Study on the Chemical Stability of Benzoxazine-Based Phenolic Resins in Carboxylic Acids

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ABSTRACT: The chemical stability of typical polybenzoxazines based on bisphenol-A and primary amines was studied. Using proton nuclear magnetic resonance spectroscopic analysis of polybenzoxazine model dimers, it was found that the Mannich base is stable in a carboxylic acid solution. It is proposed that the nature of the primary amines is responsible for the interactions which take place between the carboxylic acid and the Mannich-base model dimers. As a result, the chemical stability of polybenzoxazines may also be related to the nature of the amines, which, in turn, influence the strength of the hydrogen-bonded network structure which develops upon cure. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1207–1219, 2001

INTRODUCTION

Composite materials with organic resin matrices have received attention because they possess high strength-to-weight ratios compared to other materials, such as metals and ceramics, and are more stable to chemical attack. While metals typically require organic coatings and paints to inhibit corrosion in liquid environments, some composites exhibit good chemical resistance without any protective coatings. For these reasons, the polymer matrix composites continue to be a subject of strong interest in the aerospace, marine, and automotive industries. Marine vessels, including oil and natural gas pipelines, for instance, are typically coated with a protective composite layer to reduce the extent of corrosion. Many under-the-hood parts in automobiles have also been replaced by composite materials which are more lightweight and can tolerate prolonged exposure to organic liquids such as fuel, oil, and antifreeze.

The stability of a composite material to chemical attack depends primarily on the properties of the matrix resin. Consequently, various polymeric materials have been studied extensively as matrix materials for composite structures. Phenolic resins are also used as matrices because they have attractive properties, including good thermal and chemical resistance as well as excellent flame retardance. However, phenolic resins have well-known shortcomings including the evolution of small molecules during polymerization, the use of strong catalysts, and poor molecular design flexibility.

Recently, the polybenzoxazines, a class of phenolic resin, have been actively studied, having a number of unique properties such as excellent mechanical properties,[1,2] high char yield,[2] near zero volumetric shrinkage/expansion upon polymerization,[3] and ease of processing.[4] Furthermore, polybenzoxazines have superb molecular design flexibility and, thus, the ability for the mechanical and physical properties to be tailored to the specific requirements of individual applications.

The knowledge of the chemical nature of the material, including the crosslinked network

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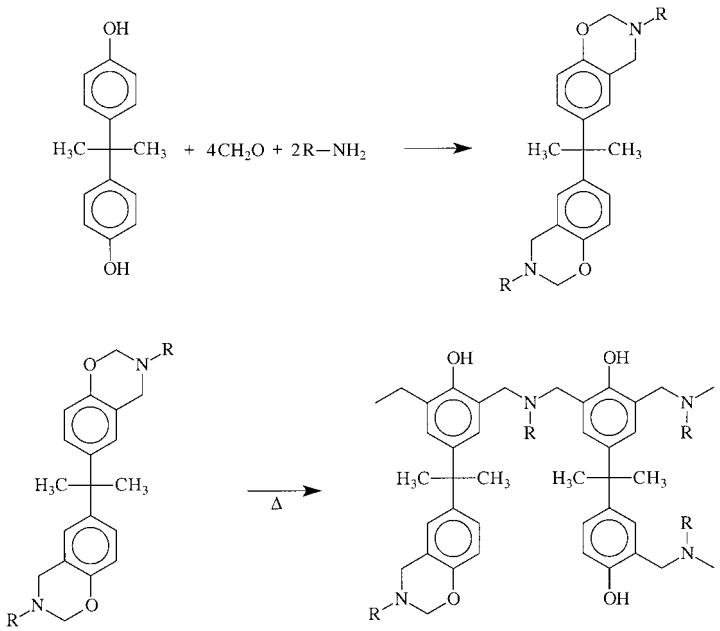


Scheme 1 Ring-opening polymerization of polybenzoxazines.

structure and the structural parameters that affect the stability of resins, is essential to obtain maximum performances and to predict the stability of the resins in a wide range of service environments. Although numerous studies have been conducted to elucidate the kinetics and mechanisms of the degradation of thermosetting resins in chemically aggressive media,[5–8] the stability of polybenzoxazines in chemical environments has been poorly understood. It has been observed that polybenzoxazines exposed to carboxylic acid show anomalous behavior as some polybenzoxazines are rapidly disintegrated in a weak carboxylic acid solution. Therefore, it was the purpose of this article to study the effect of carboxylic acids on a typical polybenzoxazine and to discern molecular interaction mechanisms using a number of newly synthesized model compounds.

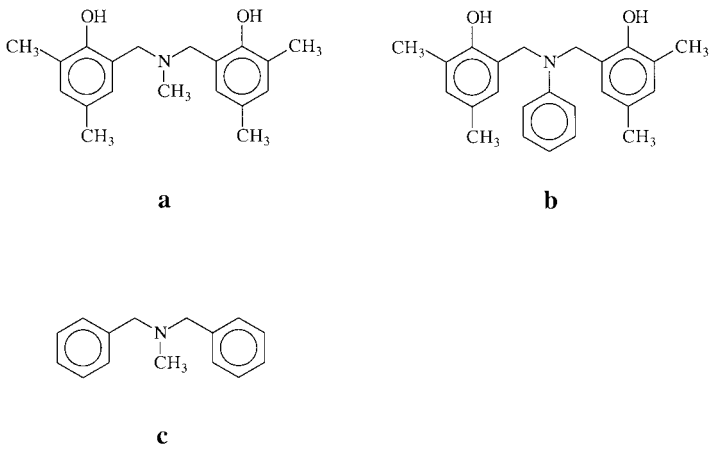
EXPERIMENTAL

All chemicals were used as received. Bisphenol-A (97%), *p*-formaldehyde (95%), aniline (99%), methylamine (40% in water), 2,4-dimethylphenol (98%), and benzylbromide (98%) were obtained from the Aldrich Chemical Co. Formaldehyde (37% in water) was purchased from Fisher Scientific and triethylenetetramine was purchased from Miller–Stephenson Chemical.

Bifunctional benzoxazine monomers were synthesized and purified according to the procedure of Ning and Ishida[9] or Ishida.[10] Two typical bifunctional benzoxazines were prepared from bisphenol-A, formaldehyde, and primary amines. One was 2,2-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazine)-propane (abbreviated BA-m) based on methylamine and the other was 2,2-bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine)propane (abbreviated BA-a) based on aniline. The purity of the compounds was determined from proton nuclear magnetic resonance (^{1}H-NMR) spectra.

The benzoxazine monomer contains an oxazine ring that opens into a phenolic structure upon thermal polymerization. All the bifunctional benzoxazines were polymerized as shown in Scheme 1 without an added initiator or catalyst according to the following schedule: 150°C, 1 h; 175°C, 1 h; and 195°C, 2 h. R in the structure denotes the substituent of the primary amine (Scheme 1).

Diglycidyl ether of bisphenol-A (DGEBA) (EPON 825, Shell) was used for the purpose of comparison. An aliphatic amine, triethylenetetramine (TETA), was used as the curing agent. Prior to mixing, both DGEBA and TETA were dried in a vacuum and then mixed immediately at room temperature. The mixture (DGEBA:TETA = 100:14) was evacuated to remove air bubbles at room temperature for 1 h and then cured at 120°C for 3 h.



Scheme 2 Structures of model dimers.

Synthesis of a Methylamine-based Polybenzoxazine Model Dimer

N,*N*-Bis(3,5-dimethyl-2-hydroxybenzyl)methylamine [Scheme 2(a)] was synthesized according to a previous study using 2,4-dimethylphenol, formaldehyde, and methylamine.[11] White, irregular crystals were obtained by recrystallization from ethyl ether for the methylamine-based dimer.

Synthesis of an Aniline-based Polybenzoxazine Model Dimer

N,N-Bis(3,5-dimethyl-2-hydroxybenzyl)aniline [Scheme 2(b)] was also synthesized by the same method as was *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine using aniline instead of methylamine. The product was recrystallized from hexane until white crystals were obtained and subsequently purified by column separation. A white needlelike crystal was obtained.

^{1}H-NMR (200 MHz, $CDCl_3$, 298K) δ: 2.16, 2.17 (12H, Ar—CH_3), 4.26 (4H, Ar—CH_2—N), 6.65, 6.82 (4H, Ar—H), and 7.00–7.31 (5H, Ar—H). ^{13}C-NMR (50.1 MHz, $CDCl_3$, 298K) δ: 15.84, 20.48 (4C, Ar—C), 55.68 (2C, Ar—C—N), and 121.60–151.70 (18C, Ar).
ANAL. Found: C, 79.89%; H, 7.69%; N, 3.91%. Calcd for $C_{24}H_{27}NO_2$: C, 79.74%; H, 7.53%; N, 3.87%.

Synthesis of Dibenzylmethylamine

N,*N*-Dibenzylmethylamine [Scheme 2(c)] was synthesized using benzylbromide and methylamine as follows[12]: A stoichiometric amount of reactants (benzylbromide:methylamine = 2:1) was reacted in ethyl ether at room temperature for 10 min and the viscous product dissolved in ethyl ether. The ether solution was washed several times with distilled water and dried over sodium sulfate for 12 h. Evaporating the ether resulted in a viscous fluid at room temperature.

The purity of the dimers was examined using a 200-MHz nuclear magnetic resonance spectrometer (^{1}H-NMR and ^{13}C-NMR) and a Hewlett–Packard 6890 gas chromatography-5973 mass selective detector (GC–MS). For simplicity, *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine, *N*,*N*-bis(3,5-dimethyl-2-hydroxybenzyl)aniline, and *N*,*N*-dibenzylmethylamine will be referred to as Methyl-dimer, Aniline-dimer, and Benzyl-dimer in this article, respectively.

Weight-retention measurements were performed by weighing samples periodically on a analytical balance following immersion in a desired acid solution at room temperature. The samples (10 × 10 × 2 mm) were removed from the solution, blotted, weighed, and finally reimmersed in the solution. The disintegrated residue in the solution was washed by distilled water several times, filtered, and dried in a vacuum for 72 h at 60°C.

Fourier transform infrared spectroscopy (FTIR) was performed on a Bomem Michelson MB110 FTIR spectrophotometer which was equipped with a liquid nitrogen-cooled, mercury–cadmium–telluride (MCT) detector with a specific detectivity, D^*, of 1×10^{10} cm $Hz^{1/2}$ W^{-1}. All spectra were recorded at a resolution of 4 cm^{-1} and displayed in the absorbance mode. Coaddition of 100 scans was sufficient to obtain good signal-to-noise ratio. The residues of acid-treated samples were pressed into a KBr pellet. A thin film of the benzoxazine monomer

was cured on a potassium bromide (KBr) plate, using the above-mentioned curing cycle.

Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2950, at a nitrogen flow rate of 90 mL/min and a heating rate of 10°C/min. A TGA–FTIR (Bio-Rad FTS 60A) interface was used for evolved gas analysis using a deuterated triglycine sulfide (DTGS) detector. The FTIR was interfaced with the TGA through a heated glass transfer line. Both the transfer line and the gas cell were heated at 260°C. FTIR spectra of the evolved gases were collected at a spectral resolution of 8 cm^{-1} and at a time resolution of 1 s.

The nuclear magnetic resonance (NMR) spectrometer used was Varian XL200. Deuterated chloroform and deuterated acetic acid were used as solvents with 0.5% tetramethylsilane as the internal standard. Coaddition of 64 transients yielded a good signal-to-noise ratio spectrum. A relaxation time ($D1$) of 10 s was used to obtain integration results.

Size-exclusion chromatography (SEC) was performed with a Waters gel permeation chromatograph equipped with Waters 510 HPLC pump and an UV detector fixed at 254 nm. High-performance liquid chromatography (HPLC)-grade tetrahydrofuran (THF) was used as an eluent.

RESULTS AND DISCUSSION

Although the extent of swelling was varied from one polymer sample to another, it was observed that both polybenzoxazines and epoxy in sulfuric acid showed swelling behavior as shown in Figure 1. Since a chemical attack usually takes place at the weakest link in the polymer chain, the tertiary nitrogens, as the weakest link, in the epoxies, are therefore more susceptible to acid attack than to base attack due to the basic nature of nitrogen.[13] However, as shown in Figures 2 and 3, polybenzoxazines in carboxylic acid solutions displayed interesting behavior. While the epoxy had shown the same swelling behavior as that of polybenzoxazine in a sulfuric acid solution, and the BA-a polymer was very stable in the carboxylic acid solution during the experimental time scale, the BA-m polymer, on the other hand, rapidly disintegrated into small fragments. Taking into account that the dissociation constant, K_a, of carboxylic acid is much lower than that of sulfuric acid (Table I), the disintegration of the BA-m polymer in carboxylic acids is unexpected. Furthermore, despite the similarity between BA-a and BA-m's chemical structures, the fact that the BA-a polymer shows outstanding stability in car-

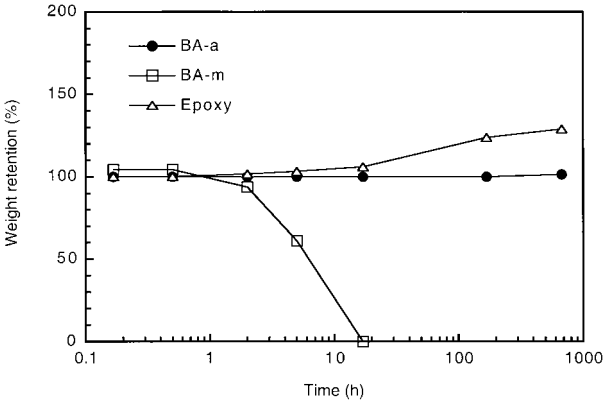


Figure 2 Weight retention of BA-a, BA-m polybenzoxazine, and epoxy in formic acid (30 wt %).

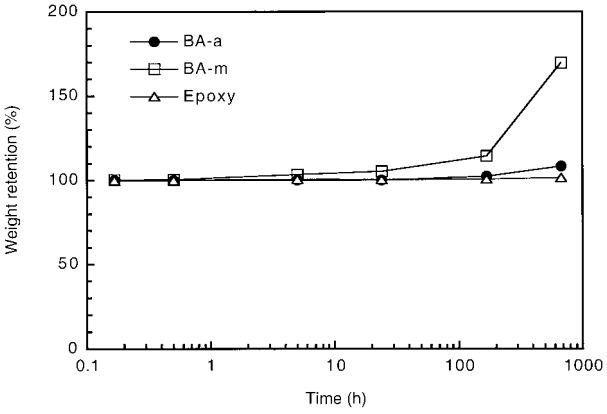


Figure 1 Weight retention of BA-a, BA-m polybenzoxazine, and epoxy in sulfuric acid (30 wt %).

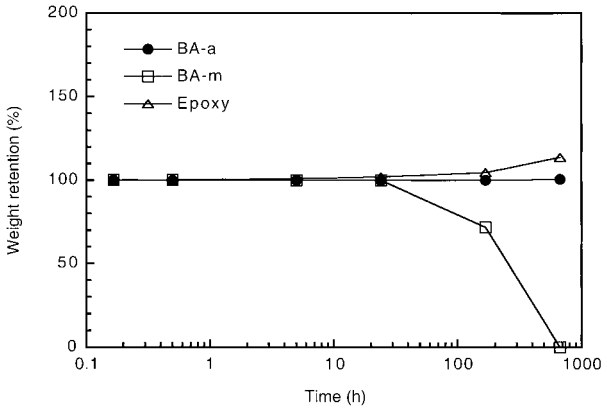


Figure 3 Weight retention of BA-a, BA-m polybenzoxazine, and epoxy in acetic acid (30 wt %).

Table I Dissociation Constants (K_a) and Boiling Points (bp) of the Used Acids[14]

	K_a	bp (°C)
Formic acid	1.77×10^{-4}	101
Acetic acid	1.75×10^{-5}	118
Sulfuric acid	1.0×10^{3}	—

boxylic acid solutions is worthy of investigation, especially due to the promise that this phenomenon might provide fundamental information as to the network structure of polybenzoxazines.

Due to the possibility that the main chain of polybenzoxazines, in particular, the Mannich base, was partially degraded by acid attack, the residues of BA-m polymer obtained after the carboxylic acid treatment were examined by FTIR analysis. As shown in Figure 4, the characteristic C═O stretching band of carboxylic acid is shown in the region of 1725–1700 cm^{-1}, although it was difficult to find evidence that the chemical structure of the BA-m polymer was changed within the experimental error. From the intensification of the multiple bands between 1750 and 1550 cm^{-1}, however, we can predict that the strong interaction between the BA-m polymer and the carboxylic acid cannot be easily removed under the drying condition employed. Compelling evidence for this interaction is demonstrated by the intensification of the characteristic band at 1560 cm^{-1}, due to the asymmetric stretch of carboxylic acid salt, and the broad multiple band in the region of 1420–1335 cm^{-1} assigned to the symmetric stretching vibration. TGA and TGA–FTIR-evolved gas analysis will

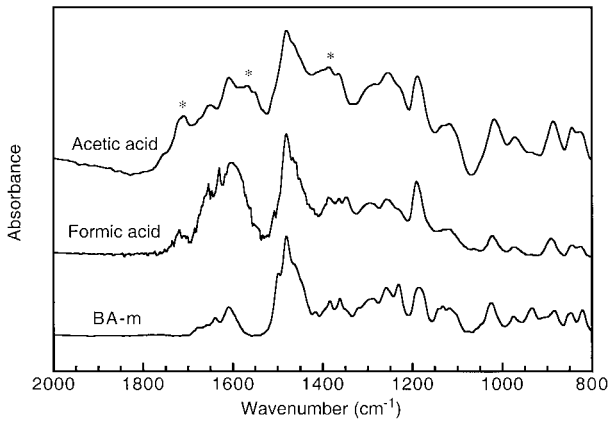


Figure 4 Comparison of FTIR spectra of BA-m polybenzoxazine residues treated with acetic acid (30 wt %) and formic acid (30 wt %) for 28 days.

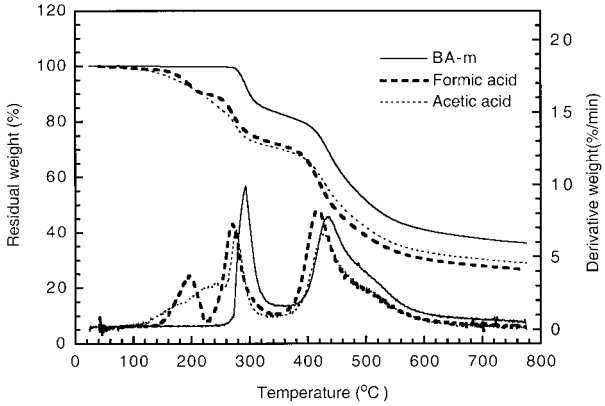


Figure 5 TGA thermograms of BA-m polybenzoxazine and the residues treated with acetic acid (30 wt %) and formic acid (30 wt %) for 28 days.

be used to clarify this subject later. The FTIR spectra of the carboxylic acid solutions, after filtering the residues, were also taken. However, any traces of small molecules, which could be fragmented by acid attack, were not found within the instrumental detectivity.

TGA thermograms of the BA-m polymer with or without acid treatment by either acetic acid or formic acid are shown in Figure 5. The initial weight loss for the acid-treated BA-m polymer was observed below 250°C with a weight loss of 10–15%, while the untreated BA-m polymer was still stable over this temperature range. After the initial weight loss was completed, the second and the third weight-loss peaks for the acid-treated BA-m polymer appeared at almost the same position as in the untreated BA-m polymer. The effect of a small particle size, and, thus, the increased surface area, might be responsible for the small reduction of the derivative peak shift for the acid-treated samples.

To obtain more detailed information as to the chemical nature of the initial weight losses of the acid-treated BA-m polymer, the evolved gases from TGA were monitored by TGA-interfaced FTIR spectroscopy. The FTIR spectra of the evolved gases for the formic acid-treated BA-m polymer, at the peak temperature, are shown in Figure 6. The spectra at the second and third peaks of the weight derivative are identical to the result of the thermal degradation for the BA-m polymer, that is, the spectrum at 270°C indicates that the amine fragment resulting from scission of the Mannich bridge by thermal degradation, as is also the case for the spectrum at 410°C, is from the thermal degradation of the phenolic moiety.[15]

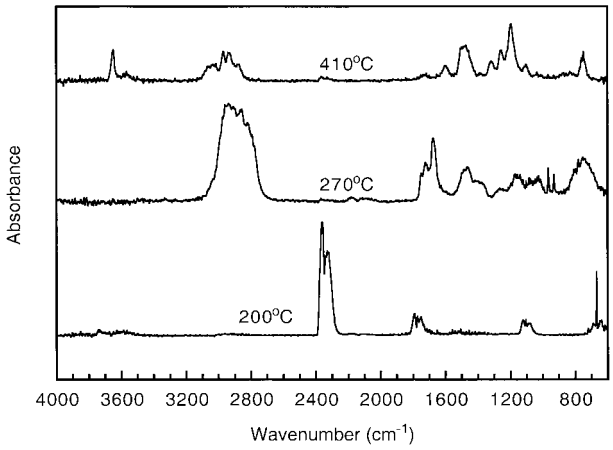


Figure 6 FTIR spectra of evolved gases from degrading BA-m polybenzoxazine residue treated with formic acid (30 wt %) for 28 days.

However, characteristic formic acid vapor bands appear in the spectrum obtained at 200°C. It was observed that the acetic acid-treated BA-m polymer also shows similar behavior to that of the formic acid-treated BA-m polymer at this low temperature regime, as shown in Figure 7. Hence, the weight loss in the vicinity of 200°C is due mainly to the evaporation of the acid from the polybenzoxazine fragments. There are two observations which suggest that carboxylic acid has a strong interaction with the polymer. First, the boiling points of formic acid (101°C) and acetic acid (118°C) are much lower than is the temperature for the onset of the initial peak. Second, the carboxylate ion is observed in the FTIR spectra. Therefore, the existence of this strong interaction with the polymer is most likely in the form of a salt.

From the above results that (1) the BA-a polymer was very stable in the carboxylic acid solution in comparison to BA-m polymer, (2) no significant changes were found in the FTIR spectrum of the polymer residue after the acid treatment except for the strong carbonyl stretching bands, and (3) the TGA thermogram of the polymer residue was the same as that of the untreated polymer except for the initial weight loss, it is concluded that the disintegration of the BA-m polymer in carboxylic acid cannot be explained by a simple degradation of the Mannich base. A different mechanism is, therefore, needed to explain this behavior.

To investigate the chemical stability of the Mannich bridge in polybenzoxazines, three model dimers were synthesized and investigated by NMR in different deuterated solvents. Methyl-dimer and Benzyl-dimer have the same structure as that of the Mannich bridge except that the Methyl-dimer has a hydroxyl group in the phenyl ring. Also, the aniline-dimer was chosen to compare the effect of the pendant group of the nitrogen atom. The NMR chemical shifts for the protons of the Methyl-dimer in deuterated chloroform solvent were assigned by Dunkers and Ishida[11] [Fig. 8(a)]. The chemical shifts for the structure of the Benzyl-dimer could also be assigned using the chemical shifts of the Methyl-dimer and confirmed by the integration analysis of the peak area [Fig. 9(a)]. Only one resonance appears for the methylene protons in the Mannich bridge, which indicates that all four methylene protons have the same electronic environment.

However, the NMR spectra of the Methyl-dimer and Benzyl-dimer in deuterated acetic acid are very different from those in deuterated chloroform [Fig. 8(b) and 9(b)]. The resonances of the methyl protons in the Methyl-dimer are well separated in deuterated acetic acid; however, they are not resolved in deuterated chloroform. According to Dunkers and Ishida,[11] the resonances for the methyl protons in the Methyl-dimer in deuterated chloroform are not resolved due to the superposition of the chemical shifts. As shown in Table II, however, when deuterated acetic acid is used as the NMR solvent, the protons near the nitrogen atom show a larger increase in the chemical shift than that of the other protons which are attached to the phenyl ring. One explanation may be that the salt formation provides a deshielding

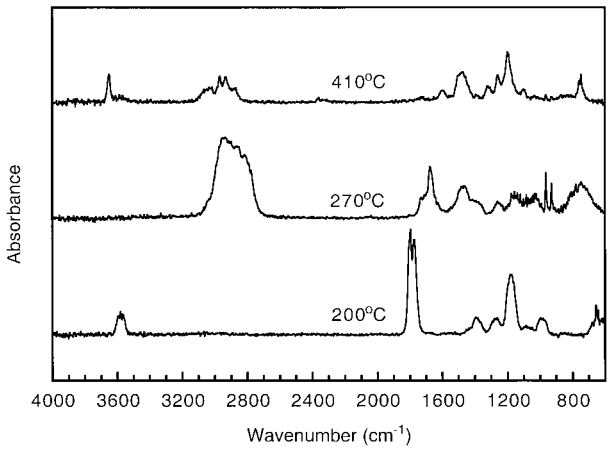


Figure 7 FTIR spectra of evolved gases from degrading BA-m polybenzoxazine residue treated with acetic (30 wt %) for 28 days.

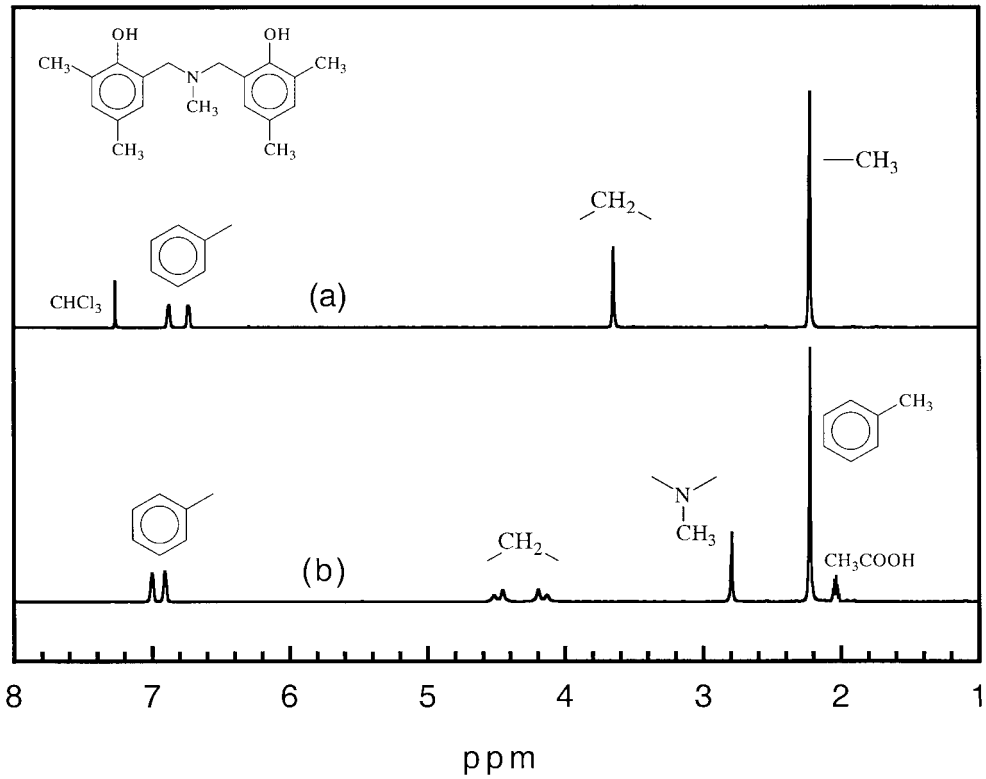


Figure 8 ^{1}H-NMR spectra of Methyl-dimer in (a) deuterated chloroform and (b) deuterated acetic acid.

effect to the protons which are adjacent to the nitrogen, causing a downfield transition of the chemical shift. Ma and Warnhoff[16] reported that the pronounced downfield shift of the resonances of basic *N*-methyl and *N*-methylene groups was observed when deuterated acetic acid or trifluoroacetic acid were used as solvents. This effect is due to the decreased shielding of the methyl and methylene protons which are attached to the protonated nitrogen atom relative to those of the amine. This result suggests that salt formation takes place between the nitrogen atom and carboxylic acid.

In addition, it should be noted that the singlet of the methylene protons in the Methyl-dimer in deuterated chloroform is split into an AB quartet centered near 4.33 ppm in deuterated acetic acid, while those of the Benzyl-dimer appear as a singlet in both solvents. These splitting peaks can be assigned to the resonances of the methylene protons by integration analysis, reflecting a change in the electronic environment around the methylene by the addition of deuterated acetic acid. The coupling of adjacent CH protons by NH is not observed for most aliphatic amines because the proton exchange rate is rapid. If the exchange rate of the proton on a nitrogen atom is slowed by a strong interaction with acids, a coupling to the adjacent protons may be observed.[17] However, it is well known that the coupling constant due to the protonated proton in the H—C—N$\cdots$H$^+$ system is small in the range of 5–6 Hz.[16–18,20] Therefore, this coupling phenomenon related to protonation cannot explain the AB quartet shown in the ^{1}H-NMR spectrum of the Methyl-dimer in deuterated acetic acid because the coupling constant (14 Hz) for this AB quartet is much higher than that of the H—C—N$\cdots$H$^+$ system.

For this protonated system, Reynolds and Schaefer[20] found that there is a methylene proton asymmetry (J_{AB} = 12.85 Hz at 299K) in *N*-methyldibenzylamine (Benzyl-dimer in this article) along the benzyl–nitrogen bond axis, when the nitrogen atom is strongly protonated by trifluoroacetic acid. This methylene proton asymmetry is similar to the nonequivalence of methylene protons in compounds of the substituted ethane type that was reported by Gutowsky,[21] that is, the structure of protonated amine is very similar to triply substituted ethane (Scheme 3). For the

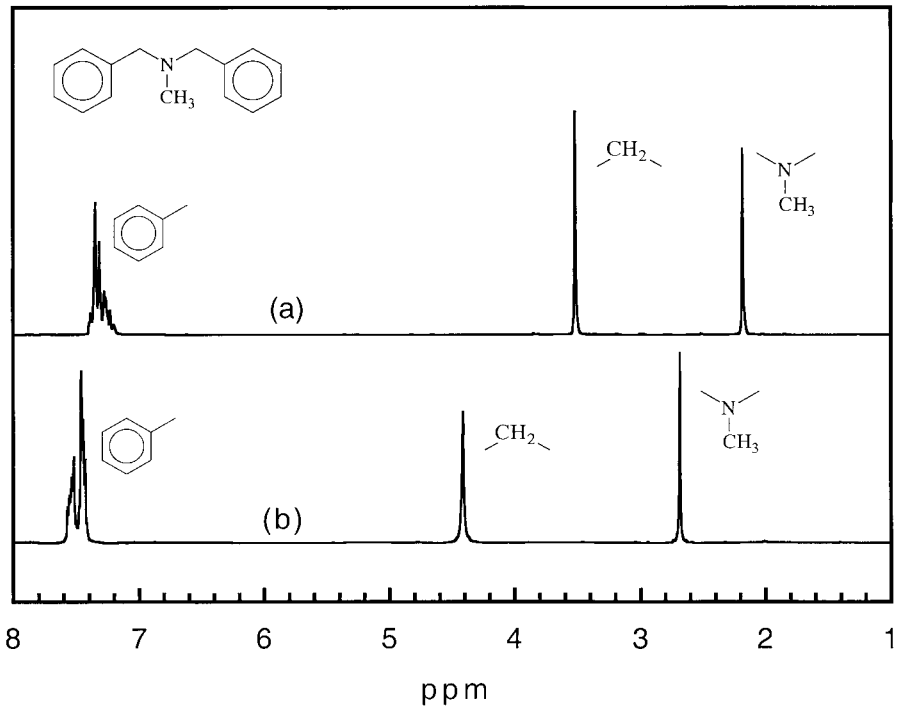


Figure 9 ^{1}H-NMR spectra of Benzyl-dimer in (a) deuterated and (b) deuterated acetic acid.

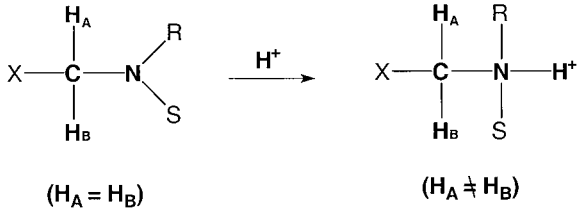
same reason, the methylene protons, which are strongly protonated in the Mannich bridge, are nonequivalent along the C—N bond axis, showing an AB quartet in ^{1}H-NMR.

In our experiments with the Benzyl-dimer, even though the chemical shift for methylene protons is shifted downfield due to the protonation of nitrogen atom by acetic acid, the proton-exchange rate between acetic acid and the Benzyl-dimer is not slowed to the extent of showing a chemical shift splitting for the methylene protons. However, because the methylene protons in the Benzyl-dimer are not split with the change of solvents, the splitting of the Methyl-dimer cannot be attributed to simple salt formation. Another mechanism may be present in the case of the

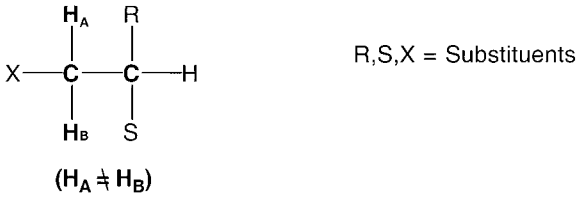
Table II Changes of Chemical Shifts of Dimers in Different Deuterated Solvents

		δ_{CDC13}	$\delta_{CD3COOD}$	$\Delta(\delta_{CD3COOD} - \delta_{CDC13})$
Methyl-dimer	N—CH_3	2.24	2.81	0.57
	—CH_2—	3.66	4.13–4.53	0.47–0.87
	Ph—CH_3	2.22	2.24	0.02
	Ph—H	6.73, 6.89	6.91, 7.00	0.11, 0.18
Benzyl-dimer	N—CH_3	2.19	2.69	0.50
	—CH_2—	3.51	4.43	0.92
	Ph—CH_3	—	—	—
	Ph—H	7.17–7.40	7.41–7.59	0.24–0.19
Aniline-dimer	N—CH_3	—	—	—
	—CH_2—	4.26	4.69	0.43
	Ph—CH_3	2.16, 2.17	2.10, 2.21	−0.06–0.04
	Ph—H	6.65, 6.82, 7.00–7.31	6.68, 6.86, 7.21–7.49	0.03–0.18

a. Protonated amine



b. Triply substituted ethane

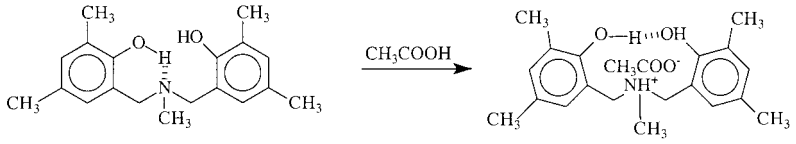


Scheme 3 Comparison between protonated amine and triply substituted ethane.

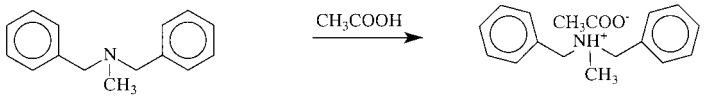
Methyl-dimer. Since strong intramolecular hydrogen bonding can be formed between the hydroxyl groups in the Methyl-dimer,[22], a steric hindrance to rotation of the molecule along the C—N bond axis may result, showing additional topological nonequivalence of the methylene protons and chemical-shift differences. Thus, we propose that this stable hydrogen bonding interferes with the movement of the molecules, making the proton-exchange rate slower to the extent of showing coupling to the geminal methylene protons. Based on the above results for dimers, a number of possible interactions between the model dimer and acetic acid are proposed in Scheme 4.

A similar experiment was carried out with the Aniline-dimer. Interestingly, as shown in Figure 10 and Table II, neither the significant chemical-shift difference nor the coupling for the methylene group is shown, despite the presence of the hydroxyl group. This means that very weak salt formation takes place between them, resulting in a rapid proton exchange because the proton-ex-

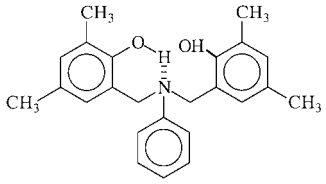
a. Methyl-dimer



b. Benzyl-dimer



c. Aniline-dimer



Scheme 4 Proposed interaction mechanism between model dimers and carboxylic acid.

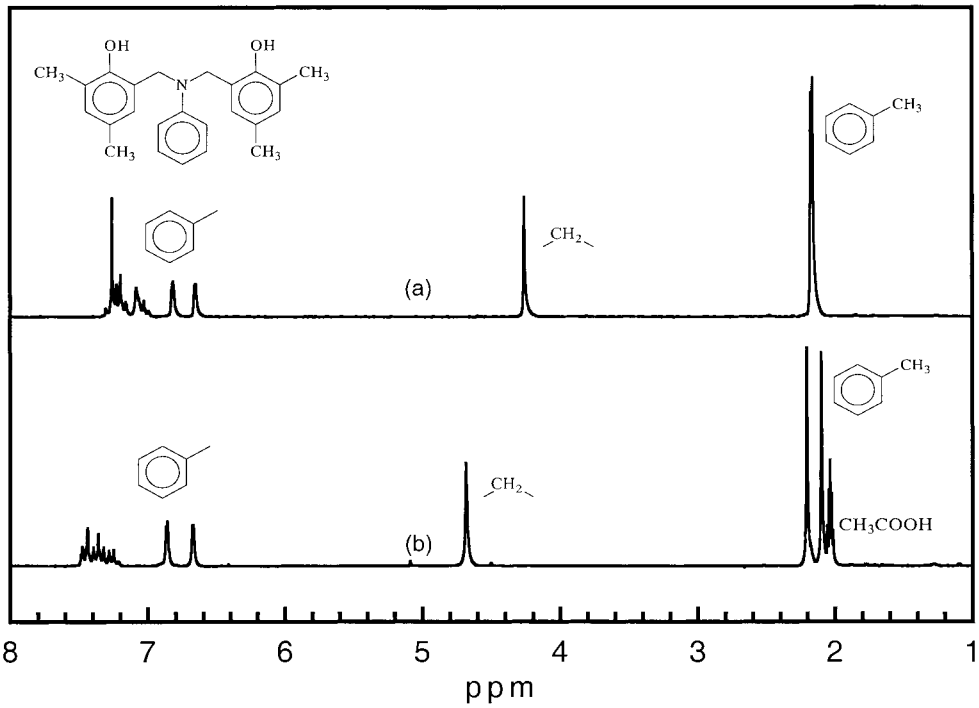


Figure 10 [1]H-NMR spectra of Aniline-dimer in (a) deuterated chloroform and (b) deuterated acetic acid.

change rate is increased with an increasing acid strength of the amino group.[22]

To examine the chemical stability of the Mannich bridge in acetic acid, NMR spectra of the Methyl-dimer were taken in a mixed solvent of deuterated acetic acid (50% wt) and deuterium oxide (50% wt) as a function of time at room temperature, the results of which are shown in Figure 11. Even after 60 days, no changes in the NMR spectrum were observed. Furthermore, this result is consistent with the result of size-exclusion chromatography which suggests that there exists only one kind of molecule after 60 days of acid treatment (Fig. 12). From the NMR study of the model dimers in deuterated acetic acid, it is concluded that the Mannich bridge is considerably stable in carboxylic acid, even at a high acid concentration.

Contrary to the stability of the Methyl-dimer in acetic acid, the corresponding polymer was physically disintegrated during the same time period. We can find clues as to the nature of this behavior by examining the network structure of polybenzoxazines. It has been reported that hydrogen bonding, both an intermolecular interaction and an intramolecular interaction between hydroxyl groups and nitrogen, exists and shows broad bands between 3600 and 2500 cm^{-1} in the FTIR spectra.[3] Dunkers et al.[22] reported, using the study of a model dimer, that an ordinary —OH· · ·O intermolecular hydrogen bonding band falls at 3380 cm^{-1} while an —OH· · ·O intramolecular hydrogen bonding results in a very broad band below 3460 cm^{-1}. In addition, they also observed that a broad—OH· · ·N intramolecular hydrogen bonding is shown around

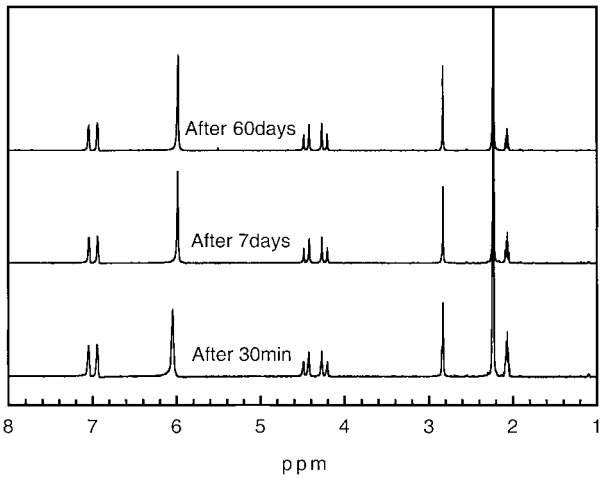


Figure 11 [1]H-NMR spectra of Methyl-dimer in the deuterated acetic acid and the deuterium oxide (50:50).

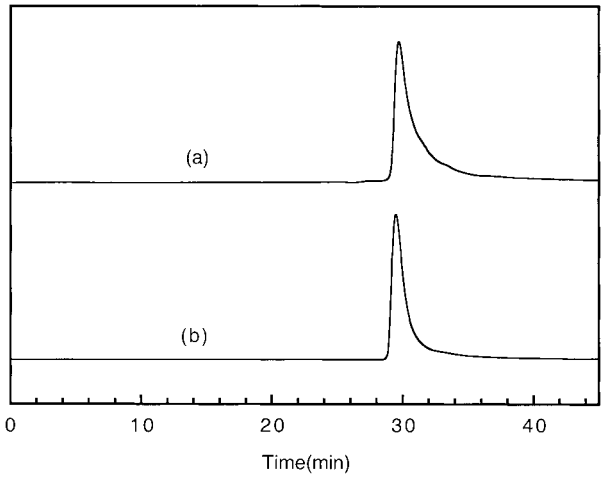


Figure 12 SEC chromatographs of (a) the purified Methyl-dimer and (b) the Methyl-dimer treated with acetic acid (50 wt %) for 60 days.

2700 cm^{-1} and a relatively free —OH group gives rise to a band at 3615 cm^{-1}. Ishida and Allen[1] reported that polybenzoxazines have high glass transition and strong mechanical properties despite their unexpectedly low crosslinking density compared to typical epoxies. They explained that this result is attributed to the network structure of polybenzoxazine, which is supported by strong hydrogen bonding in addition to chemical crosslinking.

However, as is shown in Figure 13, the nature of hydrogen bonding in the BA-a polymer is quite different from that of the BA-m polymer. A prominent band of a weakly hydrogen-bonded —OH group at 3550 cm^{-1} can be seen in the BA-a polymer along with a second band due to intermolecular hydrogen bonding. The former band is absent in the BA-m polymer and the latter is significantly smaller in size. These differences are explained by the fact that the strength of hydrogen bonding is dependent on the electronegativity of the side group that is attached to the nitrogen atom. In the case of the BA-a polymer, although the phenyl group has an electron-donating nature, the electron cloud density around the nitrogen atom attached to the benzene ring is lower than that of the BA-m polymer because the electrons on the nitrogen atom are more delocalized. This is a well-known explanation for the large difference in the basicity between the aliphatic and aromatic amines (Table III). Therefore, the —OH group in the BA-a polymer forms —OH· · ·O intramolecular hydrogen bonding or intermolecular hydrogen bonding with the other —OH groups in competition with —OH· · ·N intramolecular hydrogen bonding, whereas the BA-m polymer is dominated by the intramolecular hydrogen bonding between the OH groups and the nitrogen atom.

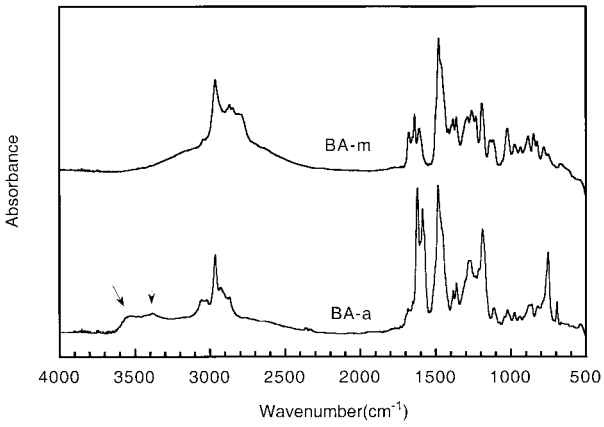


Figure 13 Comparison of the FTIR spectra between BA-m and BA-a polybenzoxazine.

Table III Dissociation Constants (K_b) of Amines[23]

	K_b
Methylamine	4.5×10^{-4}
Aniline	4.2×10^{-10}

From the results of the FTIR study on hydrogen bonding in polybenzoxazines, the differences in the network structures of polybenzoxazines can be proposed. The differences in the hydrogen-bonded structure indicate that the network structure of the BA-m polymer is supported mainly by the intramolecular hydrogen bonding rather than by the intermolecular hydrogen bonding. This intramolecular hydrogen bonding can disrupt the network formation because it makes the molecules curl[3] and sterically hinders chemically bonded crosslinking.[1] On the other hand, the relatively small amount of the hydroxyl group in the BA-a polymer participates in intramolecular hydrogen bonding. As a result, polybenzoxazine chains of BA-a can remain in a more extended state rather than curled. Moreover, interchain interaction should be stronger. Therefore, the BA-a polymer likely has more chances to form chemically bonded crosslinked structures because the carbon atoms at the *o*-position of phenolic group,

Table IV Comparison of Crosslink Density of BA-a and BA-m Polymer and Density Changes from the Monomer to the Corresponding Polymer

	Crosslink Density[1] ($\times 10^3$ mol/cm^3)	Density[3] (g/cm^3)	
		Monomer	Polymer
BA-a	1.1	1.200	1.195
BA-m	<1.1	1.159	1.122

the main reactive crosslinking site of polybenzoxazines, can more easily react with the other reactive chain ends during polymerization. Furthermore, it was reported by Low and Ishida[24] and Ishida and Sanders[25] that BA-a polybenzoxazine may have additional crosslinking reactions at the *o*- and *p*-positions of the aniline functional group as well as at the *o*-position of phenol. These aspects can also be supported by the fact that the crosslinking density of the BA-a polymer is higher and the volumetric change after polymerization of BA-a is much smaller than that of BA-m (Table IV).

Obviously, these differences in the nature of the network structure are closely related to the chemical resistance of polybenzoxazines. From the result of the model dimer study, several possibilities can be proposed to help explain the stability of the polybenzoxazine network structure. First, since the BA-m polymer chains are highly curled, due to the strong intramolecular hydrogen bonding during ring-opening polymerization, the network structure of the BA-m polybenzoxazine might be formed less tightly than that of the BA-a polybenzoxazine. Furthermore, strong salt formation may exist between the carboxylic acid and the nitrogen atom in the Mannich bridge of the BA-m polybenzoxazine. This affinity of the Mannich bridge for carboxylic acid in the BA-m polymer makes the carboxylic acid molecules penetrate into the network structure more easily by osmotic pressure, resulting in well-known macroscopic stress cracking by solvents.[7,26] However, it is difficult to strongly protonate the tertiary nitrogen of the Mannich bridge of BA-a due to the electronegativity difference from the methyl counterpart. Also, since the network structure of the BA-a polymer may have more chemically crosslinked sites due to the active reaction sites of aniline, the entangled and crosslinked network structure of the BA-a polymer is hardly affected by carboxylic acid. Therefore, the polybenzoxazine from BA-a can more effectively resist the carboxylic acid environment than can the BA-m counterpart.

CONCLUSIONS

The chemical stability of typical polybenzoxazines based on bisphenol-A and primary amines was investigated in an acid medium. While the BA-a polymer was very stable in carboxylic acids, the BA-m polymer rapidly disintegrated to a small fragmented powder form and the reference epoxy also showed a sign of swelling. Using the proton nuclear magnetic resonance spectroscopy results of the polybenzoxazine model dimers, it is found that the Mannich base is stable in a carboxylic acid solution. It is shown that strong salt formation takes place between the carboxylic acid and the Mannich base in the BA-m model dimer while the BA-a model dimer has a weak interaction with carboxylic acid. The possible interaction of carboxylic acid with model dimers has been proposed. From the results of the model dimers and the study of hydrogen bonding in polybenzoxazines, it is also proposed that the rapid disintegration of BA-m polybenzoxazine in carboxylic acid is attributed to macroscopic stress cracking and that the origin for the chemical stability of polybenzoxazines is highly related to the nature of the primary amines and the hydrogen-bonded network structure.

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