

Development of Low-Viscosity Benzoxazine Resins and Their Polymers

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ABSTRACT: With unsubstituted phenol, formaldehyde, and primary aromatic amines as the starting materials, a series of monofunctional benzoxazine resins with low viscosities at room temperature were developed. The polymerization behavior of these resins into thermosetting materials was monitored by differential scanning calorimetry. Stress

relaxation of the obtained polybenzoxazines revealed these polymers to be chemically crosslinked networks. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2953–2966, 2002

Key words: thermosets; resins; viscosity

INTRODUCTION

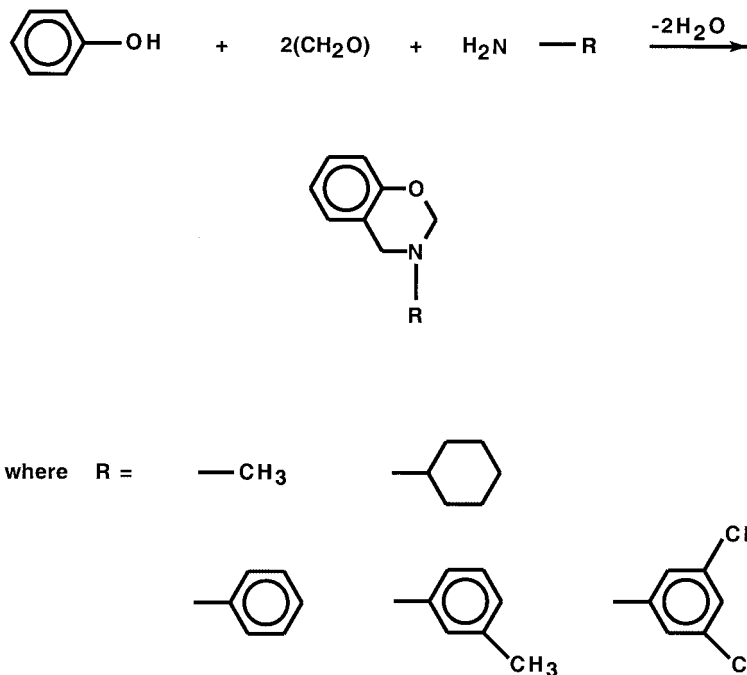
In phenolic chemistry, both the ortho and para positions on the benzene ring are reactive toward electrophilic substitution reactions due to the directing effect of the hydroxyl group.¹ This general knowledge has long been used in various phenol-related reactions. 1,3-Benzoxazines, a class of heteroatomic ring compounds derived from various phenols, formaldehyde, and primary amines, are also deemed to show multiple reactivities of the benzene ring due to the directing effect of both the alkoxy and the alkyl groups connected to the benzene ring. The free ortho position on a benzoxazine benzene ring has long been reported to have high reactivity toward thermal and phenol-initiated ring-opening polymerizations, forming a phenolic Mannich base polymer structure.^{2–5} Furthermore, the free para position has also shown reactivity toward a similar type of polymerization.^{3,6} Even the meta positions are reactive under severe curing conditions, albeit with much less reactivity.^{5,7,8} A systematic study of the regioselectivity of the benzoxazine benzene ring revealed quantitatively that both the free ortho and the para positions of the aromatic amine-based benzoxazine benzene ring showed high reactivities toward thermal polymerization, possibly resulting in a crosslinked structure.⁹ This result, as described later, opened a new insight into the thermosetting benzoxazine field.

In recent years, thermosetting polybenzoxazines derived from substituted 1,3-benzoxazines, hereafter called benzoxazines, have been actively studied because of their excellent physical and mechanical properties and high thermal stability.^{10–13} To obtain high-performance polybenzoxazines, it is almost always necessary to utilize benzoxazine monomers derived from difunctional phenols, except those made from functionalized amines. To date, no pure sense of monofunctional (mono-oxazine-ring-containing) benzoxazine-based high-performance thermosetting polybenzoxazine has been reported, although a few works concerning the monofunctional benzoxazine derivatives that contain an additional nonoxazine functionality have been studied.^{12,14} Compared to phenolic resins, benzoxazine resins generally show a substantially lower melt viscosity, which is favorable from a processing point of view. By design of the phenolic and primary amine moieties, difunctional benzoxazine resins with significantly lower melt viscosities have been achieved;¹⁴ however, they are all still solid at room temperature. Thus, benzoxazines that are liquid at room temperature and can potentially be developed into high-performance polybenzoxazines are of interest for some applications, such as coatings and highly filled compounds. In previous research on polybenzoxazine composites for electronic packaging applications, the addition of a low-viscosity reactive diluent other than the solid benzoxazine matrix was helpful to balance the steep increase of the viscosity as the filler loading was increased.¹⁵ With considerable molecular mobility, liquid benzoxazines can possibly be polymerized faster than their solid counterparts with the help of appropriate initiators/catalysts.

It was reported that the key factors affecting the viscosity of a difunctional benzoxazine resin are the

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Scheme 1 Monomer synthesis.

bulky diphenol part between two oxazine rings and the pendent amine groups.¹⁴ An intuitive approach to reducing the resin viscosity yet maintaining compara-

ble polymer properties is to replace the biphenol moiety with unsubstituted phenol, whose reactive ortho and para positions can satisfy the multifunctionality requirement for the formation of a thermosetting material. Indeed, liquid monofunctional benzoxazine monomers based on unsubstituted phenol and primary aliphatic amines were reported.² However, no intentional attempt was conducted to obtain high-performance thermosetting polymers from these monomers. Indeed, the polymerization behavior of these monomers has hardly been reported. Based on the knowledge of difunctional benzoxazines, aromatic amine-based polybenzoxazines have exhibited better properties than their aliphatic amine counterparts.^{10,16} Therefore, the objective of this study was to develop monofunctional benzoxazine resins based on unsubstituted phenol and primary aromatic amines that were liquid at room temperature. The polymerization behavior of these resins and the properties of the resulting thermosetting polymers will subsequently be studied.

TABLE I
¹³C Assignments for the Two New Aromatic
Amine-Based Benzoxazines

Carbon	Ph-mt	Ph-35x
a	154.2	154.3
b	120.9	121.0
c	127.7	127.6
d	120.6	120.6
e	126.6	126.6
f	116.8	116.8
g	79.2	79.2
h	50.2	50.2
i	148.2	148.2
j	115.0	115.8
k	128.9	138.7
l	122.1	123.1
m	138.9	138.7
n	118.7	115.8
o	21.5	21.5
p		21.5

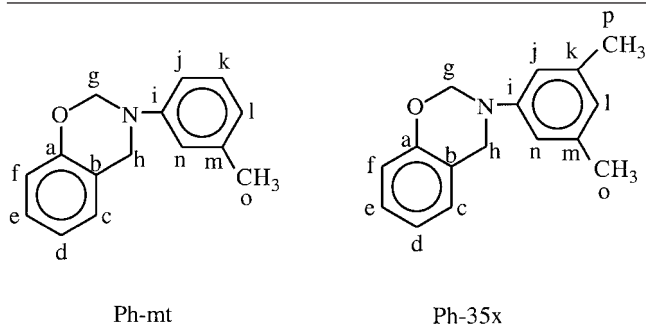


TABLE II
Monomer Viscosity by Shear Viscosity Measurement

Monomer	Viscosity (Pas)
Ph-m	5.6 ^a
Ph-cyha	1.0 ^b
Ph-a	4.6 ^b
Ph-mt	15 ^b
Ph-35x	43 ^b

^a -40°C.

^b Room temperature.

TABLE III
Relationship Between the Viscosity of Partially Cured Ph-a Resins and Their Benzoxazine Ring Contents

Benzoxazine ring content (%)	Viscosity (Pa s)
95	4.7 ^a
77	8.3 ^a
70	88 ^a
67	250 ^a
61	800 ^a
52	5.6 ^b
30	17.5 ^c

^a Room temperature.

^b 50°C.

^c 100°C.

EXPERIMENTAL

Materials

Except for the 37 wt% formalin (Fisher Scientific, Pittsburgh, PA), all the chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI). The phenol used in all monomer syntheses was of 99% purity. Paraformaldehyde used in the solventless method was of 95% purity. The amines were methylamine (40 wt % in water), cyclohexylamine (99%), aniline (99%),

m-toluidene (99%), and 3,5-xylidene (98%). All chemicals were used as received.

Monomer synthesis

The phenol–methyl amine-based monomer was synthesized by a solvent procedure.¹⁷ All the other monomers were synthesized by the solventless method,¹⁸ as shown in Scheme 1. An example of the phenol–aniline-based benzoxazine synthesis is as follows. Phenol, paraformaldehyde, and aniline at a molar ratio of 1:2:1 were mixed at room temperature in a 400-mL beaker, which was immediately immersed into an oil bath equilibrated at 100–120°C with magnetic stirring. The materials were reacted for approximately 20 min after equilibrium was reached. We then dissolved the resulting yellow liquid in ethyl ether and washed it in a separatory funnel with 2*N* NaOH solution several times until the aqueous base layer was colorless after the shaking to remove possible unreacted material or oligomeric phenolic species. The ether solution was then rinsed with deionized water until it reached a pH of 7, and then it was dried over sodium sulfate overnight. The ether was then removed with a rotary evaporator. The resulting light yellowish product was a

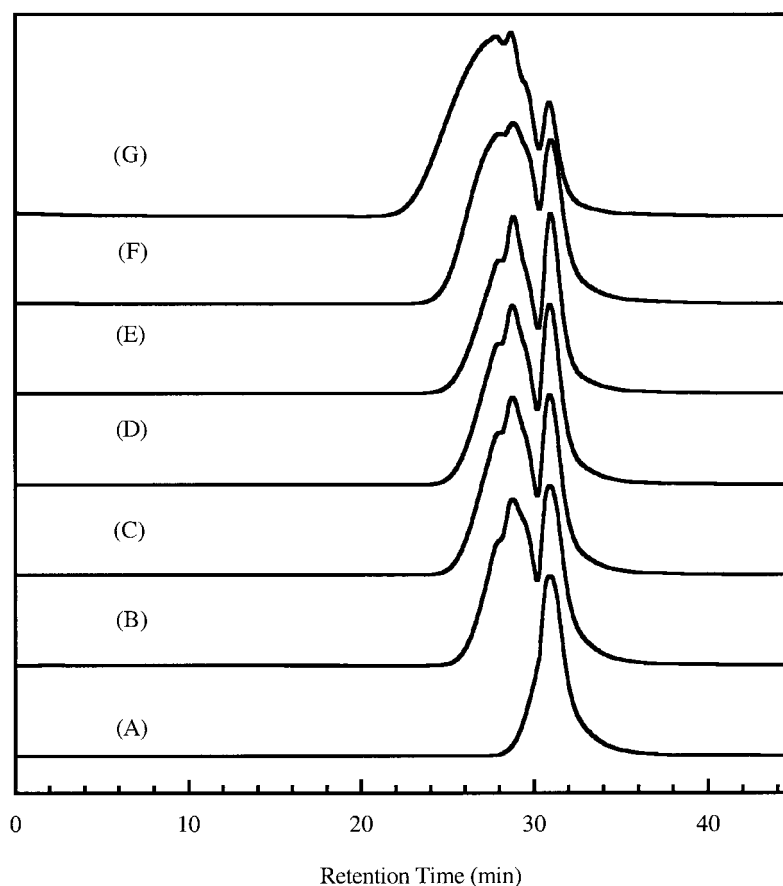


Figure 1 SEC chromatograms of Ph-a resins with different viscosities at (A) 4.7 Pa s, (B) 8.3 Pa s, (C) 88 Pa s, (D) 250 Pa s, (E) 800 Pa s at room temperature, (F) 5.6 Pa s at 50°C, and (G) 17.5 Pa s at 100°C.

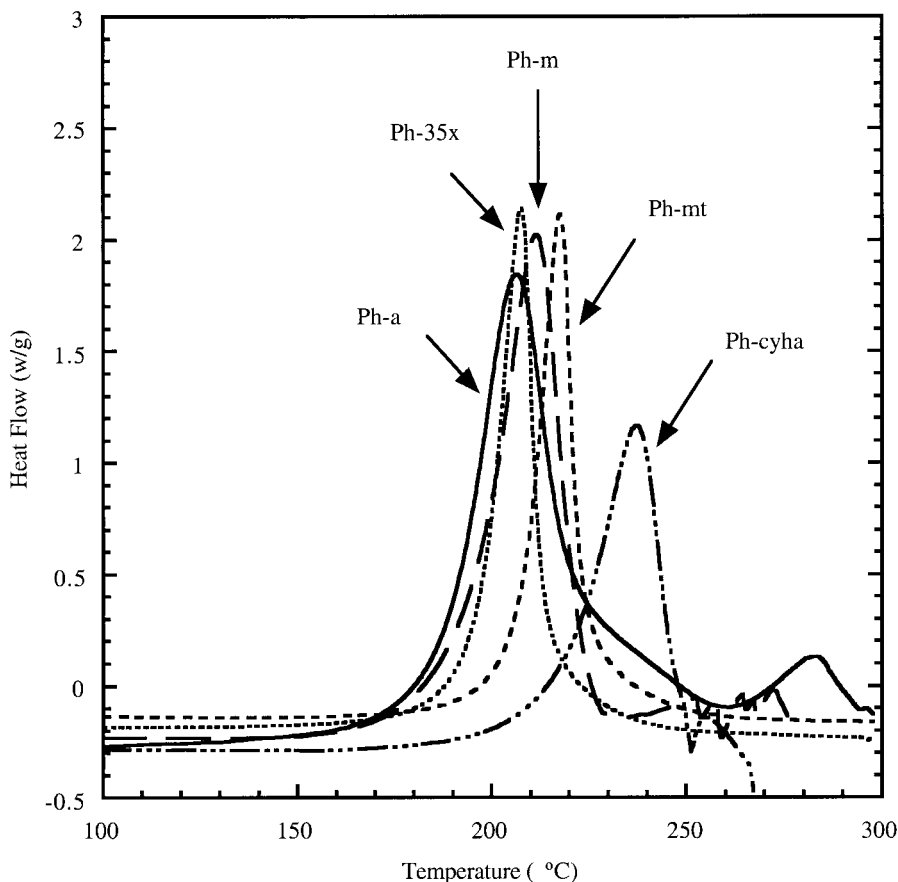


Figure 2 Nonisothermal DSC curing profiles of the five phenol-based monomers (ramp rate = 10°C/min).

liquid at room temperature and was further dried in a vacuum oven at 40°C for 2 h to remove residual solvent from the purification. The molecular structure and purity of all the monomers were verified by NMR. Monomers derived from methyl amine, cyclohexylamine, aniline, *m*-toluidene, and 3,5-xylylene, whose IUPAC names are 3,4-dihydro-3-methyl-2H-1,3-benzoxazine, 3,4-dihydro-3-cyclohexyl-2H-1,3-benzoxazine, 3,4-dihydro-3-phenyl-2H-1,3-benzoxazine, 3,4-dihydro-3-(3-methylphenyl)-2H-1,3-benzoxazine, and 3,4-dihydro-3-(3,5-dimethylphenyl)-2H-1,3-benzoxazine, will be referred to as Ph-m, Ph-cyha, Ph-a, Ph-mt, and Ph-35x herein, respectively. The detailed ¹³C-NMR assignments of the two new aromatic amine-based monofunctional benzoxazines are listed in Table I.

Ph-mt

Ph-mt was a dark brown liquid with a yield of 69% and a purity by gas chromatography/mass spectroscopy of 99.3%.

¹H-NMR (CDCl₃, 200 MHz, 298 K, δ): 2.29 (3H, Ar—CH₃), 4.60 (2H, Ar—CH₂—N), 5.33 (2H, N—CH₂—O), 6.70–7.30 (8H, Ar).

¹³C-NMR (CDCl₃, 200 MHz, 298 K, δ): 21.5 (1C, Ar—C), 50.2 (1C, Ar—C—N), 79.2 (1C, O—C—N), 115.1 (1C, Ar), 116.8 (1C, Ar), 118.7 (1C, Ar), 120.6 (1C, Ar), 120.9 (1C, Ar), 122.1 (1C, Ar), 126.6 (1C, Ar), 127.7 (1C, Ar), 128.9 (1C, Ar), 138.9 (1C, Ar), 148.2 (1C, Ar), 154.2 (1C, Ar).

Fourier transform infrared (FTIR; KBr) ν (cm⁻¹): 776 and 693 (*meta*-substituted benzene), 1033 (C—C str. aromatic

TABLE IV
Calorimetric Data of the Polymerization Reaction

	Ph-m	Ph-cyha	Ph-a	Ph-mt	Ph-35x
Exothermic peak (°C)	212	237	206	217	207
Heat of reaction (J/g)	285	214	381	333	353
T _g (°C) by second DSC run	192 ^a	225 ^a	142	122	130

^a Possibly from bisphenolic methylene structure.

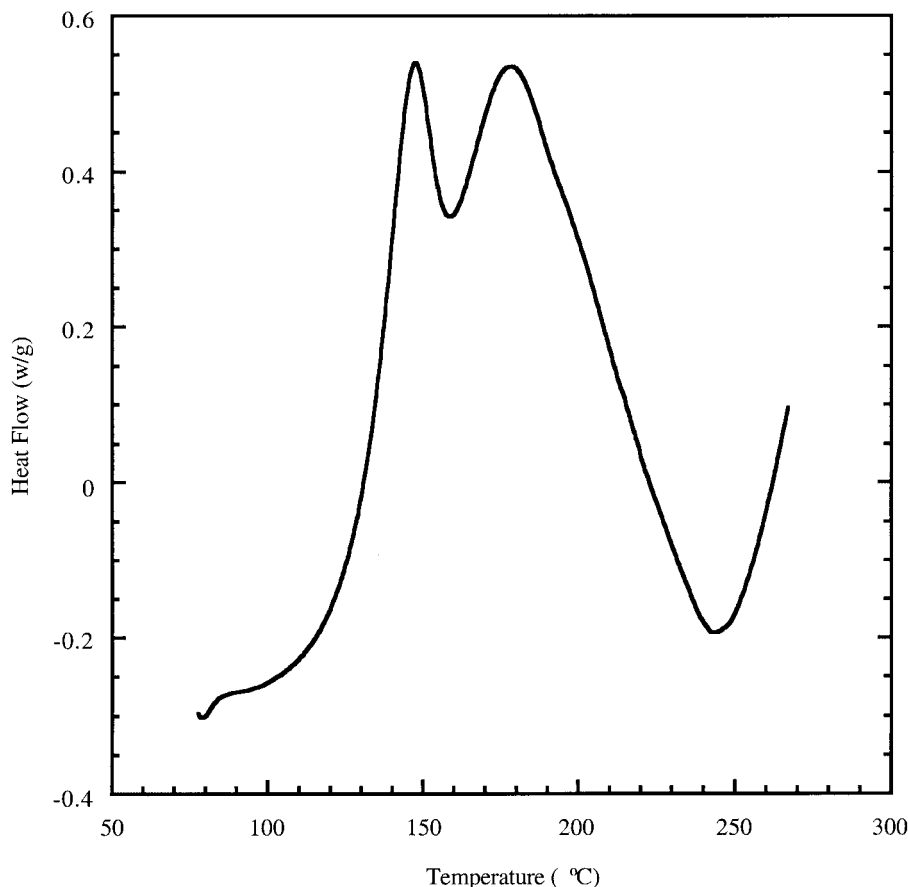


Figure 3 Nonisothermal DSC thermogram of Ph-a/5 wt % MeOTs (ramp rate = 10°C/min).

ether), 1225 (cm^{-1}) (Ar—O—C asym. str. aromatic C—O), 944 (oxazine ring).

Ph-35x

Ph-35x was a light yellow liquid with a yield of 77% and a purity by GC/MS of 99.7%.

$^1\text{H-NMR}$ (CDCl_3 , 200 MHz, 298 K, δ): 2.25 (6H, Ar— CH_3), 4.59 (2H, Ar— CH_2 —N), 5.32 (2H, N— CH_2 —O), 6.55–7.15 (7H, Ar).

$^{13}\text{C-NMR}$ (CDCl_3 , 200 MHz, 298 K, δ): 21.5 (2C, Ar—C), 50.2 (1C, Ar—C—N), 79.2 (1C, O—C—N), 115.8 (2C, Ar), 116.8 (1C, Ar), 120.6 (1C, Ar), 121.0 (1C, Ar), 123.1 (1C, Ar), 126.6 (1C, Ar), 127.6 (1C, Ar), 138.7 (2C, Ar), 148.2 (1C, Ar), 154.3 (1C, Ar).

FTIR (KBr) $\nu(\text{cm}^{-1})$: 835 and 696 (1,3,5-trisubstituted benzene), 1035 (C—C str. aromatic ether), 1226 (Ar—O—C asym. str. aromatic C—O), 945 (oxazine ring).

Instrumentation

The structure and purity of the monomers were identified via $^1\text{H-NMR}$ spectroscopy. The NMR was performed on a 200-MHz Gemini $^1\text{H-NMR}$ spectrometer. Deuterated chloroform was used as a solvent with tetramethylsilane as an internal standard.

Molecular weight (MW) was measured by size exclusion chromatography (SEC) with a Waters 510 high performance liquid chromatography pump with a U6K injector and Waters 484 tunable absorbance and Waters 410 differential refractive index detectors. The columns were Whatman Styragel 50, 10², and 10³-nm columns.

The curing profile of all the monomers were measured by differential scanning calorimetry (DSC) with a TA Instruments 2920 modulated differential scanning calorimeter. The samples were run in hermetic aluminum pans at a heating rate of 10°C/min with a nitrogen purging flow of 80 mL/min. A second run was always performed to check the glass-transition temperature (T_g). The thermal stability of the cured benzoxazines was measured by thermogravimetric analysis (TGA) using a TA Instruments Hi-Res 2950 thermogravimetric analyzer. The temperature was ramped at 20°C/min under a 90 mL/min nitrogen purge.

Steady shear viscosity measurements were performed on a Rheometrics dynamic mechanical spectrometer (RMS-800) with a 200 g cm torque force rebalance transducer. Liquid samples were transferred directly onto a 50-mm parallel plate fixture and

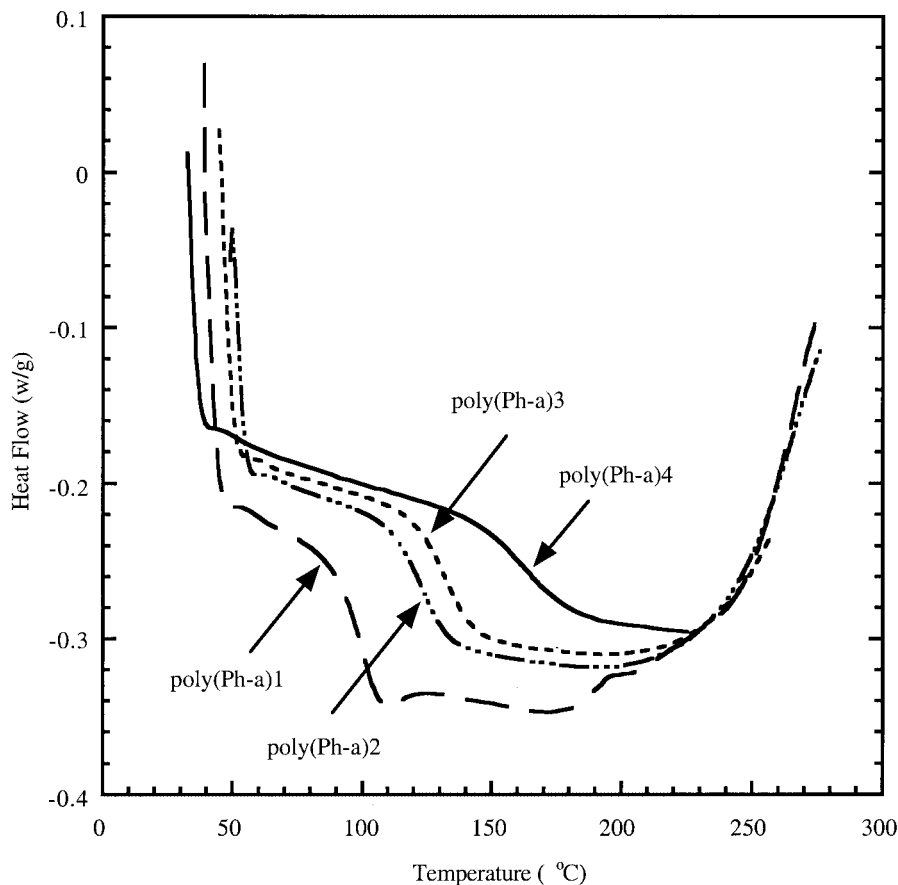


Figure 4 Effect of curing conditions on T_g of poly(Ph-a) (ramp rate = $10^\circ\text{C}/\text{min}$).

set to a gap of approximately 0.5 mm. We prepared void-free solid disks by preheating the solid samples in a room-temperature-vulcanizing silicon rubber mold. Parallel plates with a diameter of 25 mm were used for the solid sample measurements. The temperature for the viscosity measurements was varied accordingly, and the testing steady shear rate was varied from 0.01 to 100 s^{-1} .

TABLE V
Curing Conditions of the Poly(Ph-a)s Investigated
in the Thermal Properties Section

	Curing conditions
Poly(Ph-a)1	60°C , 1 h
	180°C , 40 min
	160°C , 1 h
Poly(Ph-a)2	180°C , 40 min
	200°C , 15 min
	160°C , 1 h
Poly(Ph-a)3	180°C , 40 min
	220°C , 15 min
	160°C , 1 h
Poly(Ph-a)4	180°C , 40 min
	240°C , 15 min

Dynamic mechanical spectra of the polymer samples were obtained on the same RMS-800 spectrometer with a 2000 g-cm torque force rebalance transducer. Specimens approximately $50 \times 12 \times 3$ mm in dimension were tested in a rectangular torsion fixture. A 0.1% strain was applied sinusoidally after a strain sweep was conducted to ensure that the applied strain was within the linear viscoelastic limit. The test frequency was 6.28 rad/s (1 Hz), and the temperature was increased from 25°C into the rubbery plateau region of each material.

Stress relaxation experiments were performed immediately after the temperature sweep experiments. After the temperature equilibrated at 50 , 100 , and 150°C above T_g , a 0.2% strain was applied, and the relaxation of the shear modulus was monitored for 700 s.

The room-temperature density of poly(Ph-a) and methyl *p*-toluenesulfonate (MeOTs)-initiated poly(Ph-a) was measured via gas pycnometry with a Quantachrome ultrapycnometer 1000. Helium was used as a carrying gas at 27.2°C . The samples were placed in a calibrated small sample cup with 20 measurements recorded for each sample.

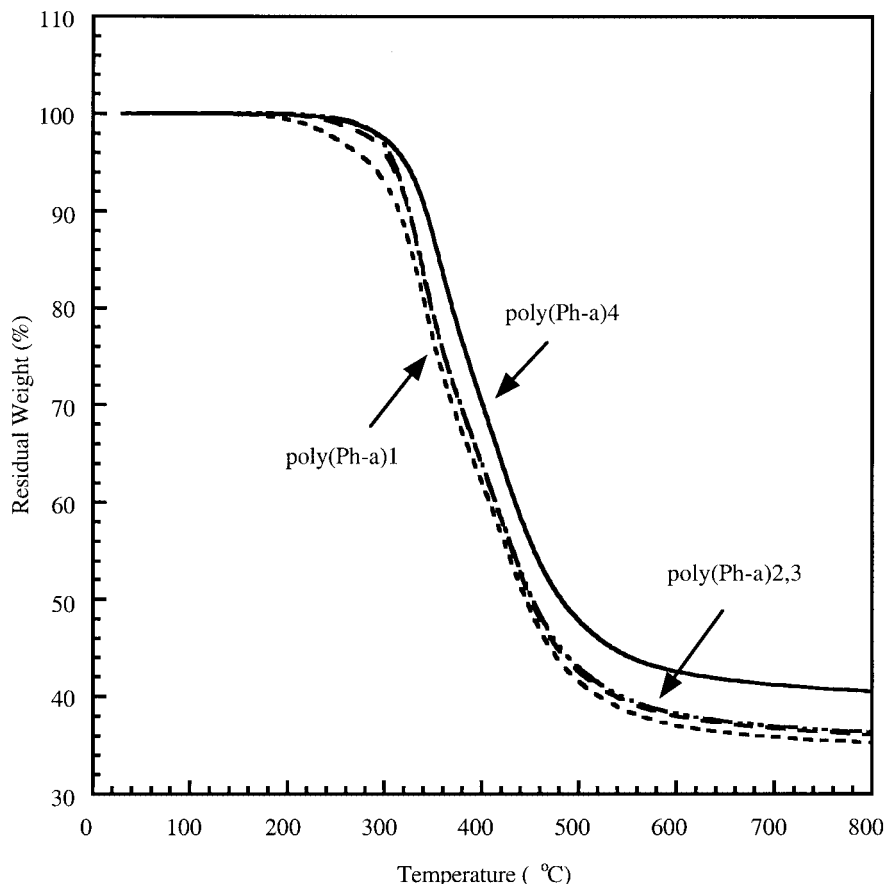


Figure 5 TGA thermograms of poly(Ph-a) (ramp rate = 20°C/min).

RESULTS AND DISCUSSION

Viscosity study

All the synthesized monofunctional benzoxazines were liquids at room temperature. This agrees with the conclusion made from the difunctional benzoxazine monomer study that viscosity is strongly affected by the size of the phenolic central linkage unit.¹⁴ Ph-a has a room-temperature viscosity of approximately 4.6 Pas; however, its difunctional counterpart stays as a solid at room temperature with a melt viscosity of 5.5 Pas at 100°C.¹⁵ The viscosities of these monomers are tabulated in Table II. In the case of the Ph-m monomer, due to its extremely low viscosity at room temperature, the data was obtained at -40°C. The effect of the amine pendent group in the benzoxazine molecule on the shear viscosity is shown in Table II. Generally, the tested aliphatic amine-based benzoxazines showed lower viscosities than the aromatic amine-based counterparts. Ph-m showed a viscosity of 5.6 Pas at -40°C, and Ph-cyha showed a viscosity of approximately 1 Pas at room temperature, whereas Ph-a, Ph-mt, and Ph-35x had viscosities of 4.6, 15, and 43 Pas at room temperature, respectively. In the same aliphatic or aromatic category, the larger the

size of the amine moiety was, the higher the viscosity of the benzoxazine monomer was.

In a patent by Harmon and Meigs in 1936,¹⁹ a similar stoichiometric starting material composition as those used in this paper to make aliphatic amine-containing benzoxazine monomers were reported, which aimed at making acid-soluble, heat hardening solid resins; however, the benzoxazine structure was not known at that time. To differentiate their resins with the benzoxazine resins under investigation, we selectively conducted experiments following their reported procedures. The phenol-formaldehyde-methyl amine-based resin according to their experimental procedure was a white solid at room temperature with a melt viscosity of 3.5×10^4 Pas at 100°C. NMR analysis of this resin revealed 7–11% benzoxazine ring content and 74% oligomeric material content, to which the solid nature of this resin at room temperature may be attributed. The phenol-formaldehyde-cyclohexylamine-based resin was a light yellow solid at room temperature with a melt viscosity of 6.8 Pas at 100°C. The composition of this resin was determined by NMR to be 20–30% benzoxazine ring content and 47% oligomeric species.

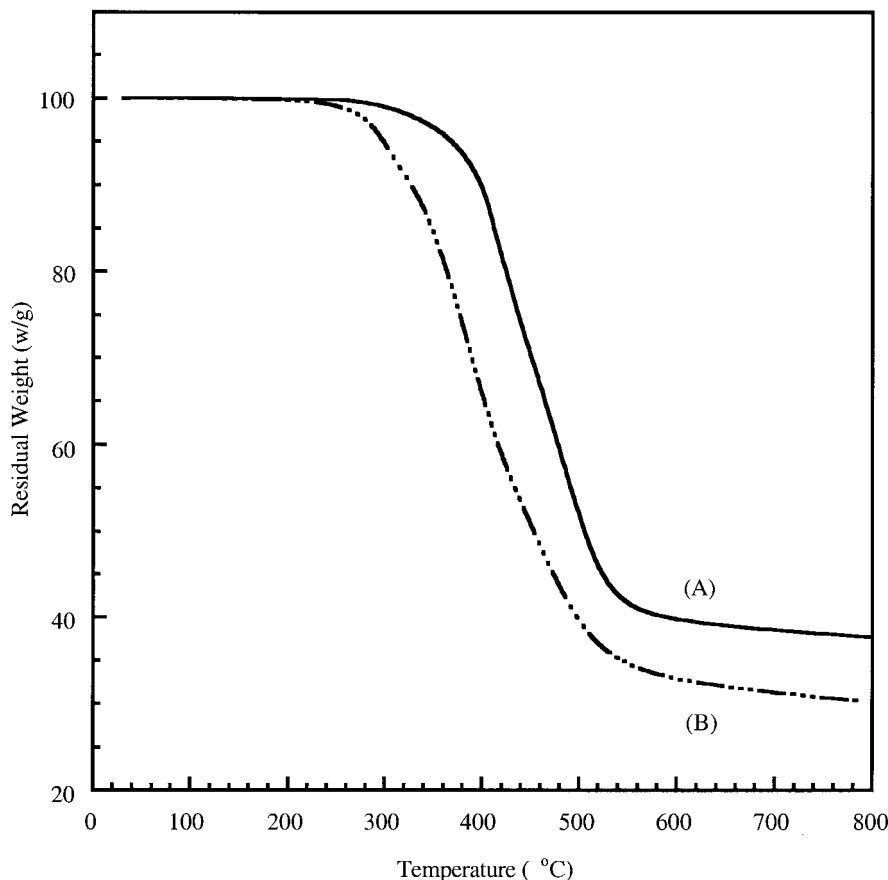


Figure 6 Comparison of the TGA thermograms of (A) poly(Ph-a) and (B) its difunctional counterpart, poly(BA-a) (ramp rate = 20°C/min).

In light of the previous analysis, we expected that the viscosity of the resin may have been related closely to the benzoxazine ring content and the oligomeric material content in the reaction product. To evaluate this hypothesis, we partially polymerized Ph-a in an oven at 160°C for different time periods. Subsequently, we subjected the partially polymerized samples to NMR analysis to determine the benzoxazine ring content, SEC analysis to monitor the MW, and steady shear measurements to measure the viscosity. The relationships of the benzoxazine ring content and the viscosity are summarized in Table III. The corresponding MW evolution is displayed in Figure 1. As shown the lesser the ring content and the higher the oligomer concentration were, in particular, the larger was the size of the oligomers and the higher was the resin viscosity. With about 52% ring content and 40% pentamer or higher oligomers (determined by a curve-fitting analysis of the SEC data), the viscosity of the Ph-a resin became too high to be easily measured at room temperature; however, the viscosity dropped drastically as the temperature increased. The viscosity of this Ph-a resin composition was about 5.6 Pas at 50°C. With a further decrease in the ring content and an increase in the higher oligomer concentration, the

Ph-a resin became a solid at room temperature. For example, at a ring content of 30% with 66% pentamer or higher oligomers, the melt viscosity rose to 17.5 Pas at 100°C.

Cure study

The polymerization behavior of all the synthesized monofunctional monomers was studied by DSC. The nonisothermal DSC thermograms of these monomers are shown in Figure 2 and summarized in Table IV. Ph-m showed an exothermic peak centered at 212°C, and another aliphatic amine-based Ph-cyha showed a reaction exotherm centered at 237°C. As shown in Figure 2, when the scanning temperature exceeded 250°C, a noisy baseline was observed for these two aliphatic amine-based benzoxazine systems, which may have resulted from the evolution of volatile aliphatic amines from these two cured systems. T_g 's after the first DSC scan to 270°C were 192°C for the cured Ph-m product and 225°C for the cured Ph-cyha product. These unusually high T_g 's for monofunctional benzoxazine-derived polymers may have reflected the formation of bisphenolic methylene linkages in the polymer structure due to the evaporation of aliphatic

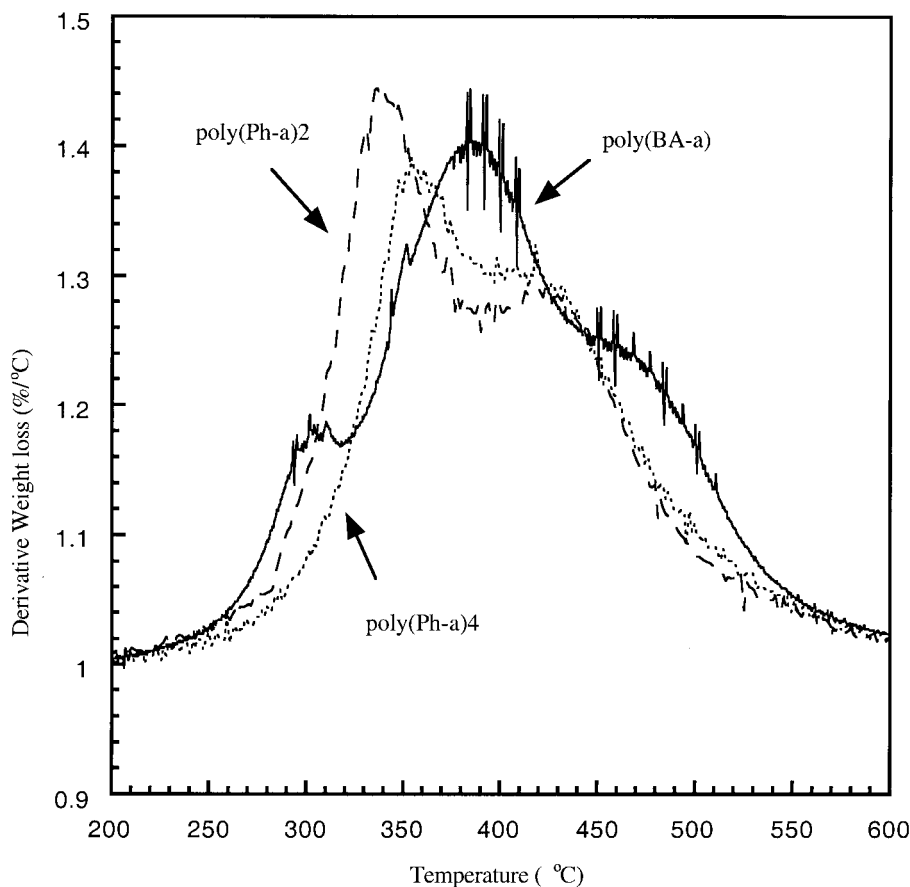


Figure 7 Comparison of the derivative TGA curves of poly(BA-a) and poly(Ph-a)s.

amine moieties. Several works studying the thermal curing mechanism of benzoxazine model compounds have demonstrated this methylene linkage formation during the ring-opening oligomerization.^{7,20,21} For the aromatic amine-based monomers, Ph-a showed a dominant exothermic peak between 150 and 260°C with the peak maximum at 206°C, which corresponded mainly to the thermal initiation and polymerization of the monomers. However, on the completion of the main exotherm, another small exothermic peak appeared in the regions of 260 and 290°C. The origin of this second peak was not clear at this point. Possibilities included a secondary reaction, later stage crosslinking, and possible degradation. Ph-mt and Ph-35x both showed singular exothermic peaks centered at 217 and 207°C, respectively. This observation differed significantly from that of their difunctional counterparts. DSC study of the difunctional analogs containing these two amines showed a dual-stage polymerization process, which suggested the participation of the aminobenzene rings into the overall polymerization process.²¹ Interestingly, this was not the case for these two monofunctional benzoxazines. T_g 's of these three systems determined by the second DSC scan were 142, 122, and 130°C for the cured Ph-a, Ph-mt, and Ph-35x, respectively.

A study of the difunctional benzoxazine monomers based on aniline showed that by the addition of cationic initiators into the reaction system, the exothermic curing peak measured by nonisothermal DSC measurement could be significantly reduced to a lower temperature.²² The same principle was expected to apply to their monofunctional analogs here. Figure 3 shows the nonisothermal DSC thermogram of Ph-a with 5 wt % MeOTs as a cationic initiator. Multiple polymerization behaviors were observed, with the first peak centered at 146°C and the second peak centered at 178°C. According to our previous study, these two peaks could be attributed to different cationic polymerization mechanisms.²² The T_g of this system was detected at 158°C by the second DSC run.

We removed each of the aforementioned polymer products from nonisothermal DSC cure from the DSC pan after two DSC runs to examine its solubility in tetrahydrofuran (THF), thereby roughly estimating whether or not it had been crosslinked during the DSC cure process.^{22,23} Results showed that other than the cured Ph-cyha, which was partially soluble in THF after 24 h, the other four tested polymers exhibited excellent resistance to prolonged exposure to both cold and hot THF.

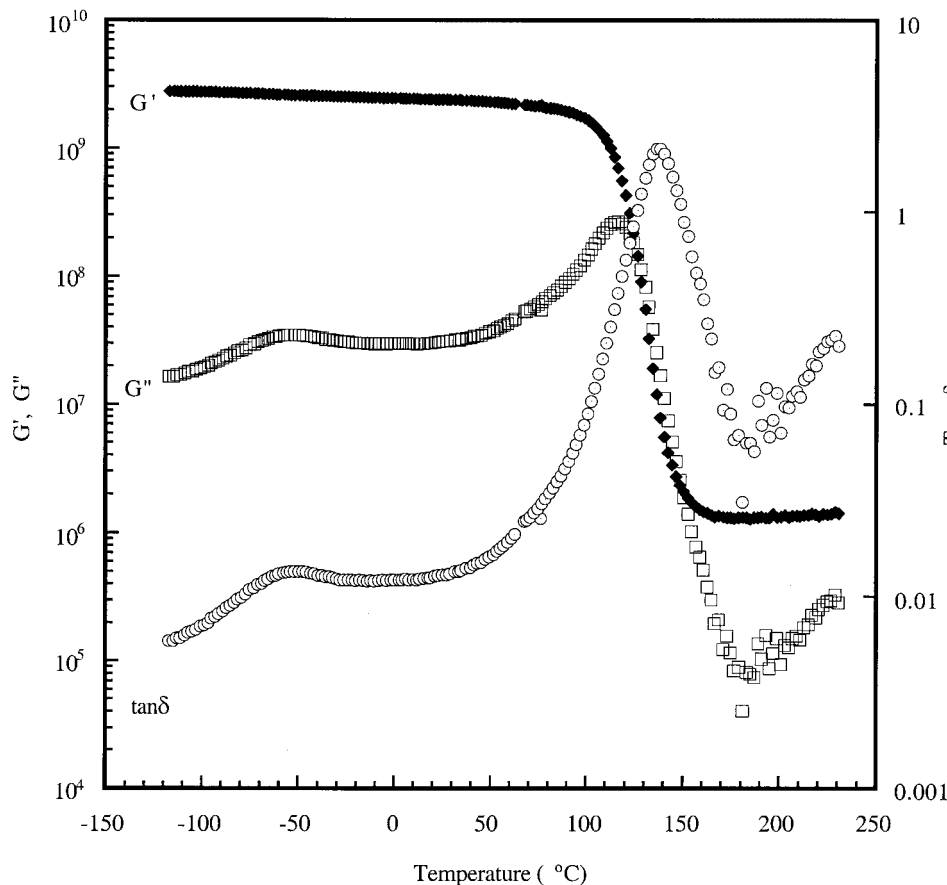


Figure 8 DMA of poly(Ph-a).

Thermal properties

To study the thermal properties of these newly developed materials, we cured Ph-a in an air-circulating oven to test the thermal properties of the resulting product with regard to the different cure conditions. Shown in Figure 4 is the T_g evolution of poly(Ph-a) monitored by DSC as a result of varying polymerization conditions. The curing conditions of these poly(Ph-a)s are listed in Table V. T_g 's determined by DSC were 96, 124, 136, and 165°C for poly(Ph-a)1, poly(Ph-a)2, poly(Ph-a)3, and poly(Ph-a)4, respectively. Residual exothermic peaks were detected in the DSC thermograms of poly(Ph-a)1, poly(Ph-a)2, and poly(Ph-a)3, indicating the incomplete cure of these polymers.

The thermal stability of these poly(Ph-a)s were investigated by TGA, as shown in Figure 5. Other than poly(Ph-a)1, all the poly(Ph-a)s were almost thermally stable up to 300°C, which was approximately 50°C higher than their difunctional counterparts based on bisphenol A. Accordingly, with the increase of the postcure temperature, the char yield of the polymer at 800°C under a nitrogen environment also increased substantially. To better recognize the good thermal stability of poly(Ph-a), we plotted the TGA thermo-

grams of both poly(Ph-a) and poly(BA-a), the difunctional counterpart, in Figure 6. Despite the much less vigorous curing condition for poly(Ph-a)4 than for poly(BA-a),¹⁵ poly(Ph-a) showed an improved thermal stability over the poly(BA-a) material.

To understand the reason why monofunctional poly(Ph-a) had much higher thermal stability than the difunctional poly(BA-a), we plotted the derivative TGA thermograms of these polymers in Figure 7. As shown in the previous study, the derivative curve of poly(BA-a) showed three well-resolved degradation events centered around 300, 390, and 470°C. The origin of these events were stated elsewhere.²⁴ Interestingly, only two well-resolved degradation peaks could be observed from the derivative curves of the poly(Ph-a)s. Increasing the postcure from poly(Ph-a)2 to poly(Ph-a)4 only affected the position of the first degradation event, which shifted from 340 to 360°C, whereas the second degradation process centered around 430°C was untouched. This could be explained by the fact that there was no isopropyl moiety in the monofunctional-based polybenzoxazines. Ultraviolet degradation studies of the bisphenol-A-based polybenzoxazines revealed that it was the isopropyl linkages in the

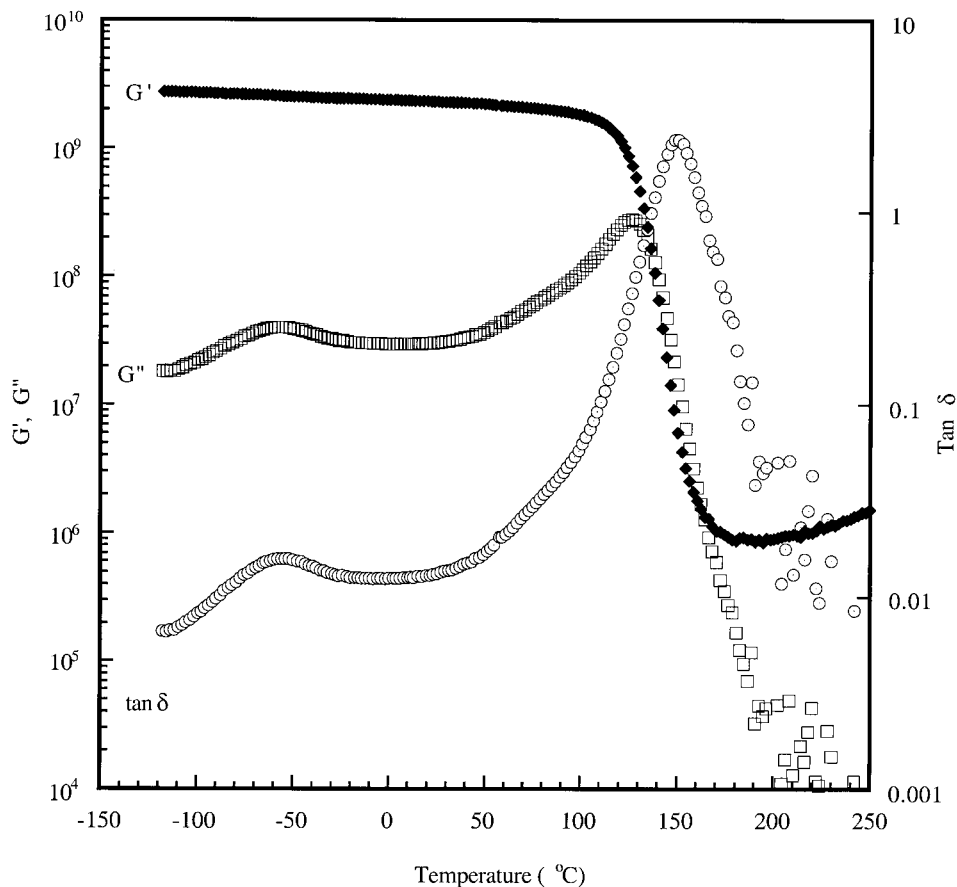


Figure 9 DMA of MeOTs-initiated poly(Ph-a).

polymer structure that first underwent degradation.²⁵ Therefore, it is reasonable to assume that by not having isopropyl linkages in the structure, we eliminated the possible weakest moieties in the polybenzoxazine structure, thereby improving the thermal stability of the polymer. Other possibilities, such as fewer short-chain branches in the structure that could serve as the initiation sites of the degradation process, could also have attributed to the improvement of the thermal stability.

Mechanical properties

Although phenol/aliphatic amine-based monofunctional benzoxazines have been reported since the 1950s,² no polymer derived from them with significant mechanical properties has ever been demonstrated in the literature. In our study, an effort was made to make phenol/aliphatic amine-based monomers into specimens suitable for mechanical testing. However, due to the foaming nature of these samples in the late curing stage, as already observed in the previous DSC cure study, it was not feasible to measure the mechanical properties of these polymers derived from the phenol/aliphatic amine-based benzoxazines. Phenol/aromatic amine-based benzoxazines, on the other

hand, could be easily cured into a rigid polymer specimen without any foaming problems. Ph-a has been chosen as an example to elucidate the mechanical properties of this kind of new polybenzoxazine. Both pure Ph-a and Ph-a/5 wt % MeOTs specimens were cured between two surface-treated glass plates with a U-shaped silicone rubber spacer. The curing condition of the pure Ph-a specimen was the same as for the aforementioned poly(Ph-a)2. The MeOTs-initiated Ph-a was cured at 150°C for 0.5 h and 180°C for 1 h.

The dynamic mechanical spectrum of poly(Ph-a) is displayed in Figure 8. A storage modulus (G') of around 2.4 GPa at 25°C was observed, which was comparable to its fully cured difunctional counterpart, poly(BA-a),¹⁰ indicating the rigid nature of this polymer at room temperature. The γ -transition was detected at around -52°C by the low-temperature loss modulus (G'') peak; however, its difunctional counterpart, poly(BA-a), exhibited a γ -transition around -70°C.²⁶ It has been proposed that the γ -process of a polybenzoxazine network relates closely to the thermal motions of the pendant groups attached to the nitrogen atoms.²⁶ Thus, the aforementioned phenomenon indicates that the motions of the pendant phenyl groups were activated at a lower temperature for poly(BA-a) than for

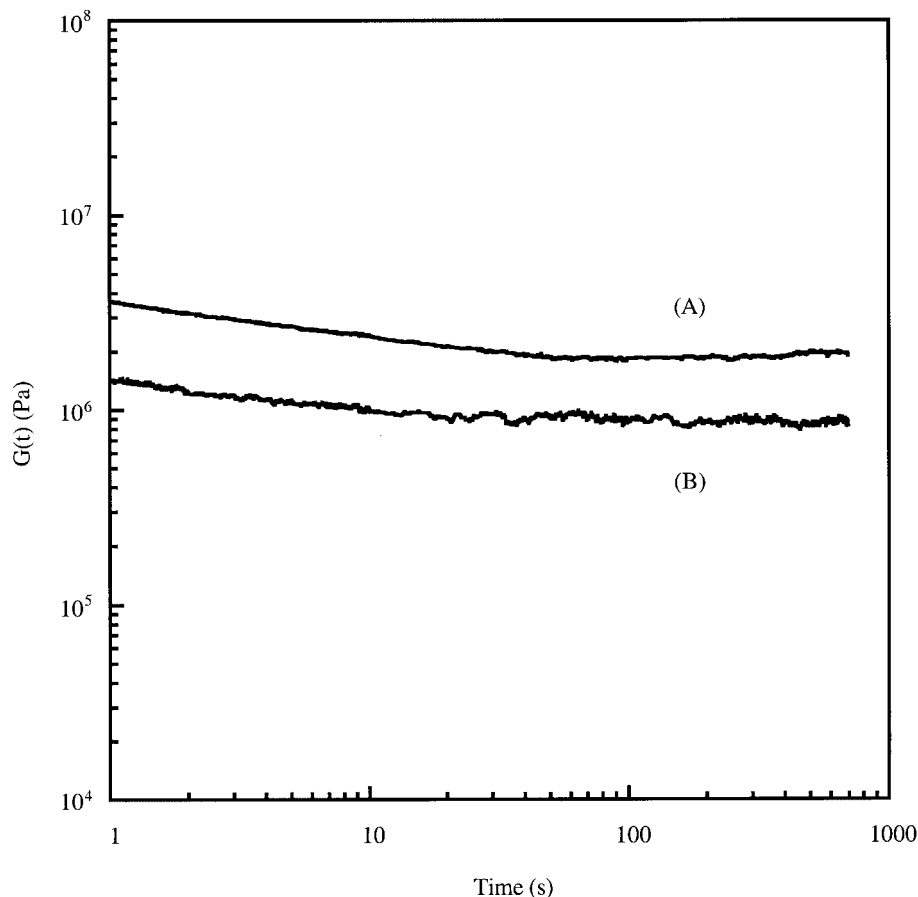


Figure 10 Stress relaxation of poly(Ph-a) at T_g + (A) 50 and (B) 100°C.

poly(Ph-a). This could be explained by an examination of the size of the repeating units of these two materials. For poly(BA-a), there were two benzene rings plus an isopropyl linkage in a repeating unit, whereas only one benzene ring existed in the repeating unit of poly(Ph-a). The resulting distance between chains in the poly(Ph-a) structure was smaller than in poly(BA-a); in other words, the pendant phenyl groups in poly(BA-a) were less confined by the surrounding polymer chains than in poly(Ph-a). Therefore, poly(Ph-a) exhibited a higher γ -transition than poly(BA-a).

Another interesting phenomenon of the dynamic mechanical analysis (DMA) spectrum of poly(Ph-a) was the lack of the β -transition. For the difunctional-based polybenzoxazines, a broad β -transition could always be observed in the temperature range of 10–100°C, which has been attributed to the incomplete network structure of these polybenzoxazines.²⁶ The great variety of the short-chain branches and defects, resulting from the incomplete polymerization of both the oxazine rings in one monomer molecule, could have been responsible for the broad nature of the β -relaxation in the difunctional polybenzoxazines, as revealed elsewhere.²⁶ In the monofunctional benzox-

azine system, because there was only one oxazine ring per monomer molecule plus two other reactive sites on the benzene ring (ortho and para),⁹ fewer defects and/or short-chain branches that were not incorporated into the network structure would be formed, thereby resulting in the insignificant β -relaxation of this polymer.

T_g of 120°C, as determined from the maximum of G'' peak agreed well with the DSC data. This T_g , lower than that of its difunctional counterpart, may have been partially explained by the lack of the rigid Ph—C(CH₃)—Ph moieties in the polymer structure, which could have confined the movement of the relatively soft Mannich bridge moieties. Another aspect that may have contributed to this low T_g was the incomplete cure of the specimen under the performed conditions. After the glass-transition region, a stable rubbery plateau was visible for a long temperature span until the highest temperature set for the experiment was reached. The plateau modulus of this polymer was 1.3 MPa.

The dynamic mechanical spectrum of Ph-a/5 wt % MeOTs is shown in Figure 9. Despite the less severe cure condition used for this specimen than for Ph-a, Ph-a/5 wt % MeOTs exhibited similar dynamic me-

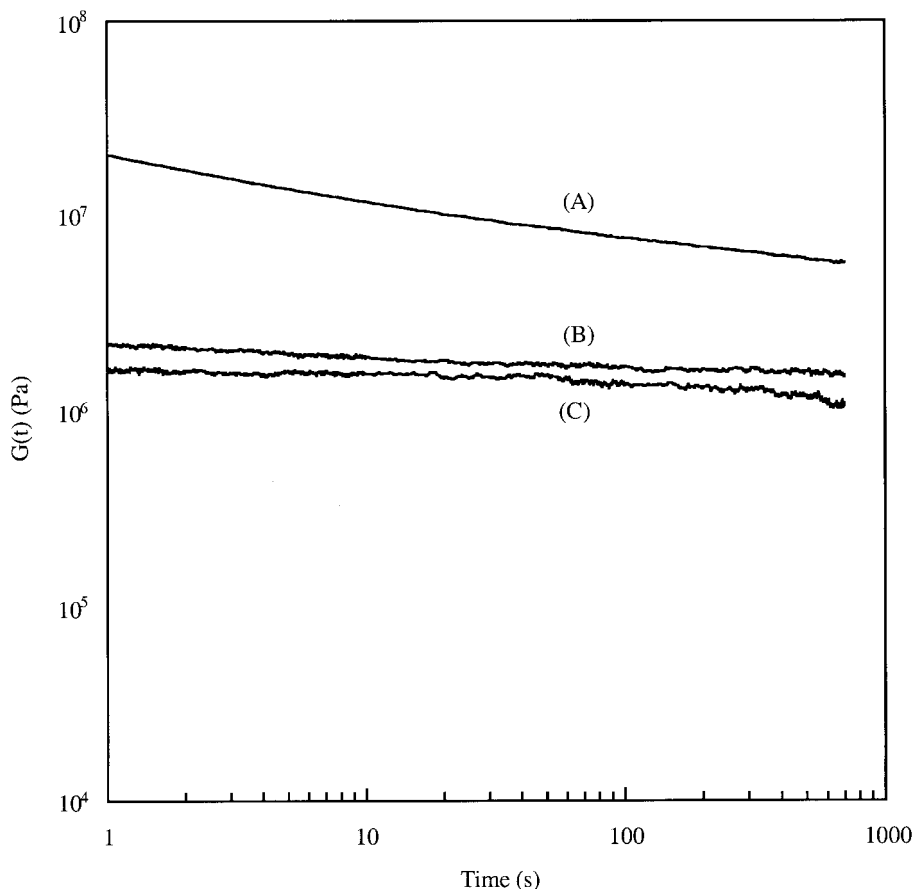


Figure 11 Stress relaxation of MeOTs-initiated poly(Ph-a) at T_g + (A) 50, (B) 100, and (C) 150°C.

chanical behavior. Both of these samples were not fully cured, as evidenced by very broad glass-transition peaks (G'') and residual exotherms in the DSC thermograms. Another interesting feature of these dynamic mechanical spectra was the curved-up trend of G' at high temperatures. Because these polymers were stable up to 300°C as characterized by TGA, this curved-up phenomenon could possibly be explained as further polymerization and/or a crosslinking reaction of these polymers rather than degradation.

An estimate of the crosslink density, (ρ_e) could be obtained from the equilibrium storage modulus (G_e) in

the rubbery region with the kinetic theory of rubber elasticity as follows:²⁷

$$\rho_e = G_e / \phi RT_e$$

where ϕ is referred to as the front factor and is typically assumed to be 1,²⁸⁻³¹ R is the gas constant, and T_e is taken as the temperature 50°C above T_g , from which the G_e values are obtained. If the density of the polymer is known, the MW between crosslinks (M_c) may also be calculated. Although this rubber elasticity

TABLE VI
Dynamic Mechanical Properties of Poly(Ph-a)s

	Poly(Ph-a)	MeOTs-initiated Poly(Ph-a)
γ -Transition (°C)	-52	-55
T_g (°C)	120	126
Storage modulus G' at 25°C (Pa)	2.4×10^9	2.3×10^9
Plateau modulus G' at 170°C (Pa)	1.3×10^6	1.1×10^6
Crosslink density (10^{-3} mol \cdot cm $^{-3}$)	0.4	0.3
Density (g cm $^{-3}$) ^a	1.23	1.20
MW between crosslinks (g mol $^{-1}$)	3075	4000

^a By pycnometer.

equation is strictly valid only for lightly crosslinked rubbers, it can still be used to provide an approximate measure of the level of crosslinking.²⁸ For highly crosslinked materials with rubbery moduli greater than 10 MPa, the rubber elasticity equation is no longer applicable.^{32,33} The rubbery moduli for poly(Ph-a) and poly(Ph-a/5 wt % MeOTs), as seen in Figures 8 and 9, were between 1 to 2 MPa and thus within the applicable range of the rubber elasticity equation. The calculated crosslink densities for these two polymers were 0.4×10^{-3} and 0.3×10^{-3} mol/cm³. M_c 's were 3075 and 4000 g/mol for poly(Ph-a) and MeOTs-initiated poly(Ph-a), respectively.

Stress relaxation measurements have been reported previously for difunctional polybenzoxazines.²⁸ It was shown that difunctional polybenzoxazines did relax stress, which suggested that they were not truly crosslinked material but might only be hyperbranched. Because the modulus and crosslink densities of these materials were high, the possibility of thermal degradation affecting these results was suspected. Thus, whether or not the thermally polymerized difunctional polybenzoxazines were crosslinked materials still remains unclear. Given a moderate T_g and a significantly higher onset degradation temperature of the specimen investigated in this study, we may have a chance to demonstrate for the first time by stress relaxation experiment that polybenzoxazines are crosslinked thermosetting materials. The stress relaxation curves for the cured Ph-a are shown in Figure 10 at temperatures of T_g plus 50 and 100°C. It can be seen that no apparent relaxation was observed up to a 700-s testing span at both temperatures. The same experiments were conducted on the MeOTs-initiated Ph-a system, and the results are shown in Figure 11. Again, no significant stress relaxation could be observed for this system at temperatures of T_g plus 50, 100, and even 150°C. These facts suggest that these polymers were chemically crosslinked networks. The mechanical data of these two polymers are summarized in Table VI.

CONCLUSIONS

Room-temperature liquid 1,3-benzoxazine resins were developed as candidates for high-performance thermosetting material applications. A close relationship between the benzoxazine ring content and the viscosity of the resins was discovered. The polymerization behavior of these resins was studied by DSC. Polyben-

zoxazines with moderate T_g 's (as high as 165°C) and highly improved thermal stability were obtained. Stress relaxation experiments revealed crosslinked structures for these polymers.

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