

Synthesis and Characterization of Benzoxazine-Based Phenolic Resins: Crosslinking Study

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ABSTRACT: Modified novolac resins with benzoxazine rings were prepared. The synthetic method involved the preparation of 1,3,5-triphenylhexahydro-1,3,5-triazine as an intermediate that further reacts with the novolac resin. The catalytic effects of phenols, carboxylic acids, and Lewis acids on the benzoxazine ring-opening polymerization were shown. The curing behavior of the benzoxazine compounds

and the thermal properties of the cured resin were studied, and the results indicated improved degradation behavior for flammability. V-0 materials were obtained when the materials were tested for ignition resistance using the UL-94 test. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 470–481, 2003

Key words: benzoxazine; phenolic resins; crosslinking

INTRODUCTION

Phenolic resins are widely used in industry because of their good heat resistance, electrical insulation, dimensional stability, low flammability, and low smoke generation. However, they do have a number of shortcomings. For example, they are brittle; they use acid or base compounds as catalysts, which corrode the processing equipment; and they release by-products such as water, ammonia compounds, and so forth during curing. These volatiles sometimes harm the properties of cured phenolic resins because of the formation of microvoids.

3,4-Dihydro-3-substituted-1,3-benzoxazines (benzoxazine) are heterocyclic compounds synthesized by the reaction of the corresponding phenols, primary amines, and formaldehyde. They were discovered as Mannich reaction products from these reactants.¹ Benzoxazine structures were also found by NMR spectroscopy as intermediates in the curing of novolac resins.²

Benzoxazine-derived phenolics are an alternative to traditional phenolics. They are synthesized by ring-opening polymerization of the aromatic oxazines. They produce no polymerization by-products and no strong catalysts are required.³ The benzoxazine ring is

known to be stable at low temperature; but a ring-opening reaction occurs at high temperature, when both the phenolic hydroxylic group and the tertiary amine group are produced. Recently, Ishida et al.^{4,5} synthesized different types of benzoxazines and studied their cure kinetics and mechanical and dynamical-mechanical properties. Jang and Shin⁶ also studied the cure kinetics of a benzoxazine-based phenolic resin.

Despite their high performance (e.g., high resistance to heat and water), the crosslinking densities of benzoxazine-based resins are believed to be surprisingly lower than those of ordinary thermosetting resins.⁷ As high performance thermosetting resins, their properties can be improved by tightening their network structure. Another problem with these systems is high cure temperature.

In this study, we modified novolac resins with benzoxazine rings to obtain higher crosslinking density from the benzoxazine-based resin and to thus lower the cure temperature. We also investigated the curing behavior and properties of the cured resins. Benzoxazine model compounds were previously synthesized by different methods to attain pure compounds that were free of amines and oligomers. We also studied the catalytic effect of phenols on a typical benzoxazine ring-opening polymerization and determined how phenols with different acidities behave. Finally, we evaluated the thermal and mechanical properties of the cured benzoxazine resins.

EXPERIMENTAL

Materials

Aniline (Aldrich), formaldehyde (35–40% aqueous, Panreac), paraformaldehyde (Probus), and *p*-cresol

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(Aldrich) were used as received. Novolac resin was kindly supplied by Aismalibar S.A. All the solvents were purified by standard procedures.

Synthesis of 3,4-dihydro-1,3-benzoxazine derivatives

Method 1

According to a published method,⁸ 0.1 mol of *p*-cresol or 0.05 mol of bisphenol A, 0.2 mol of paraformaldehyde, and 0.1 mol of aniline were placed in a 250-mL round-bottomed flask and the mixture was heated at 100°C. After 15 min the mixture was cooled and dissolved in ethylic ether and washed 3 times with 3*N* NaOH solution and water. The organic phase was dried with anhydrous MgSO₄ and filtered, and the solvent was removed at low pressure to obtain a viscous fluid. The yield of benzoxazine-based *p*-cresol was 82% and the yield of benzoxazine-based bisphenol A was 26%.

Method 2

In the second method,³ 0.2 mol of aqueous formaldehyde (37.5%) dissolved in 40 mL of dioxane were placed in a 250-mL three-necked round-bottomed flask (equipped with a condenser, thermometer, dropping funnel, and magnetic stirrer) and cooled in an ice bath. Then 0.1 mol of aniline in 10 mL of dioxane was added slowly and the mixture was stirred for 10 min. We added 0.1 mol of *p*-cresol or 0.05 mol of bisphenol A dissolved in 50 mL of dioxane, and the mixture was heated to reflux for 6 h. The solvent was removed at reduced pressure, and the viscous fluid obtained was dissolved in ethyl ether. The ether solution was washed 3 times with 3*N* NaOH solution and 3 times with water. The organic phase was dried with anhydrous MgSO₄ and the solvent was removed at low pressure. In all the cases a mixture of compounds was obtained.

Method 3

The third method was according to Brunovska et al.⁹ *Synthesis of 1,3,5-triphenylhexahydro-1,3,5-triazine*. Aniline (1 mol) was added to 1 mol of paraformaldehyde in a 250-mL two-necked round-bottomed flask with magnetic stirring. The mixture was heated to 100°C and 75 mL of toluene was added under continuous stirring for 2 h. The mixture was then cooled, filtered, and washed several times with small amounts of cold toluene. The product was dried at 60°C (79% yield). ¹H-NMR (DMSO-*d*₆/TMS, δ): 7.2 (3H, m), 7.0 (6H, dd), 6.7 (6H, dd), 4.9 (6H, s). ¹³C-NMR (DMSO-*d*₆/TMS, δ): 148.3 (s), 128.9 (d), 119.9 (d), 116.8 (d), 67.0 (t).

Synthesis of benzoxazine derivative. We placed 0.016 mol of 1,3,5-triphenylhexahydro-1,3,5-triazine, 0.048 mol of *p*-cresol or 0.024 mol of bisphenol A, and 0.048 mol of paraformaldehyde in a 50-mL round-bottomed flask at 100°C with magnetic stirring for 1 h. The mixture was cooled, dissolved in ethylic ether, and washed 3 times with 3*N* NaOH and 3 times with water. The organic phase was dried with anhydrous MgSO₄ and the ethylic ether was removed at low pressure. The obtained compounds were crystallized in hexane. Benzoxazine-based *p*-cresol (64% yield): ¹H-NMR (CDCl₃/TMS, δ): 7.3 (1H, t), 7.2 (2H, d), 7.0 (3H, m), 6.9 (1H, s), 6.8 (1H, d), 5.4 (2H, s), 4.6 (2H, s), 2.3 (3H, s). ¹³C-NMR (CDCl₃/TMS, δ): 152.0 (s), 148.4 (s), 129.9 (s), 129.2 (d), 128.4 (d), 127.0 (d), 121.3 (d), 120.5 (s), 118.2 (d), 116.6 (d), 79.4 (t), 50.3 (t), 20.5 (q). Benzoxazine-based bisphenol A (99% yield): ¹H-NMR (CDCl₃/TMS, δ): 7.3 (2H, m), 7.2 (4H, d), 7.0 (6H, m), 6.9 (2H, s), 6.8 (2H, d), 5.3 (4H, s), 4.6 (4H, s), 1.6 (6H, s). ¹³C-NMR (CDCl₃/TMS, δ): 151.7 (s), 148.0 (s), 142.8 (s), 128.9 (d), 126.1 (d), 124.5 (d), 120.9 (d), 119.8 (s), 118.2 (d), 116.6 (d), 78.9 (t), 50.7 (t), 41.9 (s), 31.2 (q).

Chemical modification of novolac resin

Commercial phenol novolac resin (5 g) was mixed with different amounts of 1,3,5-triphenylhexahydro-1,3,5-triazine and aqueous formaldehyde to obtain different modified benzoxazine-based phenol novolac resins. The general procedure was as follows: novolac resin, triazine, and aqueous formaldehyde were placed in a 100-mL round-bottomed flask and 30 mL of toluene was added. The mixture was heated at 100°C for 2 h. The toluene was removed at low pressure and the modified resin was washed with water. The resin was filtered and dried under a vacuum, and a fine orange powder was obtained. ¹H-NMR (DMSO-*d*₆/TMS, δ): 9.4–9.0 (m), 7.5–6.2 (m), 5.6–5.0 (m), 4.8–4.1 (m), 4.0–3.2 (m). ¹³C-NMR (DMSO-*d*₆/TMS, δ): 155–150 (s), 133–112 (d), 119 (d), 80 (t), 50 (t), 36–29 (t).

Curing conditions and compression molding

Mixtures of synthesized compounds with the selected curing agents were made via the dissolution of the two components in dry methanol and 1,2-dichloromethane and the subsequent evaporation of the solvent at room temperature under a vacuum. Samples for thermogravimetric analysis (TGA) were obtained by isothermal curing at the selected temperature (Table I) for 180 min.

Molded, cured benzoxazine-based novolac resins were prepared with a manual 15-ton hydraulic press sample press (SPECAC) equipped with water-cooled heated platens. The resin was placed into a 60 × 40

TABLE I
Modification Degree and Properties of Benzoxazine-Modified Novolac Resins

| | OH/Triazine Molar Ratio | Modification Degree (%) | T_{\max} (°C) | T_g (°C) | | | T_{iso} (°C) | T_{onset} (°C) | T_{\max} (°C) | Yield _{700 °C} (%) |
|---------|----------------------------|----------------------------|--------------------|-------------------|--------------|-------------------------------|--------------------------|----------------------------|--------------------|--------------------------------|
| | | | | $1/2 \Delta Cp^a$ | E_{\max}^b | $\text{Tan } \delta_{\max}^b$ | | | | |
| Novolac | — | — | — | — | — | — | — | 197 | 404, 550 | 40 |
| NB1 | 1/1 | 80 | 226 | 218 | — | — | 190 | 250 | 478 | 48 |
| NB2 | 1/0.8 | 78 | 224 | 220 | 199 | 216 | 190 | 235 | 473 | 51 |
| NB3 | 1/0.6 | 46 | 209 | 180 | 170 | 181 | 190 | 223 | 409, 518 | 53 |
| NB4 | 1/0.4 | 34 | 192 | 184 | 183 | 189 | 170 | 203 | 407, 532 | 53 |
| NB5 | 1/0.2 | 18 | 174 | 148 | 133 | 150 | 160 | 176 | 393, 552 | 50 |

T_{\max} , the temperature of the maximum of the crossing exotherm (10°C/min); T_{iso} , the isothermal cure temperature for TGA and DMA measurements.

^a Measured in a second dynamic DSC run.

^b Samples for DMA experiments were prepared as described in the Experimental section.

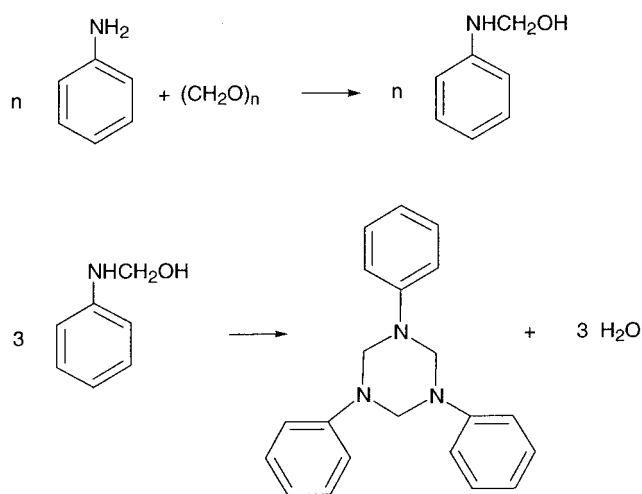
× 0.5 mm mold and compression molded at different temperatures (Table I) for 1 h under 0.1 MPa pressure. Postcuring was carried out at 220°C for 2 h.

Characterization

The quantitative analyses were carried out on a Perkin Elmer 2400 CHN microanalyzer. The ¹H-NMR (300 or 400 Hz) and ¹³C-NMR (75.4 or 100.6 Hz) spectra were obtained with a Varian Gemini 300- or 400-Hz spectrometer with a Fourier transform with DMSO-*d*₆ or CDCl₃ as a solvent and TMS as an internal standard.

Calorimetric studies were carried out on a Mettler DSC821e thermal analyzer with N₂ as a purge gas at scan rates between 5 and 20°C/min. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N₂ as a purge gas at scan rates of 10°C/min.

We measured the mechanical properties using a dynamic mechanical thermal analysis (DMTA) apparatus (TA DMA 2928). Specimens (0.5 × 10 × 40 mm, depth × width × length) were tested in a single cantilever configuration. The thermal transitions were

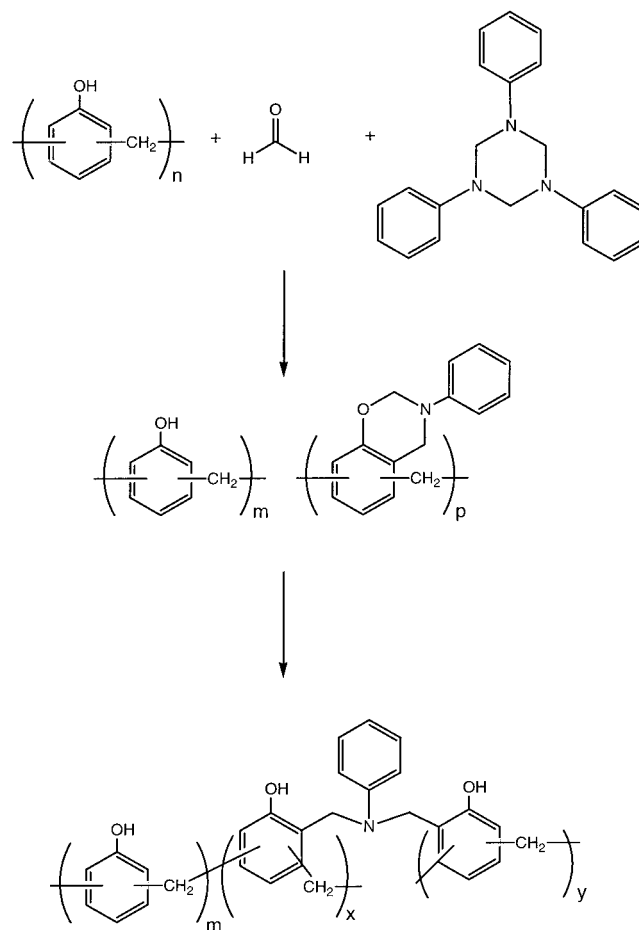


Scheme 1 The reaction of aniline and paraformaldehyde.

studied in the 35–250°C range at a heating rate of 2 or 5°C/min and at a fixed frequency of 1 Hz.

General procedure for modified UL-94 burn test

Five sample bars (0.5 × 10 × 40 mm) were used for this test. The height of the Bunsen burner flame was 25 mm and the height from the top of the Bunsen burner to the bottom of the test bar was 10 mm. All test bars



Scheme 2 The chemical modification of novolacs.

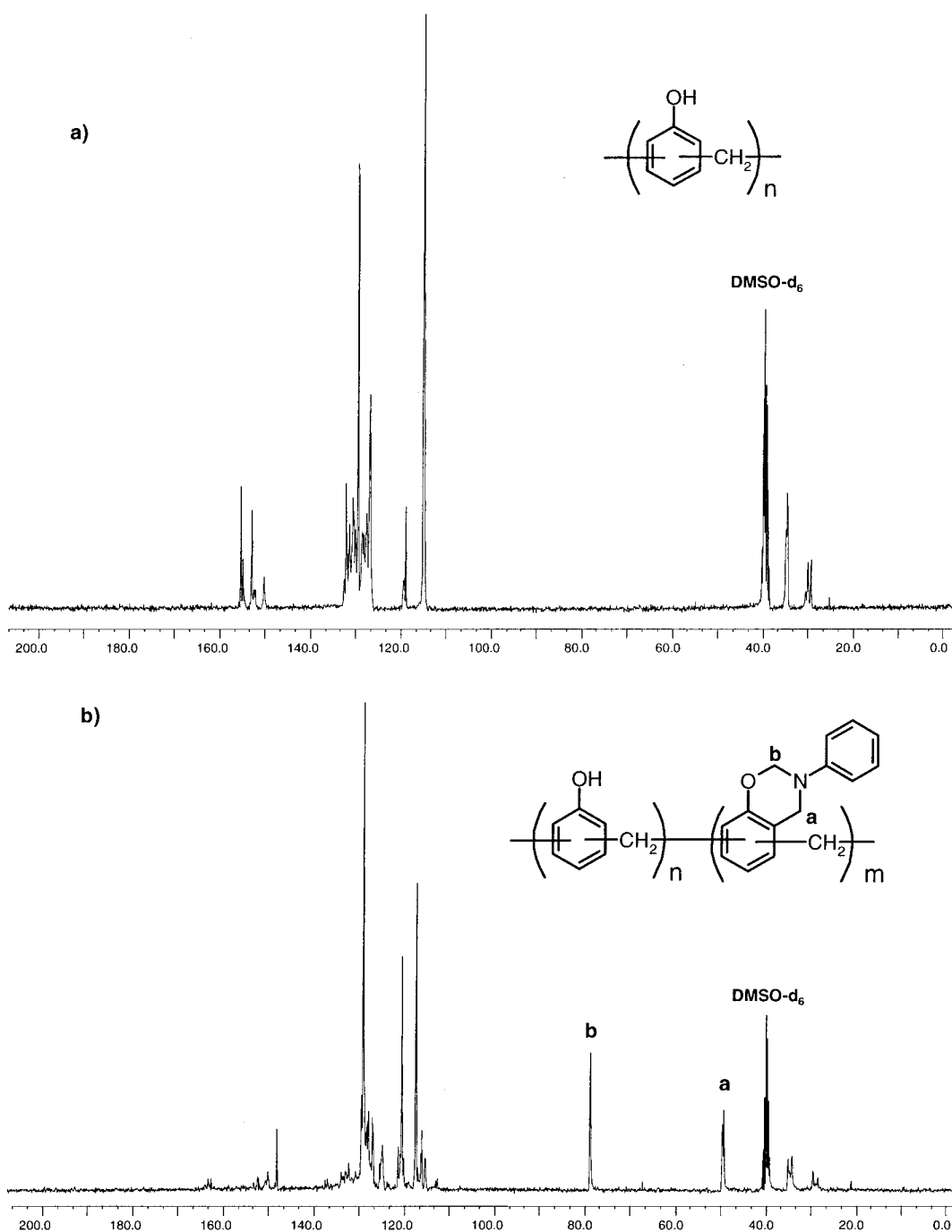
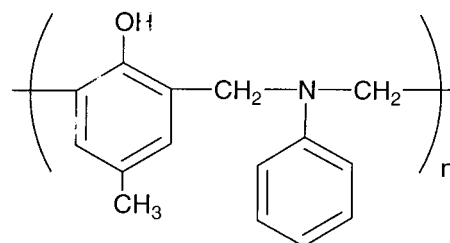


Figure 1 ^{13}C -NMR spectra of (a) novolac resin and (b) benzoxazine novolac resin with 80% modification (NB1).

underwent two trials and each trial consisted of ignition for 10 s. The flame was then removed and we recorded the time for self-extinguishing and dripping characteristics.

RESULTS AND DISCUSSION

The solventless synthesis of 3,4-dihydro-3-phenyl-6-methyl-2H-1,3-benzoxazine as a model monomer was carried out as previously reported.⁸ The reaction using



Scheme 3 The polybenzoxazine structure via thermal polymerization.

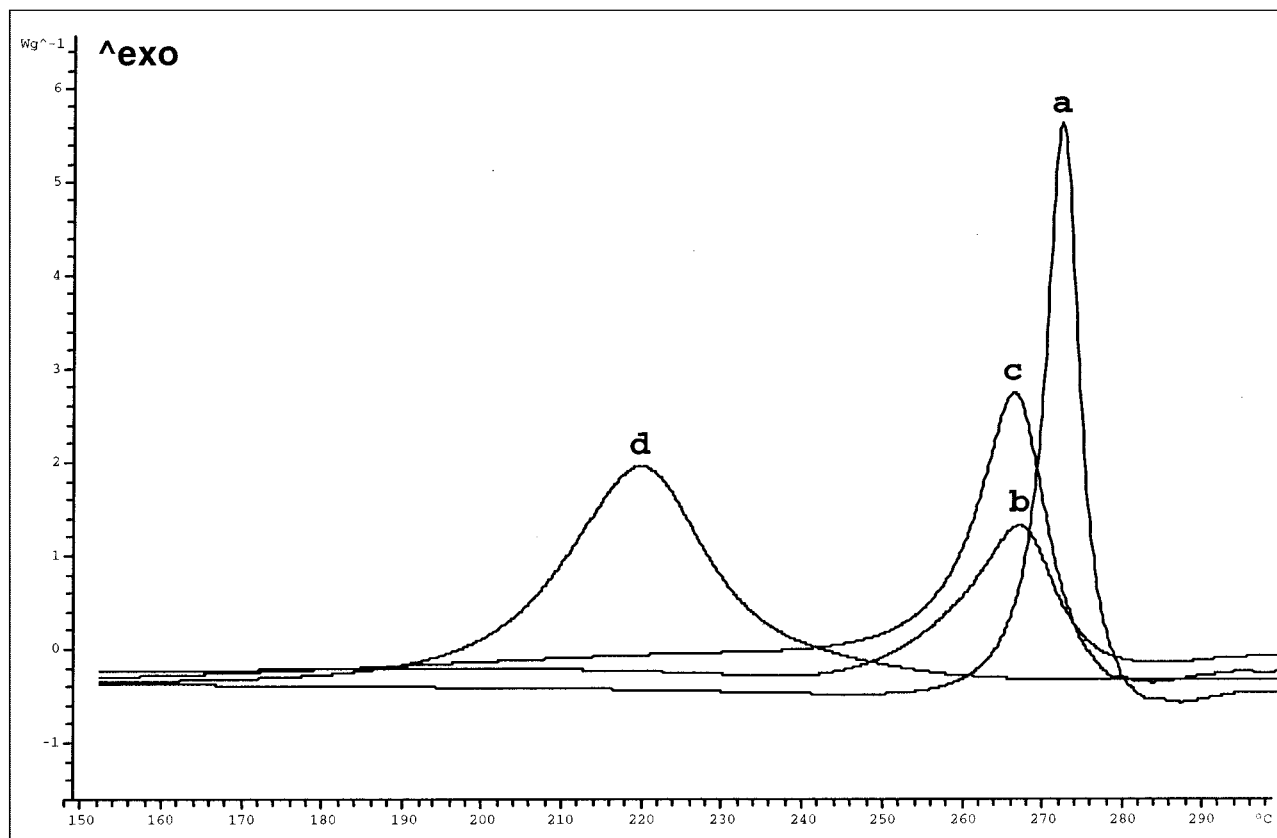


Figure 2 DSC plots (10°C/min) of pure benzoxazine-based *p*-cresol (curve a) and mixtures of this compound with 10 mol % phenol (curve b), *p*-methoxyphenol (curve c), and *p*-nitrophenol (curve d).

p-cresol as the phenol and aniline as the primary amine occurred in the melt in the absence of solvent when solid paraformaldehyde was used instead of the aqueous solution of formaldehyde, leading to benzox-

azine. However, when bisphenol A was used as the phenol, the high viscosity of the melt prevented a homogeneous reaction and unreacted formaldehyde and aniline were detected. In other words, this fact became definitive when the reaction was carried out with phenol compounds with high molecular weights.

When a formaldehyde aqueous solution was used and the reactions were carried out in dioxane solution,³ pure benzoxazine monomers were not obtained. A triazine intermediate always formed. This remained and did not evolve into the final benzoxazine.

1,3,5-Triphenylhexahydro-1,3,5-triazine is an active intermediate and precursor in the synthesis of aromatic amine-based benzoxazine structures.^{9,10} It is therefore possible to obtain 3,4-dihydro-3-phenyl-6-methyl-2H-1,3-benzoxazine of high purity and yield by a solventless reaction via the active triazine intermediate. The reaction of aniline and paraformaldehyde (Scheme 1) leads to triazine, which can be characterized by its ¹³C-NMR spectrum. The resonance at 68 ppm was assigned to the methylene carbons of the triazine ring and the resonances at 150, 130, 122, and 119 ppm were assigned to the carbons of the aromatic ring according to the proposed structure. The reaction of this triazine with *p*-cresol or bisphenol A and paraformaldehyde led to the 3,4-dihydro-3-phenyl-6-meth-

TABLE II
Catalyzed Crosslinking of Benzoxazine Based *p*-Cresol

| Catalyst | Molar Ratio (%) | T_{max} (°C) | ΔH (kJ/mol) |
|--------------------------------|-----------------------|----------------|---------------------|
| — | — | 272 | 55 |
| Phenol | 10 | 267 | 46 |
| | 50 | 257 | 72 |
| <i>p</i> -Methoxyphenol | 10 | 266 | 39 |
| | 10 | 220 | 86 |
| <i>p</i> -Nitrophenol | 20 | 194 | 87 |
| | 30 | 170 | 81 |
| | 40 | 159 | 78 |
| | 50 | 148 | 81 |
| | 5 | 243 | 39 |
| | 10 | 238 | 69 |
| 1,12-Dodecanedicarboxylic acid | 15 | 231 | 49 |
| | 20 | 219 | 82 |
| | 30 | 200 | 91 |
| | 40 | 193 | 87 |
| | 50 | 196 | 99 |
| | BF ₃ · MEA | 1 | 250 |
| 5 | | 222 | 66 |
| 10 | | 204 | 57 |

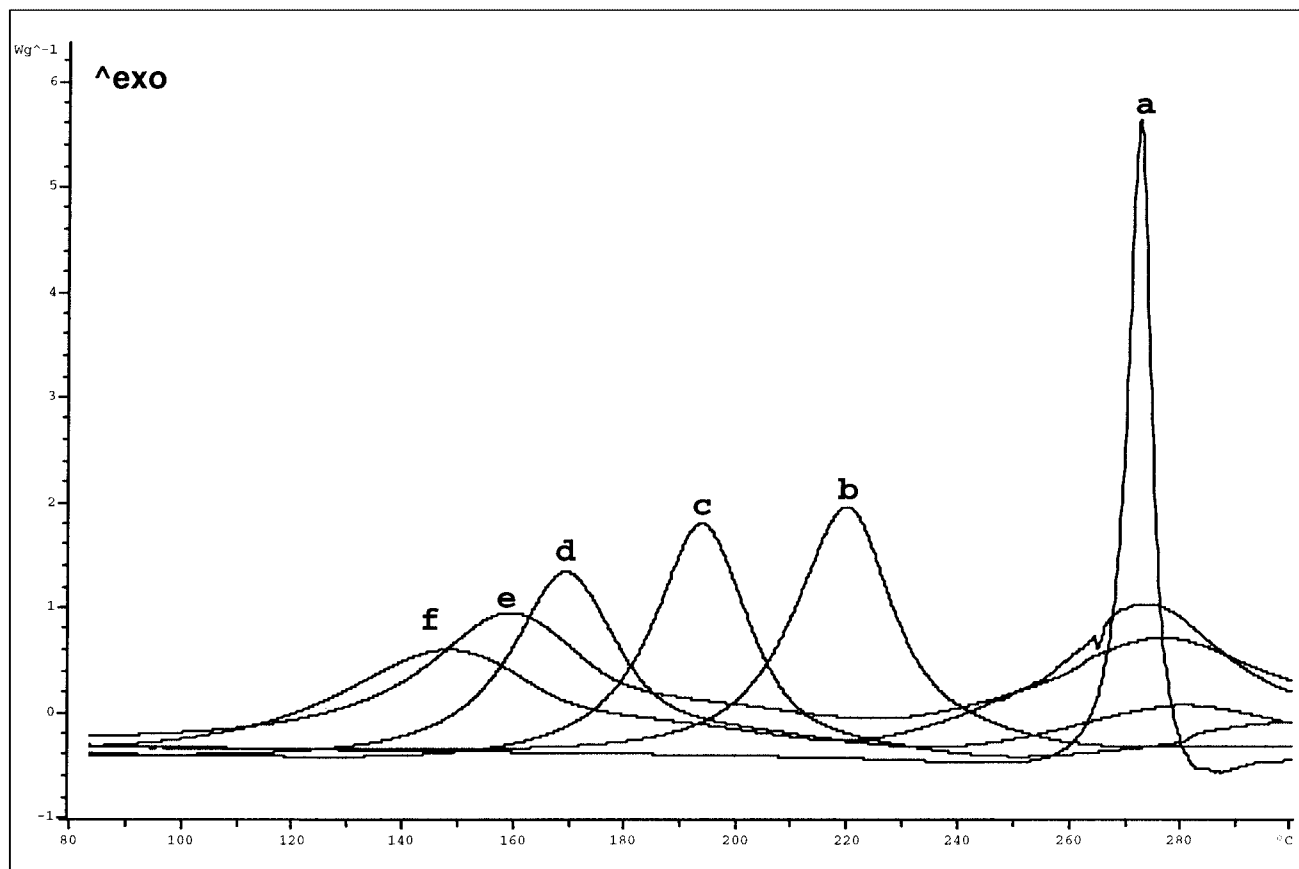


Figure 3 DSC plots (10°C/min) of pure benzoxazine-based *p*-cresol (curve a) and mixtures of this compound with molar amounts of 10 (curve b), 20 (curve c), 30 (curve d), 40 (curve e), and 50% (curve f) *p*-nitrophenol.

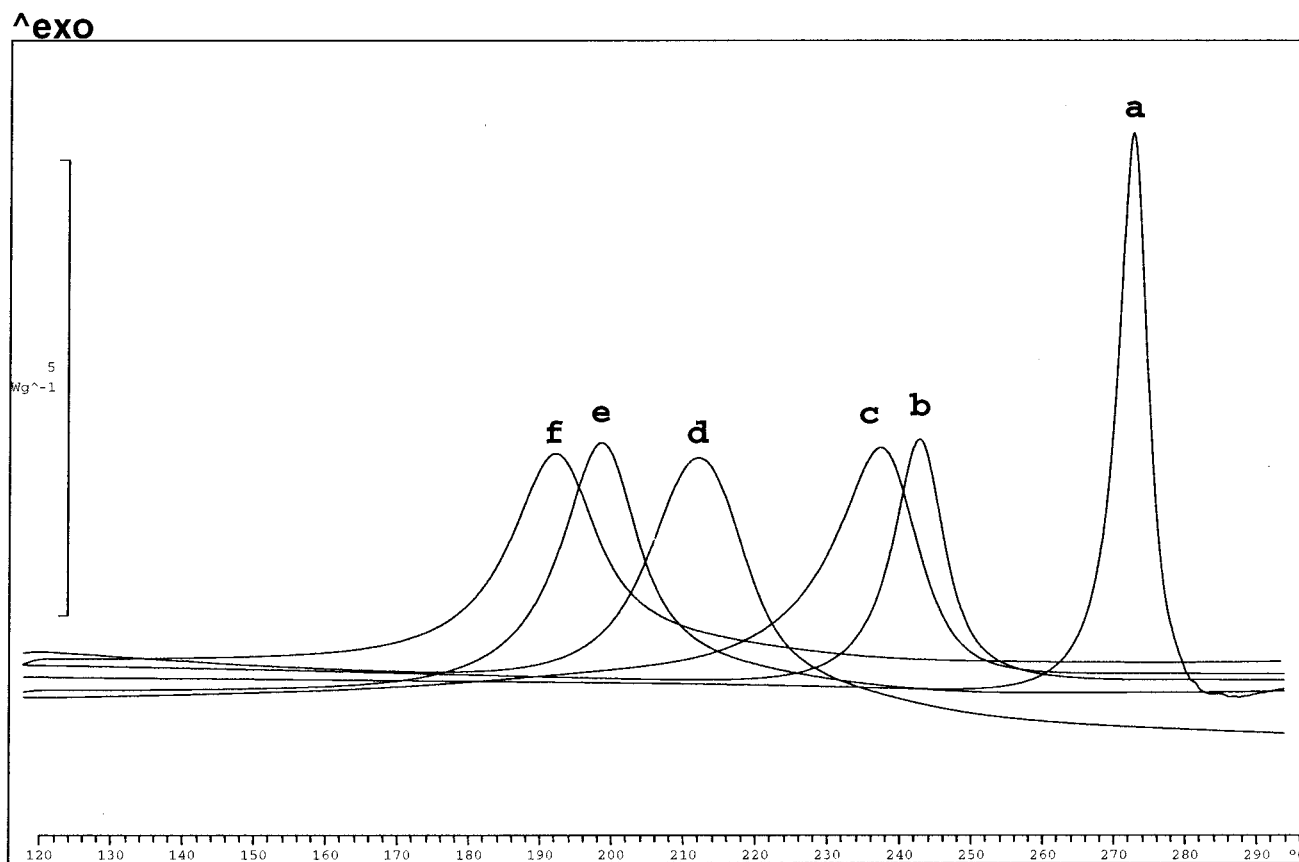


Figure 4 DSC plots (10°C/min) of pure benzoxazine-based *p*-cresol (curve a) and mixtures of this compound with molar amounts of 5 (curve b), 10 (curve c), 20 (curve d), 30 (curve e), and 40% (curve f) 1,12-dodecanedicarboxylic acid.

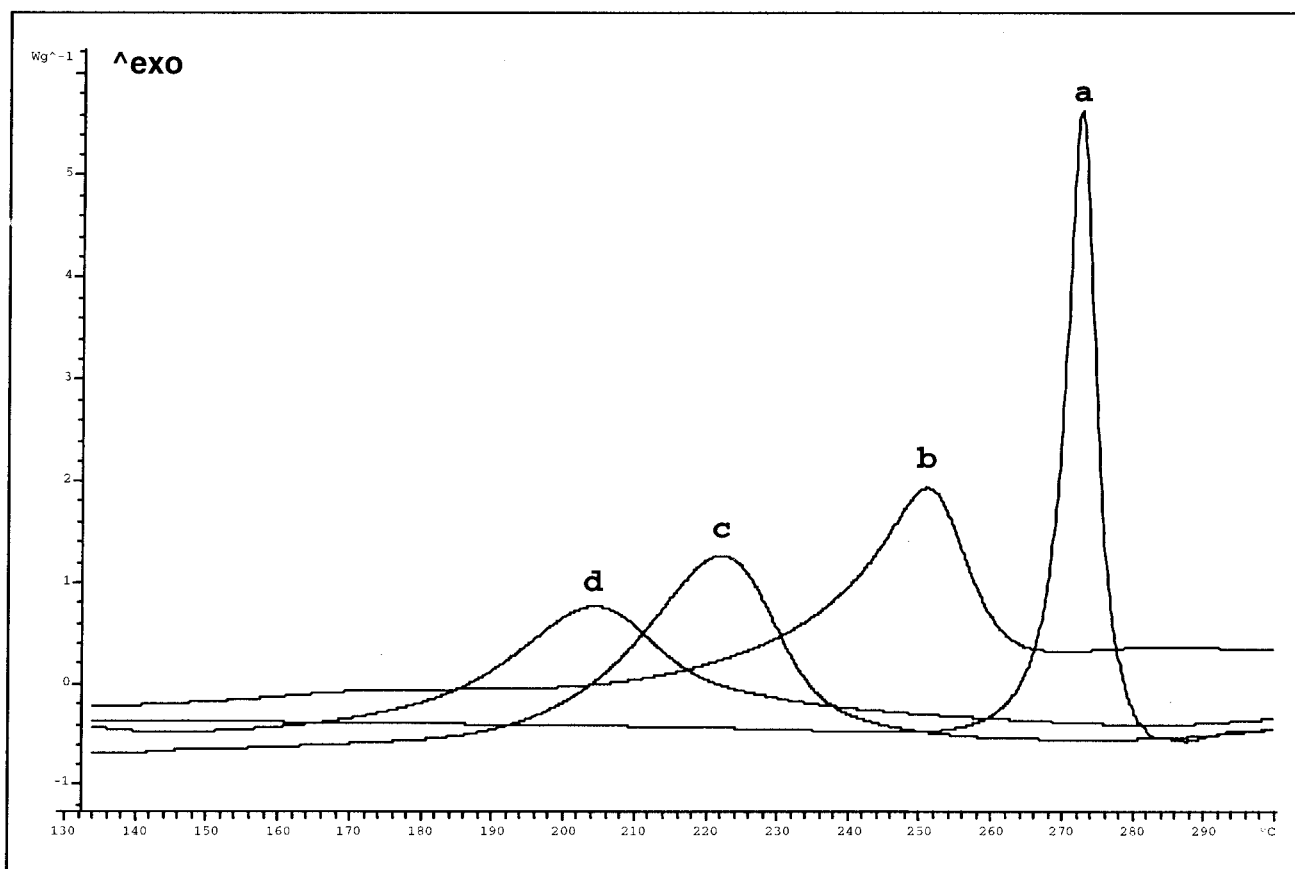


Figure 5 DSC plots (10°C/min) of pure benzoxazine-based *p*-cresol (curve a) and mixtures of this compound with molar amounts of 1 (curve b), 5 (curve c), and 10% (curve d) $\text{BF}_3 \cdot \text{MEA}$.

yl-2H-1,3-benzoxazine or bis(3,4-dihydro-2H-3-phenyl-1,3-benzoxazinyl)isopropane, respectively, in high yield and purity.

Following this synthetic method, the chemical modification of novolacs was carried out using different amounts of the intermediate triazine and aqueous formaldehyde (Scheme 2). Novolacs were therefore obtained with a different percentage of benzoxazine rings. Table I shows the triazine/phenol ratio and the modification degree as calculated by the elemental analysis of nitrogen. A stoichiometric amount of triazine obtained an 80% modification, as did the 1/0.8 ratio, which indicates that this is the maximum degree of modification that can be reached with these reaction conditions.

The benzoxazine novolac resins were characterized by NMR spectroscopy. As seen in Figure 1, the spectra of the starting novolac and the modified benzoxazine novolac are similar. The two new methylene benzoxazine signals at 80 and 50 ppm confirm the cyclization of the benzoxazine ring. There are also changes in the pattern of the aromatic signals.

The typical method for obtaining polybenzoxazines is to polymerize the corresponding monomers at high temperatures without catalysts, although catalyst-as-

sisted polymerization of benzoxazines has also been reported. Benzoxazine rings react preferentially with the ortho positions of free phenolic compounds to form a dimer with a Mannich-based bridge structure.¹¹ Also, the reactivity of bisphenol A based benzoxazines has been studied using a series of acids, alkalis, and Lewis acids as catalysts.^{12–14} The accepted polybenzoxazine structure via thermal polymerization (Scheme 3) is formed by inserting the monomer through the reaction of the benzene ortho position to produce a Mannich-based phenolic-type polymer.

Because the benzoxazine novolac resins obtained herein had different amounts of phenolic groups, focus was placed on the phenol-initiated polymerization of benzoxazines. A model compound used in a previous study, benzoxazine-based *p*-cresol, was used with various phenolic compounds containing electron-withdrawing and electron-donating substituents to determine how the phenol acidity affects the ring opening of benzoxazine.

Nonisothermal differential scanning calorimetry (DSC) experiments were performed on benzoxazine-based *p*-cresol and mixtures of this compound with 10% phenol, *p*-nitrophenol, and *p*-methoxyphenol. The results are shown in Figure 2 and Table II. As can be

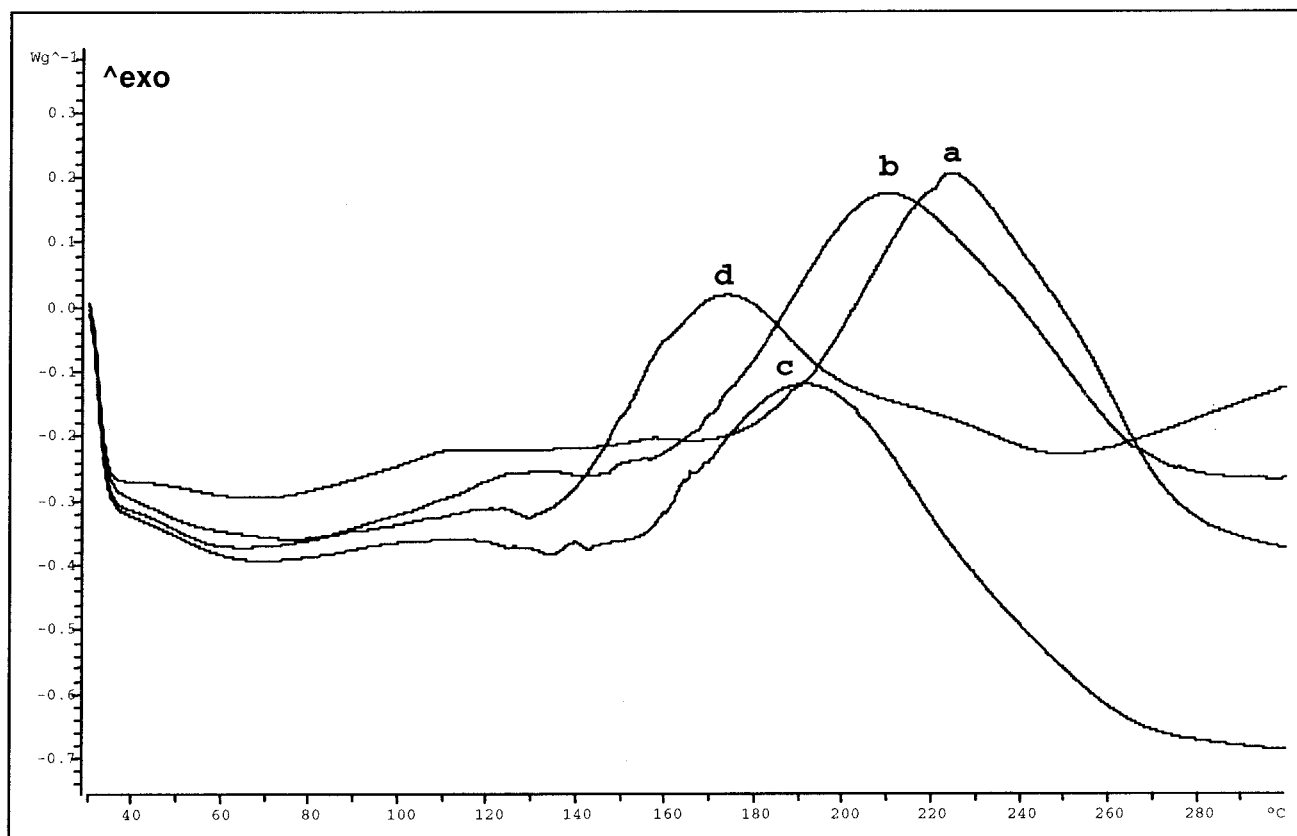


Figure 6 DSC plots (10°C/min) of benzoxazine novolac resins with modification degrees of 78% for NB2 (curve a), 46% for NB3 (curve b), 34% for NB4 (curve c), and 18% for NB5 (curve d).

seen, benzoxazine-based *p*-cresol reacted with a maximum temperature of 272°C and an enthalpy of 55 kJ/mol. When the reaction took place in the presence of *p*-methoxyphenol, the maximum temperature was similar and the enthalpy was 39 kJ/mol. The maximum temperature was slightly lower when phenol was used (46 kJ/mol). On the other hand, when *p*-nitrophenol was used, the maximum temperature decreased considerably and there was a significant increase in enthalpy (86 kJ/mol). These results show that the acidity of the phenol plays an important role in the catalysis.

The influence of the catalyst concentration was studied using various proportions of *p*-nitrophenol. Dynamic DSC plots of these experiments are shown in Figure 3. The maximum temperature of the polymerization exotherms decreased sharply when the amount of catalyst was increased from 10 to 50%. There are no significant variations in the enthalpy of the process in the data in Table II.

To further determine the acidic effect, 1,12-dodecanedicarboxylic acid was tested. The results are given in Figure 4. It is seen that the maximum temperature of the polymerization exotherms decreased significantly when the amount of catalyst was increased from 10 to 50%. Lewis acid catalysts such as $\text{BF}_3 \cdot \text{MEA}$

were also tested (see Fig. 5). The maximum temperature of the polymerization exotherms clearly decreased when the amount of catalyst was increased from 1 to 10%.

The crosslinking of benzoxazine novolac resins was monitored by DSC. As shown in Figure 6, a broad reaction exotherm was centered at 224°C when the modification degree was 78% (NB2). The lower the modification degree, the lower the maximum temperature of the crosslinking exotherm, in accordance with a higher fraction of free phenolic groups that catalyze the ring-opening crosslinking. Table I shows the maximum temperatures of the crosslinking exotherms for novolac resins with different benzoxazine contents. The glass-transition temperature (T_g) of the crosslinked materials was measured in a second dynamic DSC scan. As expected from the higher content of reactive moieties, the T_g value increased as the modification degree increased, in accordance with a higher crosslinking density.

Polymerization of the benzoxazine-modified novolac (NB2) with the highest crosslinking temperature was examined using 1,12-dodecanedicarboxylic acid and $\text{BF}_3 \cdot \text{MEA}$ as catalysts. Figure 7 shows the DSC plots. Note that the effect of the carboxylic acid catalyst is a slight decrease in the maximum crosslinking

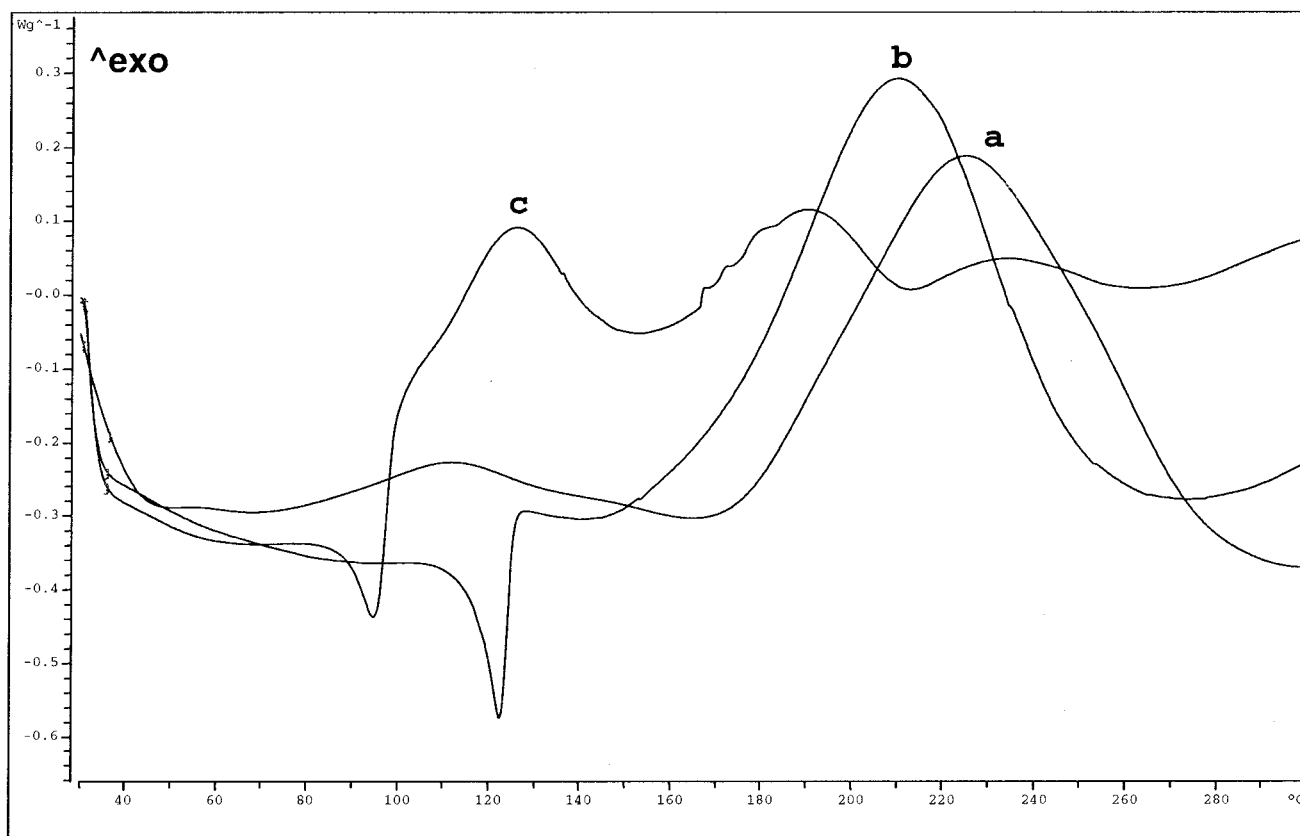


Figure 7 DSC plots of NB2 (curve a) with 10 mol % 1,12-dodecanecarboxylic acid (curve b) and 10 mol % $\text{BF}_3 \cdot \text{MEA}$ (curve c).

temperature. When $\text{BF}_3 \cdot \text{MEA}$ was used, an exotherm at 120°C appeared. This was due to the previously reported thermal conversion of $\text{BF}_3 \cdot \text{MEA}$ to HBF_4 .¹⁵ The second exotherm at 190°C was attributed to the catalyzed benzoxazine ring opening. Catalytic activity was higher for this Lewis acid.

Table I also gives TG data of the materials obtained after curing the benzoxazine-modified resins for 180 min at the selected temperature. The TGA thermograms clearly show that more than one process occurred during thermal degradation. The weight loss increased as the degree of modification increased. The experimental char yield indicates that benzoxazine-modified novolac resins have the highest char yield, which is as expected for a crosslinked thermoset. However, there were no significant differences in the degree of modification. The derivative of weight loss gets broader and more overlapped as one moves from the initial novolac resin to the most modified benzoxazine novolac. This is indicative of the greater complexity of the polymer structure. Degradation occurs at a slower rate and over a wider temperature range than in the initial novolac curve. These broad ranges are better from the viewpoint of flammability.

The dynamic mechanical behavior of conventional phenolic materials has rarely been reported. This may

be because of the extremely fragile nature of the conventional material. For this reason, the phenolics that are most often supplied are highly filled systems. The current benzoxazine system has good mechanical integrity according to the DMA.

The dynamic mechanical properties of the polymers were obtained as a function of temperature beginning in the glassy state of each composition, through the T_g and well into the rubbery plateau of each material. These plots are shown in Figures 8 and 9. Several important material parameters can be derived from the dynamic mechanical data. The storage modulus of a solid sample at room temperature provides a measure of the material stiffness under deformation. As seen in Figure 8, the storage moduli increased as the degree of modification increased. In the glassy state, stiffness is related to changes in the stored elastic energy upon small deformation as the molecular segments resist motion. The benzoxazine-rich polymers appear more able to resist segmental motion and are therefore more able to store elastic energy, thus resulting in a higher glassy modulus.

DMA also allows the determination of the T_g of the crosslinked materials. It is detected as the maximum of the loss modulus (E''), which corresponds to the initial drop from the glassy state into the transition.

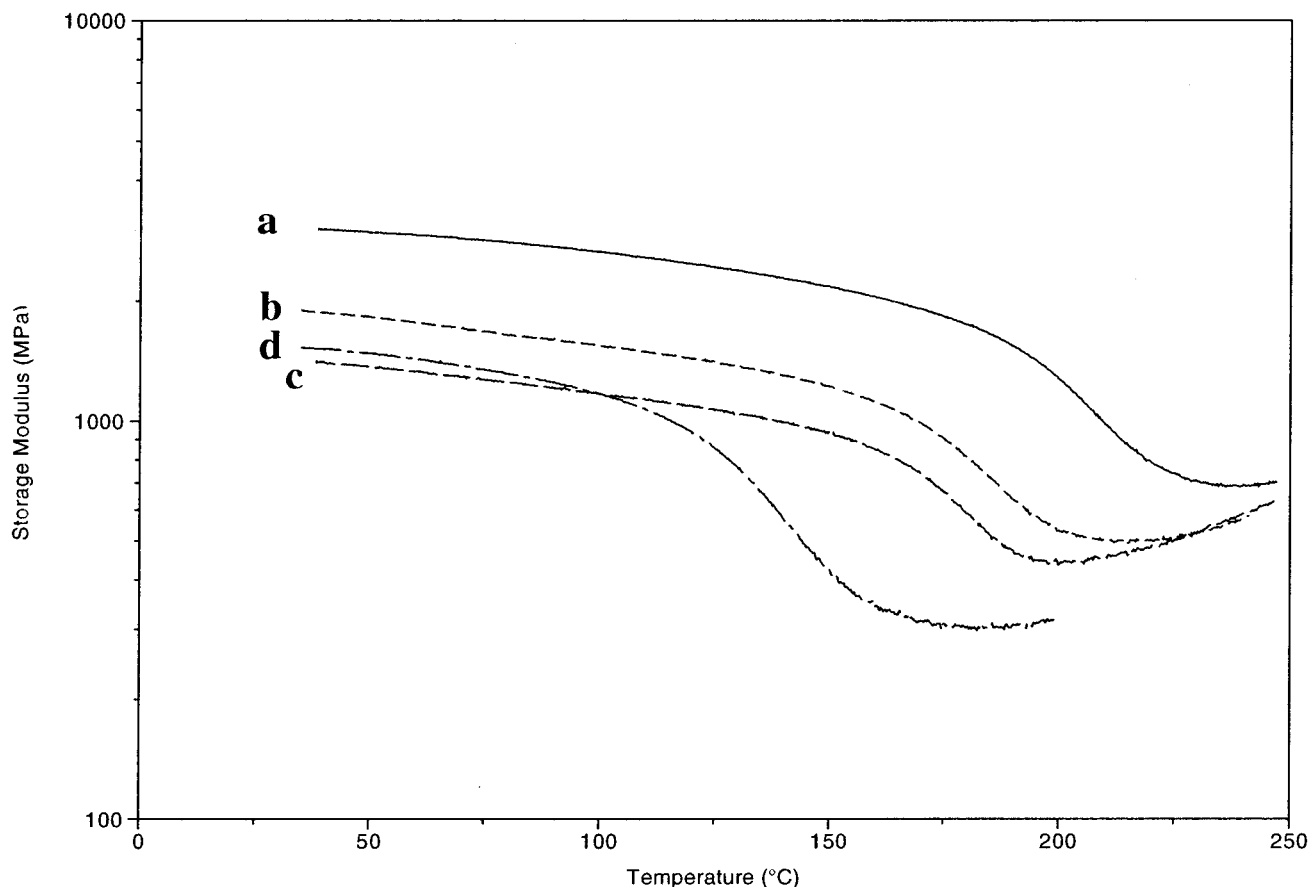


Figure 8 The storage modulus as a function of the temperature of NB2 (curve a), NB3 (curve b), NB4 (curve c), and NB5 (curve d).

Moreover, the α -relaxation peak of the loss factor ($\tan \delta$) is associated with the T_g and corresponds to the transition midpoint of the log of the storage modulus (E') curve. The T_g values from both measurements are shown in Table I. As expected, the temperature of the $\tan \delta$ peak is higher than the E'' peak. From a practical point of view, the maximum E'' is the most appropriate value because it corresponds to the upper use temperature. The T_g values obtained by DSC measurements are similar to those of the maximum of the $\tan \delta$ peak.

One can also analyze the loss factor peak to provide a qualitative insight into the network structure and the height and width of the α -relaxation peak to find trends in the crosslinking density and network homogeneity as the composition of the material changes. As Figure 9 shows, the height of the $\tan \delta$ peak, which is associated with the crosslink density, increased as the degree of modification of the starting polymer decreased. Because $\tan \delta$ is the ratio of viscous components to elastic components, one can assume that the decreasing height is associated with lower segmental mobility and fewer relaxing species and is therefore indicative of a higher degree of crosslinking for the benzoxazine-rich samples. The peak width at half-

height broadens as the number of modes of branching increases, which produces a wider distribution of structures. The range of temperatures at which the different network segments gain mobility therefore increases. There were no significant differences among the benzoxazine-modified samples. The crosslink density of each polymer can be estimated from the plateau of the elastic modulus in the rubbery state using the statistical theory of rubber elasticity.¹⁶ However, this theory is strictly valid only for lightly crosslinked materials and was therefore only used to qualitatively compare the level of crosslinking among the various polymers. As shown in Figure 8, the value of the E' in the rubber plateau increased as the degree of modification increased. The crosslinking density of the thermosets therefore appeared to increase as the content of benzoxazine rings increased.

Flame retardant testing of the synthesized material was done using the UL-94 flame test, in which the sample was suspended above cotton.¹⁷ The sample was subjected to two 10-s ignitions with a calibrated methane-fueled flame in a controlled-size unit that was free of passing air currents. After the first ignition, the flame was removed and the time for the polymer to self-extinguish was recorded. The second ignition

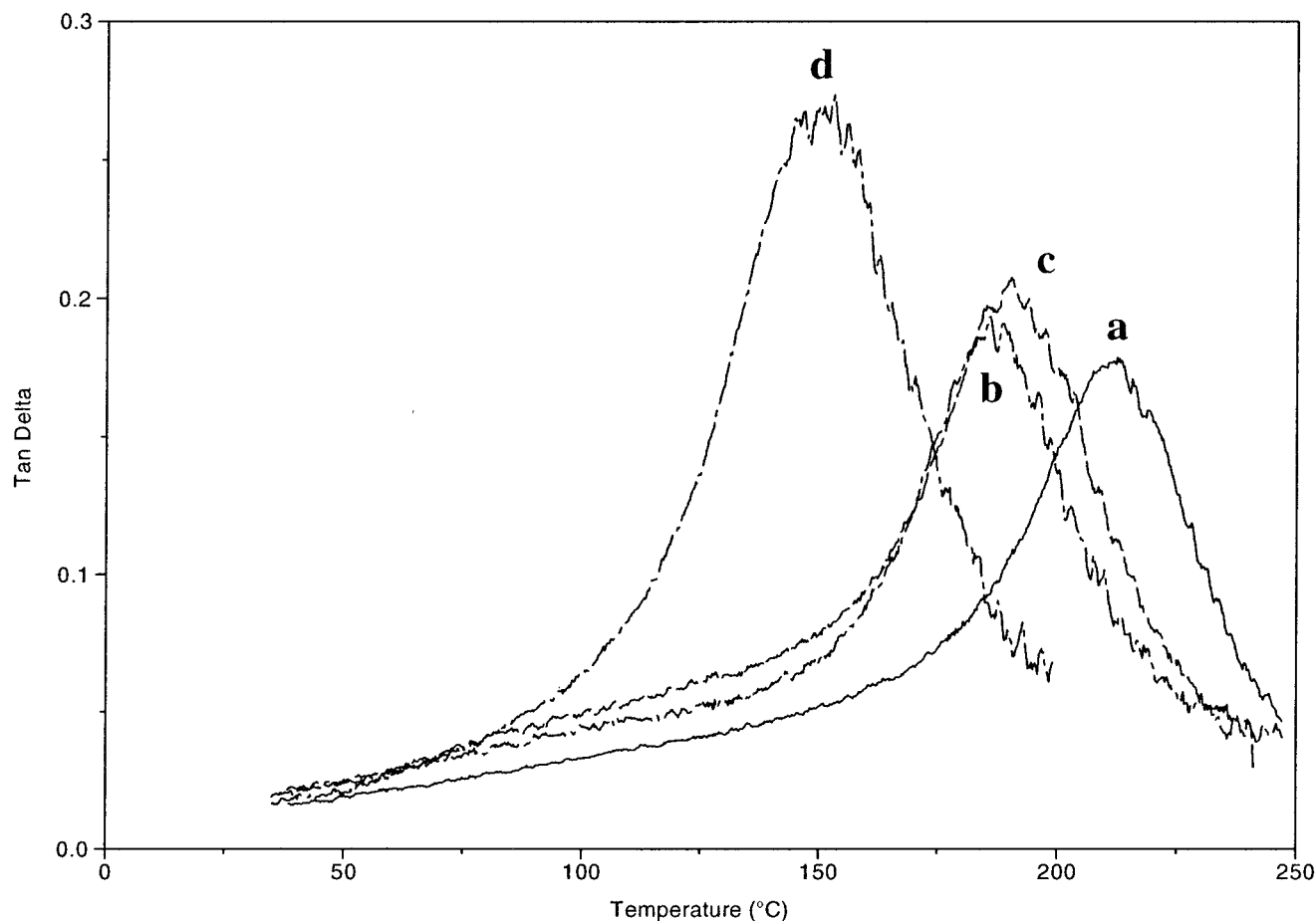


Figure 9 Tan δ as a function of the temperature of NB2 (curve a), NB3 (curve b), NB4 (curve c), and NB5 (curve d).

was then performed on the same sample and the self-extinguishing time and dripping characteristics were recorded. If the sample self-extinguished in less than 10 s with no dripping, it was considered to be a V-0 material, which is an industry standard for flame retardancy. The results of burn tests are shown in Table III. It is seen that, according to the UL-94 test, almost all the benzoxazine-modified novolac samples produced a V-0 material. This new class of benzoxazine-modified novolac resins therefore exhibits the outstanding fire-related behavior of phenols, along with better mechanical properties.

CONCLUSION

Modified novolac resins containing benzoxazine rings were synthesized. In this way, higher crosslinking density and lower curing temperatures were obtained compared to novolac resins. Our TGA showed that degradation of these new materials occurs at a slow rate and over a broad range of temperatures, thus being advantageous from the viewpoint of flammability. These benzoxazine systems showed mechanical integrity via DMA. The storage modulus increases with an increasing degree of modification. The flame

TABLE III
UL-94 Flame Test Results for Modified Novolac Resins

| | First Ignition ^a (s) | Dripping ^b | Second Ignition (s) | Dripping | UL-94 Test |
|-----|------------------------------------|-----------------------|------------------------|----------|------------|
| NB2 | 12, 15, 17, 9, 10 | No | 1,0,0,0 | No | V-1 |
| NB3 | 1, 1, 1, 8, 1 | No | 2,1,0,0 | No | V-0 |
| NB4 | 2, 1, 9, 5, 4 | No | 0,8,0,8 | No | V-0 |
| NB5 | 5, 7, 5, 12, 5 | No | 0,0,0,0 | No | V-0 |

^a Time to self-extinguish after ignition. The five numbers are for five separate tests on separately rectangular samples.

^b Indicates that the sample did or did not drip onto the cotton patch.

retardant UL-94 test showed outstanding fire-related properties.

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