stability due to the arylamine Mannich bridge structure and triazine ring in their crosslinked structure.

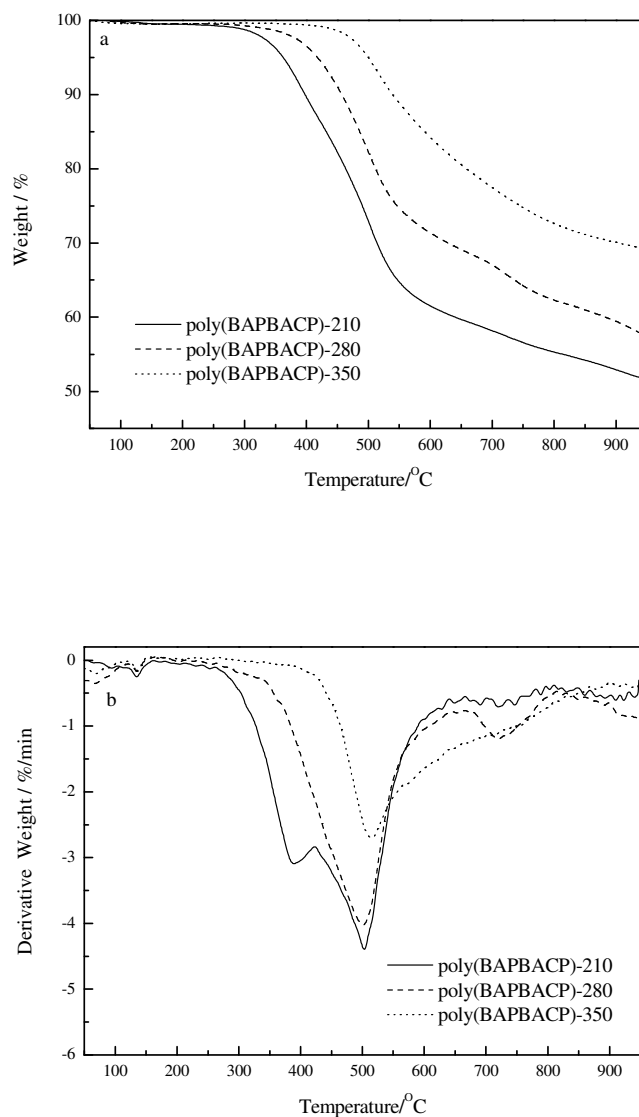


Fig.6 TG curves (a) and DTG curves (b) for poly(BAPBACP) resins with 3.5% Fe(AcAc)₃ under nitrogen atmosphere.

Table 4 TGA results of poly(BAPBACP) resin with 3.5% Fe(AcAc)₃ under nitrogen atmosphere.

Sample ID.	T_e (°C)	T_{max1} (°C)	Mass ₁ (%)	Peak ₁ value (wt%/°C)	T_{max2} (°C)	Mass ₂ (%)	Peak ₂ value (wt%/°C)	Char (%)
Poly(BAPBACP)-210	338.5	389.0	13.6	3.09	503.1	31.2	4.40	55.3
Poly(BAPBACP)-280	392.8	-	-	-	501.1	30.6	4.02	62.8
Poly(BAPBACP)-350	464.8	-	-	-	515.2	27.4	2.71	72.6

Fig. 6 shows TG thermograms and DTG curves of poly(BAPBACP) resins with 3.5% $\text{Fe}(\text{AcAc})_3$, with the detailed data summarized in Table 4. For the poly(BAPBACP)-210 resin, its DTG curve still presented a two-stage weight loss process after adding 3.5% $\text{Fe}(\text{AcAc})_3$, however the first peak value of its DTG curve was decreased from 4.56 to 3.09 and its char residue at 800 °C was increased from 50.7 to 55.3%, meaning the thermal stability of poly(BAPBACP) resins had been improved by the addition of $\text{Fe}(\text{AcAc})_3$. As seen from Fig. 4, for the poly(BAPBACP)-210 resin with $\text{Fe}(\text{AcAc})_3$, the conversion rate of cyano group increased from 31.1 to 48.3%, resulting in a higher triazine ring content, which was beneficial to the thermal stability of poly(BAPBACP) resin. For the poly(BAPBACP)-280 and poly(BAPBACP)-350 resins with $\text{Fe}(\text{AcAc})_3$, their DTG curves only presented a one-stage weight loss process, T_e s and char residues at 800 °C increased markedly and the peak values of their DTG curves decreased. The above results indicated that the thermal stability of poly(BAPBACP) resins could be improved evidently by the addition of $\text{Fe}(\text{AcAc})_3$. It was because the cyclotrimerization of cyano group was prompted by $\text{Fe}(\text{AcAc})_3$ to produce more triazine ring in the structure of poly(BAPBACP) resin. These results illustrated that triazine ring structure played a very important role towards the thermal stability of poly(BAPBACP) resin.

3.4. Flammability properties of poly(BAPBACP) resin

In order to further analyze the correlation between the crosslinked structure and flammability for the poly(BAPBACP) resins, their aerobic pyrolysis and the subsequent reactions between the volatile pyrolysis products and a mixture of nitrogen/oxygen (80/20) gas under high temperatures were simulated by microscale combustibility calorimeter experiments (MCC). The key combustion parameters, including heat release capacity (HR Capacity), total heat release (THR), the peak for total heat release (PHRR) and the temperature for the PHRR (T_{PHRR} , which is a good predictor of flammability), could be obtained. The representative heat release rate curves of the poly(BAPBACP) resins are presented in Figs. 7 and 8, with the detailed data summarized in Tables 5 and 6.

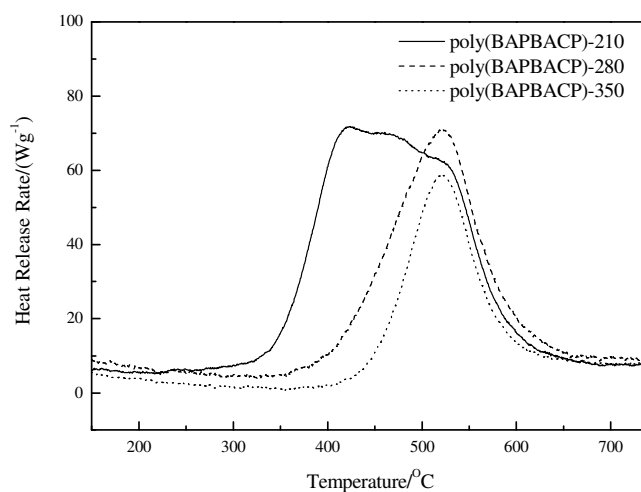


Fig.7 MCC curves for the poly(BAPBACP) resins

Table 5 MCC results of the poly(BAPBACP) resins

Sample ID.	HR Capacity ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$)	THR ($\text{kJ}\cdot\text{g}^{-1}$)	PHRR ($\text{W}\cdot\text{g}^{-1}$)	T_{PHRR} ($^{\circ}\text{C}$)
BAPBACP-210	64±1	11.7±0.1	70.1±1.5	411.5±3.2

BAPBACP-280	50±2	6.5±0.4	71.2±2.1	520.0±0.8
BAPBACP-350	43±3	3.4±0.4	58.6±2.0	520.9±2.3

As shown in Fig. 7 and Table 5, there is one wide overlapping exothermic peak from 300 to 650 °C in the MCC curve of the poly(BAPBACP)-210 resin, and its THR, HR Capacity and PHRR are 11.7 kJ·g⁻¹, 64 J·g⁻¹·K⁻¹ and 70.1 W·g⁻¹ respectively. Compared to the poly(BAPBACP)-210 resin, the exothermic peak of the poly(BAPBACP)-280 resin is narrowed and retarded to a higher temperature, T_{PHRR} increase remarkably from 411.5 to 520.0 °C and its THR and HR Capacity decrease remarkably to 6.5 kJ·g⁻¹ and 50 J·g⁻¹·K⁻¹. Further, poly(BAPBACP)-350 resin showed the lowest value of HR Capacity, THR and PHRR, indicating that triazine ring generated by the cyclotrimerization of cyano group could retard the combustion of poly(BAPBACP) resin, reducing its combustion speed, burning degree and combustion heat release.

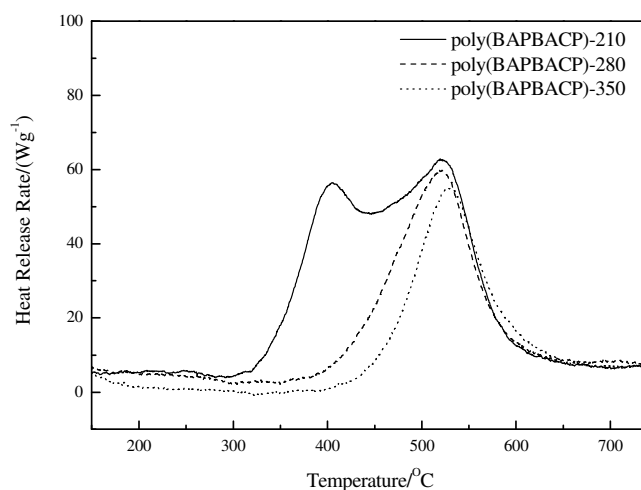


Fig.8 MCC curves for the poly(BAPBACP) resins with 3.5% Fe(AcAc)₃

Table 6 MCC results of the poly(BAPBACP) resins with 3.5% Fe(AcAc)₃.

Sample ID.	HR Capacity ($\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$)	THR ($\text{kJ}\cdot\text{g}^{-1}$)	PHRR ₁ ($\text{W}\cdot\text{g}^{-1}$)	T_{PHRR1} ($^{\circ}\text{C}$)	PHRR ₂ ($\text{W}\cdot\text{g}^{-1}$)	T_{PHRR2} ($^{\circ}\text{C}$)
BAPBACP-210	57±2	10.3±0.3	56.5±0.2	404.4±1.7	63.5±0.6	520.1±0.8
BAPBACP-280	45±1	4.2±0.1	-	-	59.5±0.5	520.4±1.7
BAPBACP-350	38±1	2.8±0.1	-	-	52.8±2.0	526.6±1.4

As shown in Fig. 8 and Table 6, after adding 3.5% $\text{Fe}(\text{AcAc})_3$, the MCC curve of the poly(BAPBACP)-210 resin presents a two-stage combustibility process, and its THR, HR Capacity and PHRRs decrease to $10.3 \text{ kJ}\cdot\text{g}^{-1}$, $57 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, $56.5 \text{ W}\cdot\text{g}^{-1}$ and $63.5 \text{ W}\cdot\text{g}^{-1}$. The results further demonstrate that more triazine ring, generated from the cyclotrimerization of cyano group catalyzed by $\text{Fe}(\text{AcAc})_3$, enables strong hindering combustibility of arylamine Mannich bridge structure, leading to a gradual reduction in heat release rate. With increasing curing temperature, the first peak of combustibility of the poly(BAPBACP) resin disappears completely, and its THR, HR Capacity and PHRR further decrease. The T_{PHRR} values of all poly(BAPBACP) resins, except poly(BAPBACP)-210 without $\text{Fe}(\text{AcAc})_3$, are almost consistent, signifying that triazine ring structure plays a crucial effect on the flammability stability of poly(BAPBACP) resin. These results show a similar trend obtained from the TGA result under nitrogen atmosphere.

4. Conclusions

In this study, the effect of $\text{Fe}(\text{AcAc})_3$ on the complex curing process, thermal and flammability properties of BAPBACP resin were investigated using DSC, FTIR, TG and MCC. The DSC curves of the BAPBACP monomer systems showed a clear two-stage curing. When adding 3.5% $\text{Fe}(\text{AcAc})_3$, the first curing exotherm shifted to a lower temperature, but the second curing exotherm was little altered. According to the

FTIR spectra of the BAPBACP monomer system without catalyst, the ring-opening polymerization of oxazine ring occurred to generate the arylamine Mannich bridge structure at low curing temperature, the cyclotrimerization of cyano group was only prompted at high curing temperature stage and was still not completed after curing at 350 °C for 0.5h. After adding 3.5% Fe(AcAc)₃, the curing procedure of the BAPBACP monomer system did not change, but the cyclotrimerization of cyano group became easier and was completed after curing at 350 °C for 0.5h. The TG results showed that T_e and T_{max2} of poly(BAPBACP)-350 resin were improved to 457.4 and 507.0 °C, and its char residue at 800 °C was also heightened to 68.1%. These results indicate that the poly(BAPBACP) resin possesses better thermal stability than the classic benzoxazine resin due to the existence of the arylamine Mannich bridge structure and triazine ring. Likewise, the flammability stability of poly(BAPBACP) resin was retarded remarkably by the arylamine Mannich bridge structure and triazine ring. Thus, the poly(BAPBACP) resins possess excellent thermal and flame retardant properties due to the arylamine Mannich bridge structure and triazine ring in their crosslinked structure. Thus, these results highlight the importance of controlling the crosslinked structure of the poly(BAPBACP) resins and an role of triazine ring on their thermal and flame retardant properties.

Acknowledgements

We gratefully acknowledge the financial supports from the National Natural Science Foundation of China (No. 51103129), Zhejiang Provincial Natural Science Foundation of China (LY14E030006), the Ningbo Natural Science Foundation (No.

2012A610084), and the Open Fund of Zhejiang Provincial Top Key Discipline of New Materials and Process Engineering (20110939 and 20121126).

References

- 1 H. Ishida, D.P. Sanders, *J. Polym. Sci., Part B: Polym. Phys.*, 2000, 38, 3289-3301.
- 2 R. Andreu, M. A. Espinosa, M. Galià, V. Cádiz, J. C. Ronda and J. A. Reina, *J. Polym. Sci. Part A: Polym. Chem.*, 2006, 44, 1529-1540.
- 3 N. N. Ghosh, B. Kiskan and Y. Yagci, *Prog. Polym. Sci.*, 2007, 32, 1344-1391.
- 4 A. Chernykh, T. Agag and H. Ishida, *Macromolecules*, 2009, 42, 5121-5127.
- 5 X. Liu and Y. Gu, *J. Appl. Polym. Sci.*, 2002, 84, 1107-1113.
- 6 A. Chernykh, J. Liu and H. Ishida, *Polymer*, 2006, 47, 7664-7669.
- 7 K. S. Santhosh Kumar, C. P. R. Nair, T. S. Radhakrishnan and K. N. Ninan, *Eur. Polym. J.*, 2007, 43, 2504-2514.
- 8 H. Qi, H. Ren, G. Pan, Y. Zhuang, F. Huang and L. Du, *Polym. Adv. Technol.*, 2009, 20, 268-272.
- 9 T. Agag and T. Takeichi, *J. Polym. Sci. Part A: Polym. Chem.*, 2006, 44, 1424-1435.
- 10 Q. C. Ran and Y. Gu, *J. Polym. Sci. Part A: Polym. Chem.*, 2011, 49: 1671-1677.
- 11 S. Rimdusit, W. Bangsen and P. Kasemsiri, *J. Appl. Polym. Sci.*, 2011, 121, 3669-3678.
- 12 C. Jubsilp, K. Punson, T. Takeichi and S. Rimdusit, *Polym. Degrad. Stab.*, 2010, 95, 918-924.

- 13 C. H. Lin, S. J. Huang, P. J. Wang, H. T. Lin and S. A. Dai, *Macromolecules*, 2012, 45, 7461-7466.
- 14 X. D. Li, Y. Q. Xia, W. L. Xu, Q. C. Ran and Y. Gu, *Polym. Chem.*, 2012, 3, 1629-1633.
- 15 T. Agag and T. Takeichi, *J. Polym. Sci. Part A: Polym. Chem.*, 2007, 45, 1878-1888.
- 16 T. Agag, L. Jin, and H. Ishida, *Polymer*, 2009, 50, 5940-5944.
- 17 C. H. Lin, S. L. Chang, C. W. Hsieh and H. H. Lee, *Polymer*, 2008, 49, 1220-1229.
- 18 T. Zhang, H. Q. Yan, Z. P. Fang and M. Peng, *Chinese J. Polym. Sci.*, 2013, 31, 1359-1371.
- 19 Y. X. Wang and H. Ishida, *Polymer*, 1999, 40, 4563-4570.
- 20 H. Y. Low and H. Ishida, *Polym. Degrad. Stab.*, 2006, 91, 805-815.
- 21 Q. C. Ran, D. X. Zhang, R. Q. Zhu and Y. Gu, *Polymer*, 2012, 53, 4119-4127.
- 22 H. Q. Yan, L. Ji and G. R. Qi, *J. Appl. Polym. Sci.*, 2004, 91, 3927~3939.
- 23 H. Q. Yan, S. Chen and G. R. Qi, *Polymer*, 2003, 44, 7867~7867.
- 24 D. Mathew, C. P. R. Nair and K. N. Ninan, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, 37, 1103-1114.
- 25 L. Zhang, , H. Peng, J. Sui, C. Soeller, P. A. Kilmartin and J. Travas-Sejdic, *J. Phys. Chem. C.*, 2009, 113, 9128-9134.
- 26 H. Ishida and D. P. Sanders, *Polymer*, 2001, 42, 3115-3125.
- 27 J. Dunkers and H. Ishida, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, 37, 1913-1921.

- 28 C. P. R. Nair, C. Gopalakrishnan and K. N. Ninan, *Polym. & Polym. Compos.*, 2001, 9, 531-539.
- 29 H. Y. Low and H. Ishida, *J. Polym. Sci. Part B: Polym. Phys.*, 1998, 36, 1935-1946.
- 30 H. Y. Low and H. Ishida, *Polymer*, 1999, 40, 4365-4376.