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Cationic ring-opening polymerization of benzoxazines

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

With certain cationic initiators benzoxazine rings can be opened and polymerized at room temperature. Fourier transform infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy, size exclusion chromatography, differential scanning calorimetry, and thermogravimetric analysis have been used to monitor the polymerization process and to characterize the obtained polymers. High performance bisphenol-A/aniline based polybenzoxazine with glass transition (T_g) at 220°C and char yield of approximately 60% at 800°C under nitrogen is obtained. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Benzoxazine; Cationic polymerization; Ring-opening polymerization

1. Introduction

In recent years the development of the benzoxazine-based family of phenolic resins has attracted significant attention. Various phenols and primary amines have been used to synthesize benzoxazine resins. As a result of the ring-opening polymerization, polybenzoxazines overcome many shortcomings associated with traditional phenolic resins such as releasing condensation by-products and using strong acids as catalysts, while retaining good thermal properties and flame retardance of phenolics [1]. Also, like epoxies and polyimide, polybenzoxazines have excellent mechanical properties and molecular design flexibility. Benzoxazine resins undergo near-zero volumetric changes or expansion upon polymerization [2]. By using particular types of amine and phenol, polybenzoxazines with char yield as high as 80% have recently been obtained [3].

The typical method of obtaining polybenzoxazines is to polymerize the corresponding monomers at elevated temperatures without catalysts. Some work has been done involving the catalyst-assisted benzoxazine curing, and the results show that by adding certain catalyst, the induction time for the benzoxazine precursor curing can be reduced and the reaction rate can be accelerated [4]. However, the reduction of the maximum exotherm temperature was modest and no significant polymerization has been observed under 100°C.

The benzoxazine ring is a six-membered heterocyclic ring with N and O as two of the constitutive elements. Molecular modeling results show that the oxazine ring in a benzoxazine molecule assumes a distorted semi-chair structure in terms of minimum energy model [5,6]. The resulting ring strain makes it possible for this kind of molecule to undergo ring-opening polymerization under certain reaction conditions. Moreover, the strong basicity of the N and O atoms by Lewis definition makes the ring very likely to be opened via a cationic mechanism.

The objective of this study is to perform a comprehensive survey of initiators and/or catalysts for the polymerization of benzoxazine monomer and search for the effective compounds to reduce the curing temperature and time of these new benzoxazine resins and, in this way, make them more attractive from a processing point of view. For this purpose a bisphenol-A/aniline based benzoxazine monomer, 6,6′-bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazinyl) isopropane, designated as BA-a, was chosen. The structure of this monomer is shown below. Various cationic initiators, an anionic initiator and a free radical initiator for comparison were investigated in this study.

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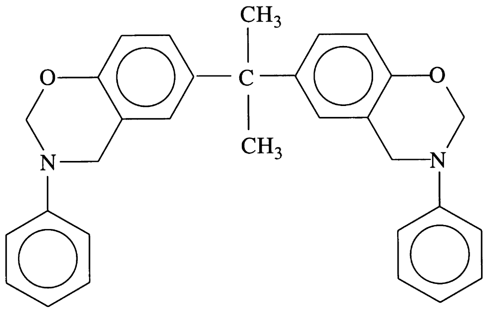
Table 1
Examination of the polymerization of BA-a with various initiators (M/I mole ratio is 20:1)

Run no.	Initiator	Temperature (°C)	$CHCl_3$ insoluble part yield (%)
1	Phosphorus pentachloride	20	56.2
2	Phosphorus trichloride	20	19.6
3	Phosphorus oxychloride	20	15.0
4	Titanium(IV) chloride	20	19.4
5	Aluminum chloride	20	46.8
6	Triphenylcarbenium hexachloroantimonate	20	8.7
7	Antimony pentachloride	53	10.1
8	Antimony pentachloride/oxetane	20	12.3
9	Methyl tosylate	—	—
10	Methyl triflate	—	—
11	Aluminum phthalocyanine chloride	20	20.4
12	Triflic acid	—	—
13	Boron trifluoride diethyl etherate	53	0
14	Boron trifluoride diethyl etherate/oxetane	20	0
15	*p*-Tolyl triflate	53	0
16	Methyl iodide	53	0
17	Butyl lithium	20	0
18	Benzoyl peroxide	110	0



BA-a monomer

2. Experimental

2.1. Materials

Benzoxazine monomers were synthesized and purified according to the procedure of Ning and Ishida [1]. All the initiators listed in Table 1 were purchased from Aldrich Chemical Company and used without further purification. The solvents, 1,2-dichloroethane anhydrous and 1,2-dichlorobenzene anhydrous, with purities as 99.99 + %, were purchased from Aldrich and used directly without further purification. Another solvent, chloroform, was purified by washing with water, drying over sodium sulfate, and refluxing and distilling over phosphorus pentoxide under N_2 protection. All reagents and solvents were stored in a dry box with the moisture rating of 1 ppm except those that needed to be refrigerated.

2.2. Measurements

Fourier transform infrared (FT-IR) spectra were obtained on a Bomem Michelson 110 MB Fourier transform infrared spectrometer with 100 coadded scans at a resolution 4 cm^{-1}. Proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were taken on a Varian Gemini-200 spectrometer with proton frequency of 200 MHz. Deuterated chloroform was used as the solvent and tetramethylsilane (TMS) was used as an internal standard. Size exclusion chromatographic (SEC) analyses were performed on a Waters 510 instrument equipped with three styrogel columns of molecular weight range from 200 to 200 000, with a 254 nm fixed wavelength ultraviolet (UV) detector and a refractive index (RI) detector. Chromatographic grade tetrahydrofuran (THF) was used as the eluent. Differential scanning calorimetric (DSC) measurements were made with a TA Instruments Modulated DSC 2920. All DSC experiments were carried out under nitrogen purge at a flow rate of 80 ml min^{-1}. Standard hermetic DSC pans were used. A TA instrument 2950 thermogravimetric analyzer (TGA) was used for all the TGA experiments. All TGA experiments were carried out under nitrogen purge at a flow rate of 90 ml min^{-1}. A heating rate of 10°C min^{-1} from room temperature to 850°C was used.

2.3. Typical procedure for the polymerization of benzoxazine

A three-necked flask was flame-dried under vacuum and filled with argon. All the other operations were carried out in a dry glove box under argon protection. In a run of the initiation reaction with PCl_5, the sample was prepared as follows. To a mixture of 0.54 mmol of BA-a and 1 ml of

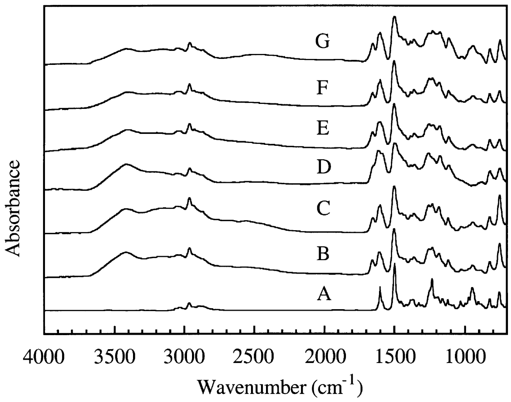
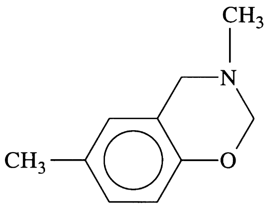


Fig. 1. FT-IR spectra of (A) BA-a monomer, and the polymers obtained from (B) $SbCl_5$, (C) $SbCl_5$ + oxatane, (D) $TiCl_4$, (E) PCl_3, (F) $POCl_3$, and (G) PCl_5 initiating systems.

chloroform in a 25 ml three-necked flask equipped with a magnetic stir bar, 0.027 mmol of PCl_5 was added at room temperature, the flask was then sealed off and the reaction was allowed to continue at room temperature for the desired time. After polymerization, the precipitated material was separated by filtration, washed with chloroform, and dried under vacuum.

For SEC analysis, BA-a was polymerized in chloroform at room temperature by means of PCl_5 initiator at monomer:initiator mole ratio (M/I) of 100:1. Small portions of samples were removed from the reaction mixture at time intervals of 1, 2, 2.5, 3.5, 5 and 7 h by a syringe and poured into a large amount of methanol. The precipitated materials were isolated by filtration, dried under vacuum at room temperature for 1 h, and then subjected to SEC analysis.

For NMR study, a *p*-cresol/methyl-amine based monofunctional benzoxazine monomer, 3-methyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine, designated as *p*C-m, was used. Again, PCl_5 was chosen as the initiator and deuterated chloroform as solvent (M/I = 20). A portion of the reaction mixture was sealed in a NMR tube, the reaction was allowed to continue in the tube at 25°C, and monitored in situ by recording the NMR spectrum at certain time intervals.



*p*C-m monomer

3. Results and discussion

3.1. Polymerizations of BA-a benzoxazine with a variety of initiators

Examination of the polymerization of BA-a with 5 mol% of a variety of cationic initiators, an anionic initiator and a free radical initiator was carried out with either 1,2-dichloroethane, chloroform, or 1,2-dichlorobenzene as the tentative solvent at a desired temperature for 20 h. The results are shown in Table 1.

As evidenced by both yields and spectral analyses, six Lewis acids, phosphorus pentachloride (PCl_5), phosphorus trichloride (PCl_3), phosphorus oxychloride ($POCl_3$), titanium chloride ($TiCl_4$), aluminum chloride ($AlCl_3$), and antimony pentachloride ($SbCl_5$), or a strong alkylating agent, triphenyl cabenium hexachloroantimonate ($(C_6H_5)_3C^+(SbCl_6)^-$), or a metalloporphyrin compound, aluminum phthalocyanine chloride, afforded polymers which precipitated from the reaction medium as a brown solid in different yields. However, no precipitants of BA-a have been observed with borontrifluorodietherate ($BF_3(OEt)_2$), or $BF_3(OEt)_2$ with a promoter (oxetane), or a covalent initiator, methyl iodide, or an anionic initiator, butyl lithium, or a free radical initiator, benzoyl peroxide, as initiator. As to the methyl triflate, methyl tosylate, and triflic acid initiated polymerizations of BA-a, no products precipitated during the solution polymerization process. However, the color of these three reaction systems changed from colorless to dark red, as well as the viscosities increased significantly. After evacuating the solvent and drying in vacuo at 100°C for 2 h, a tough polymer with brown color was generated. Another triflate, *p*-tolyl triflate, failed to significantly initiate the BA-a ring-opening polymerization.

3.2. FT-IR study

Fig. 1 shows the FT-IR spectra of the polymers obtained from various Lewis acid initiating systems. Fig. 2 illustrates the FT-IR spectra of all the other effective initiating systems. Compared to the monomer BA-a spectrum (Figs. 1(a) and 2(a)), the dramatic change of the peaks in the

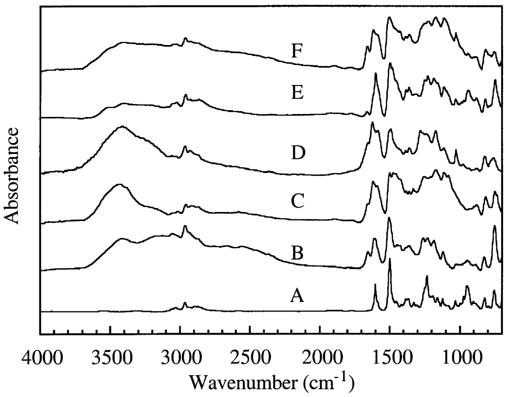


Fig. 2. FT-IR spectra of (A) BA-a monomer, and the polymers obtained from (B) $(C_6H_5)_3C^+(SbCl_6)^{-1}$, (C) aluminum phthalocyanine chloride, (D) triflic acid, (E) MeOTs, and (F) MeOTf initiating systems.

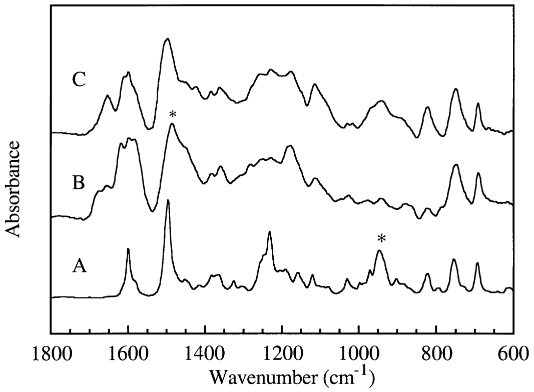
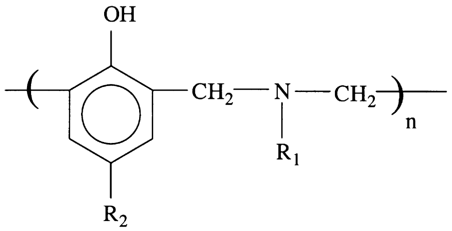


Fig. 3. Comparison of FT-IR spectra of (A) BA-a monomer, (B) thermally polymerized, and (C) PCl_5-initiated poly(BA-a) benzoxazines.

region of 1350–1000 cm^{-1}, arising from the CH_2 wagging mode (1327 and 1305 cm^{-1}), C–O–C asymmetric stretching mode (1233 cm^{-1}), C–N–C asymmetric stretching mode (1159 cm^{-1}), and C–O–C symmetric stretching mode (1031 cm^{-1}) of the oxazine ring, respectively, as well as the decrease of the peak resolution, indicate the opening of the oxazine ring and the polymerization of the monomers into oligomers and polymers.

It is worth noting the spectral differences between the thermally polymerized polybenzoxazine and some of the cationically polymerized polybenzoxazines. As an example, the comparison of the FT-IR spectra of the thermally polymerized and the PCl_5-initiated poly(BA-a) benzoxazines is shown in Fig. 3. In the spectrum of BA-a monomer, the peaks centered at 1500 and 949 cm^{-1} are characteristic of the tri-substituted benzene ring in the benzoxazine structure, corresponding to the in-plane C–C stretching and the out-of-plane C–H deformation of tri-substituted benzene ring, respectively. These two peaks almost disappear in the thermally polymerized polybenzoxazine spectrum, meanwhile a new peak centered at 1489 cm^{-1}, representing tetra-substituted benzene ring mode, appears. The results are in accordance with the well accepted polybenzoxazine structure as shown below.



Polymer Structure I

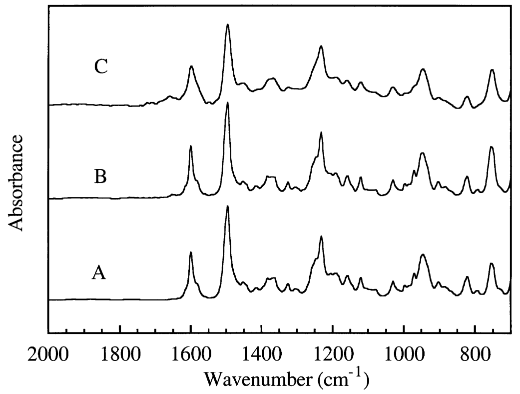


Fig. 4. FT-IR spectra of the products from (A) $BF_3(OEt)_2$, (B) butyl lithium, and (C) benzoyl peroxide-initiated BA-a polymerization systems.

Table 2
DSC and TGA results of polybenzoxazines obtained from different initiating systems

Initiator	T_g by DSC (°C)	Char yield at 800°C by TGA (%)
PCl_5	215	50.26
PCl_3	216	48.93
$POCl_3$	210	50.53
$TiCl_4$	222	61.78
Metalloporphyrin	186	43.59
MeOTf	193	31.48
MeOTs	142	28.06
Triflic acid	—	31.29
$AlCl_3$	186	44.50
Thermally cured	177	28.56

However, with some initiators, here PCl_5 has been chosen as an example, those two peaks at 1500 and 949 cm^{-1} remain unaffected except for the peak broadening. This indicates that in the obtained polybenzoxazine structure, instead of tetra-substituted, the majority of the benzene rings should still be tri-substituted. Further NMR results are in support of this hypothesis.

As to the other initiators listed in Table 1, there is little or no difference between the spectra of the products obtained from initiating systems No. 13 to No. 18 (Fig. 4) and that of the BA-a benzoxazine monomer (Figs. 1(a) and 2(a)), implying that no significant ring-opening reactions took place under the chosen polymerization condition. In Fig. 4, borontrifluorodietherate initiated product was chosen among the tested ineffective cationic initiators along with an anionic (butyl lithium) and a free radical (benzoyl peroxide) initiators to illustrate the lesser extent or absence of polymerization of these initiating systems. In general, the FT-IR results are in good agreement with the yield results.

3.3. Thermal analysis

A very important property of polybenzoxazine is its good thermal stability. This property along with its other prominent features such as high char yield, near zero shrinkage or even slight volumetric expansion upon polymerization provides polybenzoxazines high potential for structural applications [2,7]. To check the thermal properties of the polymers obtained from different effective initiating systems, thermal analyses (DSC and TGA up to 850°C)

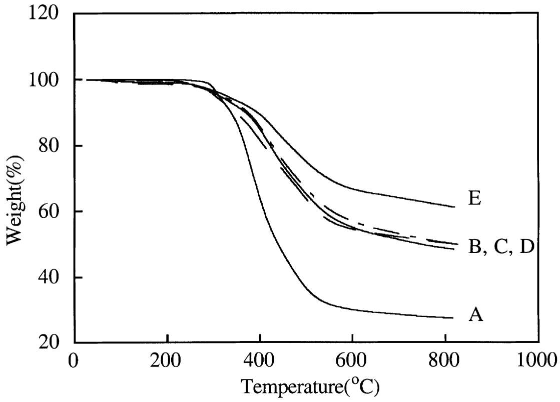


Fig. 5. TGA thermograms of (A) thermally polymerized, (B) PCl_3 (solid line), (C) PCl_5 (long dash), (D) $POCl_3$ (broken dash), and (E) $TiCl_4$-initiated poly(BA-a) benzoxazines.

were performed on these polymers in order to test the glass transition temperature (T_g) and the weight loss. Moreover, in order to obtain reproducible results, the amount of solvent was minimized by drying each as-synthesized polymer at 100°C for 2 h before the DSC measurement.

Typical glass transition temperature of the fully thermally polymerized BA-a polymer is about 170°C and char yield at 800°C under nitrogen environment is about 30%. As can be seen in Table 2, by using some initiators to initiate the polymerization, poly(BA-a) benzoxazines with better thermal properties were obtained. Particularly, with Lewis acids PCl_5, PCl_3, $POCl_3$, and $TiCl_4$ as initiators, polybenzoxazines with T_g higher than 200°C and char yield around 50% or even up to 61% at 800°C under nitrogen were obtained. The thermal analysis results are summarized in Table 2.

Initially, it was thought that the high T_g of these polymers may come from the neat cationic polymerization conditions. When carrying out thermal polymerization, the reaction system was subjected to a less controlled environment, as a result, many defects may exist in the final polybenzoxazine structures. However, when polymerized in solution, under almost oxygen and water free conditions, the propagating chains suffered less chain transfer and termination reactions. Meanwhile, the reaction system was well stirred and mixed so that the reaction heat could diffuse easily, resulting in a polymer with more ordered molecular structure.

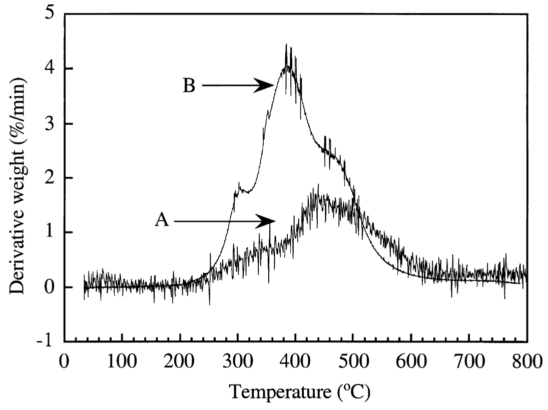


Fig. 6. Comparison of the TGA derivative curves of (A) poly(BA-a) initiated by $TiCl_4$ (50 times of its original derivative curve value) and (B) thermally polymerized poly(BA-a) benzoxazines.

The TGA thermograms of some of these polymers are shown in Fig. 5. As seen from the TGA thermograms, the onset degradation temperature of these polymers is almost the same (about 250°C). Nevertheless, the most interesting aspect of this thermal analysis goes to the significant improvement of the char yield of those polymers with initiators. Basically, the char yield of a polymeric material relates directly to its composed elements, structure, crosslink density, etc. [8]. It has been reported that polymers with phosphorus–carbon bonds as part of its structure gave higher char yield than its non-phosphate analogues [9]. However, in this study, the content of the phosphorus or titanium initiator was between 1 and 2 wt.%. It is unlikely that the increase of the char yield by as much as double that of the thermally polymerized one was totally due to the typical mechanisms associated with the phosphorous and titanium compounds. To have a better look on the degradation process of these Lewis acid-initiated high performance polybenzoxazines, derivatives of the TGA thermograms, which can illustrate better the degradation process, of thermally polymerized BA-a and Lewis acid-initiated BA-a are plotted in Fig. 6, here $TiCl_4$-initiated poly(BA-a) has been chosen as an example. As expected, thermally polymerized BA-a shows an overlapped trimodel derivative curve with the first peak around 300°C assigned as the degradation of the Mannich base, and the second major peak around 380°C as the degradation of the phenolic linkage in polymer structure **I** [10]. Interestingly, the derivative of the $TiCl_4$-initiated poly(BA-a) TGA thermogram differs substantially from that of the thermally polymerized polymer. On the onset of the degradation around 250°C, the first weight loss event occurs at a slow rate until reaching the first insignificant maximum around 340°C, which has been improved by about 40°C compared to the first peak of the thermally polymerized BA-a. In addition, the second major weight loss event was retarded to 450°C, which is about 70°C higher than that of the thermally polymerized material. Fig. 6(a) also shows broadening of the derivative peaks. This effect, which represents a slower decomposition rate over a wider temperature range, is beneficial from the flammability point of view. These features may imply different degradation mechanisms of these two types of poly(BA-a)s, which may be a result of the different structures that these two polymers assume. Other possibilities can also be associated with the high char yield results, for example, at elevated temperatures, possibly during the primary weight loss temperature range, the phosphorus or titanium atom became covalently bonded to the benzene ring or the nitrogen bridge, thus anchoring the potentially weak moieties in the polybenzoxazine structure, and as a consequence, improving the thermal stability of the polymer.

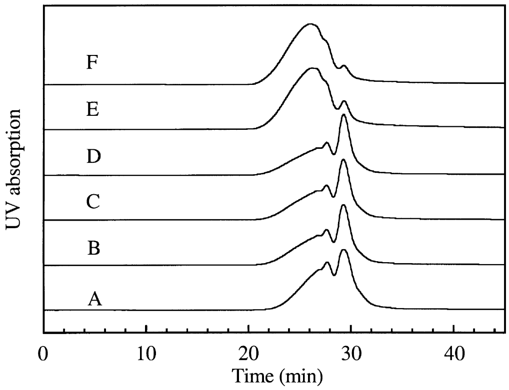


Fig. 7. SEC chromatograms of the PCl_5-initiated BA-a system at time intervals of (A) 1 h, (B) 2 h, (C) 2.5 h, (D) 3.5 h, (E) 5 h, and (F) 7 h at room temperature.

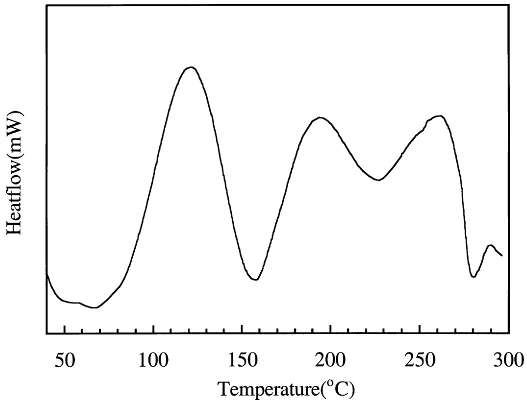


Fig. 9. Dynamic DSC thermogram of BA-a/PCl_5 system (M/I mole ratio = 20:1).

3.4. SEC analysis

The aforementioned polymers show excellent solvent resistance; however this advantage also makes it impossible to measure the molecular weight of the polymers. In order to acquire a basic knowledge of the polymerization process, SEC was used to monitor the molecular weight changes of the growing chains (oligomers) before they precipitated out of the reaction medium.

Fig. 7 shows the SEC chromatograms of the methanol-precipitated materials from the PCl_5-initiated system at different reaction times. The peak at 29.3 min retention time is assigned to the BA-a benzoxazine monomer. As the polymerization time was prolonged, this peak decreased gradually. At the same time, the broad peak in the left-hand side represents the slow shift to the shorter retention time and intensification because of the gradual oligomer formation. This phenomenon reflects the gradual increase in molecular weight during the polymerization. The molecular weight of the polymer eventually reached the extent where they were no longer soluble in the solvent used for polymerization.

By using curve fit as shown in Fig. 8, a dominant peak centered at 25.2 min was resolved from the 7 h GPC chromatogram, which means that a Mn over 2800 in terms of polystyrene standards was already achieved before the polymer precipitated out of the reaction system, suggesting the minimum limit of the molecular weight of the precipitated polymers.

3.5. Mechanistic aspects

A typical dynamic DSC curve for the BA-a benzoxazine monomer with PCl_5 as initiator (M/I = 20) is shown in Fig. 9. Multiple exotherms centered at 122, 189 and 264°C, respectively, are seen. The glass transition temperature, T_g, measured on the second DSC scan, was 174°C. The exotherm at 264°C was due to degradation rather than further curing as shown by the TGA experiment indicating that degradation of the corresponding polymer to volatile products began at about 250°C, which is consistent with the previous work [10]. The DSC curve of the pure BA-a monomer showed only one exothermic peak centered at 231°C, thus, the two low temperature exotherms should be due to the cationic initiation and polymerization of the benzoxazine resin by the initiator with the possibility of multiple polymerization reactions occurring simultaneously or

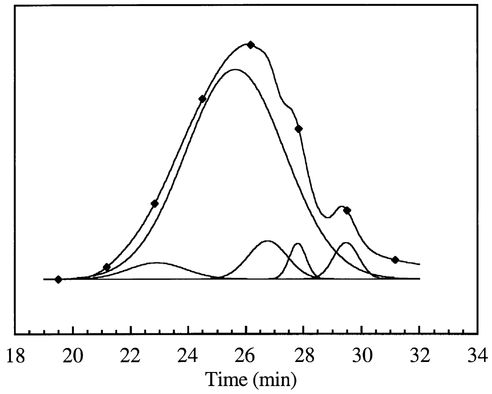


Fig. 8. Curve fit of the 7 h SEC chromatogram (marked line).

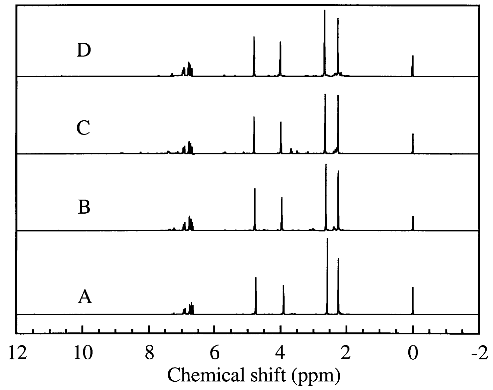


Fig. 10. In situ ^{1}H NMR spectra of the PCl_5-initiated polymerization of *p*C-m at: (A) 0 min, (B) 30 min, (C) 1 h, and (D) 20 h at room temperature.

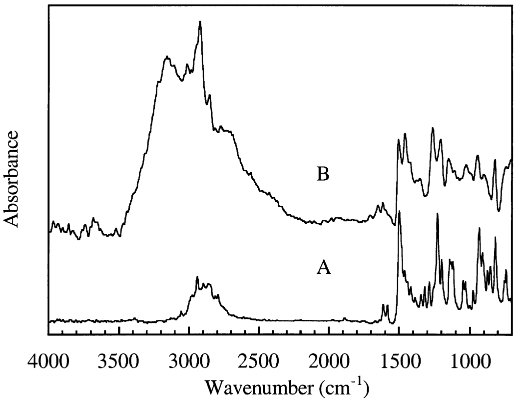


Fig. 11. Comparison of the FT-IR spectra of: (A) *p*C-m monomer and (B) poly(*p*C-m) initiated by PCl_5 at room temperature.

sequentially. Multiple peaks have been observed in the DSC cure profile for several cationically cured epoxy systems [11–13]. Various mechanisms have been proposed for this phenomenon, such as activated monomer (AM) vs. activated chain end (ACE) mechanism, different initiating species mechanism, protic impurities mechanism, and so on.

Earlier studies have shown that there may exist different types of intermediate species in the process of benzoxazine ring-opening polymerization. Dunkers and Ishida proposed that the intermediate was an iminium-ion/carbenium-ion resonance structure [14]. Another alternative mechanistic proposal involved a Schiff base both as an intermediate structure in the polymerization and as a possible side product [15]. These intermediate species provided a possible basis for the appearance of multiple curing peaks.

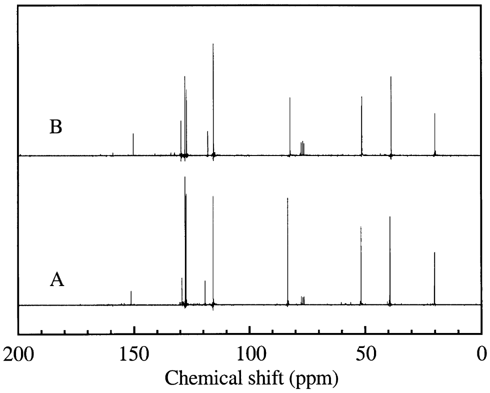


Fig. 13. ^{13}C NMR spectra of: (A) *p*C-m monomer; and (B) in situ PCl_5-initiated polymerization of *p*C-m after 20 h at room temperature.

^{1}H and ^{13}C NMR have been utilized to monitor the polymerization process of benzoxazine with PCl_5 as initiator. For simplicity, *p*-cresol and methyl amine-based monofunctional benzoxazine, designated as *p*C-m, was used as the starting material. The in situ ^{1}H NMR spectra taken at several time intervals are shown in Fig. 10. Complicated reaction intermediate peaks emerged during the early stage of polymerization, however nearly disappeared as the polymerization came to an end. The FT-IR spectrum of this final product is shown in Fig. 11, showing that this is a ring-opened polymer structure instead of still being the monomer. In comparison, the ^{1}H NMR spectra of the samples thermally polymerized from the same monomer at 160°C for various times without the catalyst are also given in Fig. 12. For the thermally cured samples, the appearance of the peak at 3.6 ppm along with the disappearance of the two peaks centered at 4.7 and 3.9 ppm indicates the formation of the symmetric Mannich bridge structure ($-CH_2-N-CH_2-$), which is in accordance with the well-known polybenzoxazine structure **I**. For the cationically polymerized sample, even after 20 h, four major aliphatic proton peaks with chemical shift at 2.3, 2.7, 4.0, and 4.8 ppm still exist, suggesting that besides the benzene protons, there are four different kinds of proton environments in the obtained polymer structure. The ^{13}C NMR of this PCl_5-initiated sample are shown in Fig. 13, and the peak assignments of the monomer are tabulated in Table 3. As

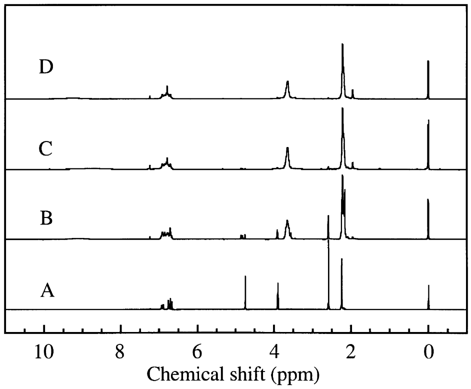
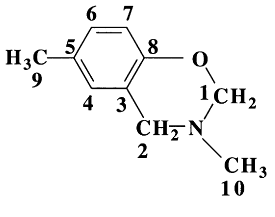
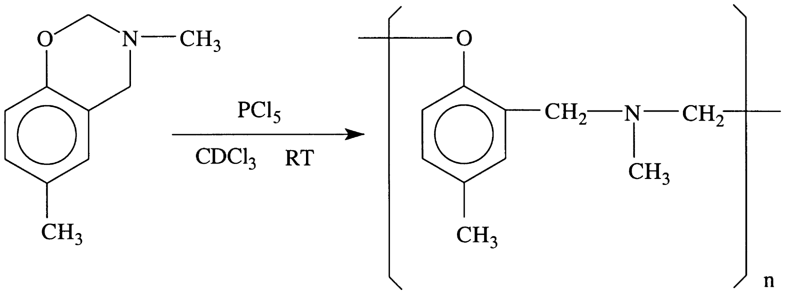


Fig. 12. ^{1}H NMR spectra of thermally polymerized poly(*p*C-m) at: (A) 0 min, (B) 10 min, (C) 30 min, and (D) 2 h at 160°C.

Table 3
^{13}C NMR assignment of *p*C-m monomer



Assignment	^{13}C chemical shift (ppm)
C1	83.7
C2	52.2
C3	119.5
C4	128.1
C5	129.6
C6	127.7
C7	116.0
C8	151.6
C9	20.4
C10	39.7



Scheme 1. Postulated structure of PCl_5-initiated poly(*p*C-m) benzoxazine.

seen from Fig. 13(a) and (b), the polymerization process barely changes the chemical shift of C9, C10, C7 and C4(C6), while slightly shifting the peak position of C1, C2, C3, and C8 upfield as a result of the opening of the oxazine ring.

Based on the FT-IR and NMR analyses, the structure of this PCl_5-initiated *p*C-m polymer has been tentatively postulated as Scheme 1.

4. Conclusions

Various initiators were studied for the polymerization of BA-a benzoxazine resin. Several initiators, PCl_5, PCl_3, $POCl_3$, $TiCl_4$, $AlCl_3$, and MeOTf, were found to be effective for the ring-opening polymerization of benzoxazine resins at moderate temperatures. Several attractive polymers with high T_g and high char yield under nitrogen environment were produced from these initiating systems. A dynamic DSC study revealed multiple exotherms upon the use of these initiators, indicating a complex polymerization mechanism. Polybenzoxazines with different structures from those of the thermally polymerized materials may be generated. Further detailed studies are needed to verify the structures of these polymers.

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