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# Catalyzing The Curing Reaction of a New Benzoxazine-Based Phenolic Resin

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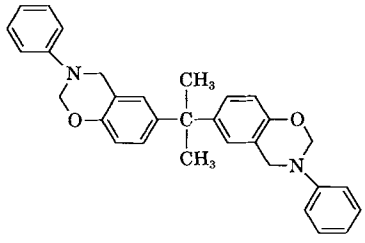
**SYNOPSIS**

The effect of potential catalysts on the curing reaction of a new type of phenolic resins obtained from benzoxazine precursors is studied. These novel resins solve the shortcomings of traditional phenolics because they cure by a ring-opening mechanism that avoids the release of volatiles. Isothermal and nonisothermal differential scanning calorimetry (DSC) data is used to determine the influence of the catalysts on the curing kinetics. Fourier transform infrared (FTIR) spectroscopy is also applied. The benzoxazine chosen for this study is a purified benzoxazine monomer based on bisphenol-A, formaldehyde, and aniline. The as-synthesized benzoxazine precursor is also studied to determine the influence of the dimers and higher oligomers in the curing mechanism. The presence of these structures seems to catalyze the curing reactions. The activation energy and overall reaction order of the as-synthesized precursor are determined. Among the catalysts tested, adipic acid shows the most promising results. For all the cases studied the curing reaction is autocatalyzed up to a diffusion-controlled stage. © 1995 John Wiley & Sons, Inc.

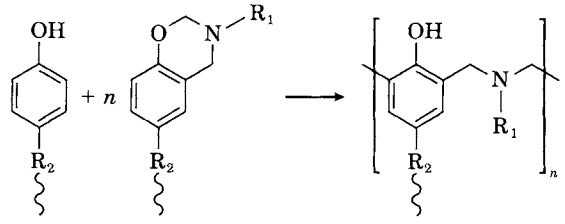
## INTRODUCTION

A novel type of phenolic resins can be prepared by ring-opening reactions of benzoxazine structures.[1] These resins overcome the shortcomings associated with traditional phenolic resins because they cure without releasing any condensation products, and the precursors have low viscosity. They also offer wide design flexibility and, as is determined in this study, they do not need strong acids as catalysts.

The objective of this work was to survey potential catalysts to assist the curing reactions of these new benzoxazine resins, and in this way, make them more attractive from the processing point of view. For this purpose a benzoxazine precursor synthesized from bisphenol-A, formaldehyde, and aniline was chosen. The structure of the monomer is shown below.



Burke et al.[2,3] found that benzoxazine rings react preferentially with the *ortho* positions of free phenolic compounds to form a dimer with a methylene–amine–methylene bridge structure. More recently, Riess et al.[4] demonstrated the high reactivity of the *ortho* position by following the kinetics of monofunctional benzoxazines with 2,4-di-*tert*-butylphenol as catalyst. Therefore, the curing reaction can be drawn as follows. For simplicity, only one functionality is illustrated.



The self-dissociation of the benzoxazine ring could also produce free phenolic structures at elevated temperatures[4] that may act as catalysts for further ring-opening reactions. Benzoxazine rings can also be opened in the presence of certain acids or alkalies.[3] Traditional phenolics use strong acids (e.g., sulfonic acids) or alkalies (e.g., sodium hydroxide, ammonia, and tertiary amines) as catalysts resulting in corrosion of the processing equipment.[5] Thus, mild acid or alkalies will be preferentially

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considered in this study for the final formulation. Because the as-synthesized precursor includes dimers and higher oligomers that have phenolic structures with free *ortho* positions, the reaction kinetics of this as-synthesized precursor will be also studied as a special case of catalyzed curing.

## EXPERIMENTAL

A benzoxazine precursor based on bisphenol-A, formaldehyde and, aniline was synthesized according to the procedure reported by Ning and Ishida.[1] All chemicals were used as received. The bisphenol-A was supplied by the Shell Chemical Company. The formaldehyde (37% by weight in water), aniline, and dioxane were purchased from Aldrich Chemical Co. The precursor obtained is a mixture of monomer, dimers, and other oligomers formed in subsequent reactions during the synthesis. Some of the possible structures in this as-synthesized precursor are shown in Figure 1.

To isolate the monomer, the reaction product was redissolved in ethyl ether, the solids were filtered out, and the solution was washed three times with a 3*N* NaOH aqueous solution in a separatory funnel, and three times with a 2*N* HCl aqueous solution; distilled water was used for the final wash. The ether phase was dried over sodium sulfate and the solvent evaporated in a rotary evaporator. A very fine white powder was obtained. Caution was taken to store the synthesis and purification products in a dry and cold environment ($\sim -4°C$) to ensure that no reaction occurred prior to any experiment.

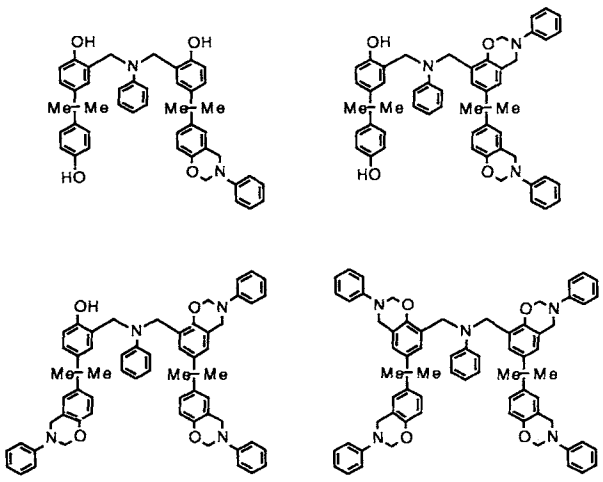

**Figure 1** Some of the possible structures in the as-synthesized precursor (Me = methyl groups).

$^1$H-NMR spectra were taken to check the effectiveness of the separation process described above. The benzoxazine ring content of the as-synthesized precursor was calculated by this technique to be always around 85%. The instrument used was a Varian XL-200, operating at 200 MHz. Deuterated chloroform was used as a solvent and tetramethylsilane (TMS) was used as an internal standard.

A Perkin–Elmer TAS-7 Differential Scanning Calorimeter was used to study the curing kinetics. Indium was used for temperature calibration and nitrogen as the flushing gas. Temperature and power calibration were optimized for the range of 30–300°C. Standard hermetic DSC pans (maximum pressure 3 atm) were used. Sample weights were between 2 and 5 mg because small samples are necessary to ensure isothermal conditions. Isothermal and nonisothermal experiments were conducted.

Nonisothermal experiments on uncured samples were carried out at 5°C/min, from 30 to 300°C. A steady baseline was established before each run by using two empty sample pans with the same heating rates. The reaction is considered complete when the curves leveled off to the baseline and no more drastic changes in heat are observed. Experiments were always performed below 300°C to prevent any possible degradation reactions inside the chamber. After this first heating run, the sample was cooled at 80°C/min to 30°C and a second heating was conducted at 10°C/min to check for complete cure. Purified benzoxazine monomer was used to perform controlled experiments with the potential catalysts. Other nonisothermal experiments on the as-synthesized precursor were performed at different heating rates to determine its activation energy, $E_a$.

For the isothermal experiments with the as-synthesized precursor and the purified monomer with adipic acid, the samples were placed in the cell at 30°C and the temperature was raised to 100°C and kept for 90 s. After thermal stability was reached, the temperature was raised again to the selected value for each isothermal experiment. At the experimental temperature, the instrument achieved stability after 80–100 s. This was determined by the time that the heat readings had variations less than ±0.002 mW. The data acquisition was then initiated. After the exothermic peak, when the DSC curve reached the baseline level again, the sample was cooled rapidly (80°C/min) to 30°C. Further heating of the sample was done at 10°C/min, from 30 to 300°C, to determine the residual heat of reaction.

The areas under the curves were quantified by drawing a straight line extension of both sides of each exotherm. These calculations and the normal-

ization procedures were performed by the DSC software. Sample weights were taken after each test. The weight losses, if there were any, were negligible.

As a first approach several potential catalysts were selected. They were phenols with a free *ortho* position (biphenols and higher functionality phenols: bisphenol-A, 2,2′-dihydroxy biphenyl, poly(*p*-hydroxystyrene), 2,2′-dihydroxybenzophenone, and 2,6-di-*tert*-butyl-*p*-cresol), mild and strong acids [acetic, adipic, sebacic, benzoic, sulfuric, *p*-toluenesulfonic, phosphoric acids, and $BF_3O(C_2H_5)_2$], and mild and strong alkalies (sodium hydroxide, hexamethylene tetramine, and methylamine). They were mixed with the purified monomer at several concentrations (2, 6, 20, and 30 mol %), and cured at 200°C for periods of 5, 10, and 20 min. Those cured samples were crushed, weighed, immersed in tetrahydrofuran (THF) at room temperature for 7 days, and then dried under vacuum (70°C, 8 h). The weight loss was measured to estimate the relative extent of cure of each sample.

The potential catalysts with the best performance based on the curing and solubility tests were selected for nonisothermal experiments. They were mixed with the benzoxazine monomer in THF solutions. The solvent was evaporated under vacuum at 65–70°C for one h. These mixtures were tested within 72 h of preparation.

As an alternative way to analyze the effect of catalysts on the curing, Fourier transform infrared (FTIR) spectra of the isothermal reaction were taken for samples of the pure monomer and the monomer with 6 mol % adipic acid. The spectra were recorded every minute, at a resolution of 2 $cm^{-1}$, coadding eight scans. The instrument used was a Bomem Michelson MB Fourier transform infrared spectrophotometer equipped with a high sensitivity, liquid nitrogen cooled, mercury–cadmium–telleride (MCT) detector and a hot cell with a temperature control of ±1°C. The specific detectivity, $D^*$, of the detector was $1 \times 10^{10}$ cm $Hz^{1/2}$ $W^{-1}$. Nitrogen was used to purge the chamber. Sample preparation involved the dissolution of the benzoxazine with and without adipic acid in THF. Cast dry films between two potassium bromide (KBr) plates were examined. The plates were loaded in a preheated hot cell at the experimental temperature. The hot cell was placed rapidly in the spectrometer. The collection of spectra started exactly 1 min after placing the sample in the hot cell. The reference spectra were taken using exactly the same procedure for two clean KBr plates. Spectra of the monomer and precursor at room temperature were taken between two KBr plates, at a 2-$cm^{-1}$ resolution with 40 scans.

## RESULTS AND DISCUSSION

### Curing Kinetics of As-Synthesized Precursor by DSC

DSC isothermal curves for the as-synthesized benzoxazine based on bisphenol-A, formaldehyde, and aniline, at different temperatures, are depicted in Figure 2. The curves show the same shape as those for the purified monomer and the same trend with temperature.[6] The maximum reaction rate is faster than that of the purified monomer and the onset of the curing reaction occurs sooner at a higher cure temperature. Isothermal tests at temperatures above 180°C are not reported, because the reaction starts prior to data acquisition.

The as-synthesized benzoxazine precursor follows the same trend as the purified monomer[6] regarding the heat evolved during isothermal experiments ($\Delta H_{iso}$) and also the residual heat ($\Delta H_{resid}$) from the scanning experiments made immediately after the isothermal experiments. The higher the cure temperature, the higher $\Delta H_{iso}$ and the lower $\Delta H_{resid}$ (see Fig. 3). The total heat of curing corresponds to the sum of the two $\Delta H$ values mentioned previously[7] and is nearly constant for the cure temperatures studied.

Because a single peak is observed in the DSC curves, it is assumed that there is a single chemical process occurring. However, an overall process formed by two or more simultaneous or very close chemical reactions cannot be ruled out. In addition, it is assumed that all the heat generated is a result of the curing reaction, which is irreversible ring-opening and formation of the methylene bridge. It is further assumed that no reaction takes place before the experiments started, and there is no vola-

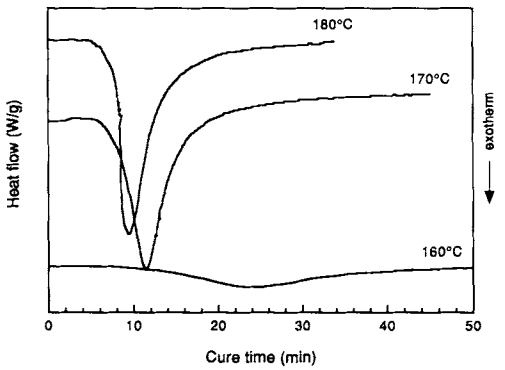


**Figure 2** Curves from DSC isothermal experiments for the as-synthesized precursor at different cure temperatures.

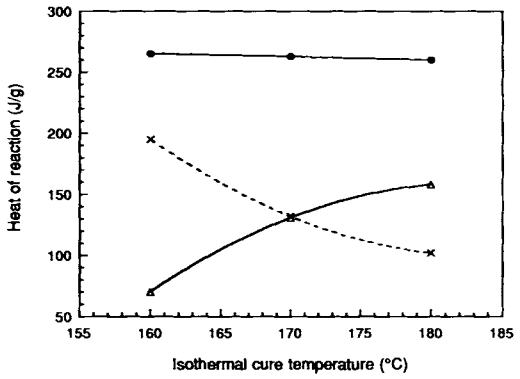


**Figure 3** Heat generated by the curing reaction of the as-synthesized precursor at different isothermal cure temperatures. (△) Heat from the isothermal reaction, (X) residual heat of reaction, and (●) total heat of reaction.

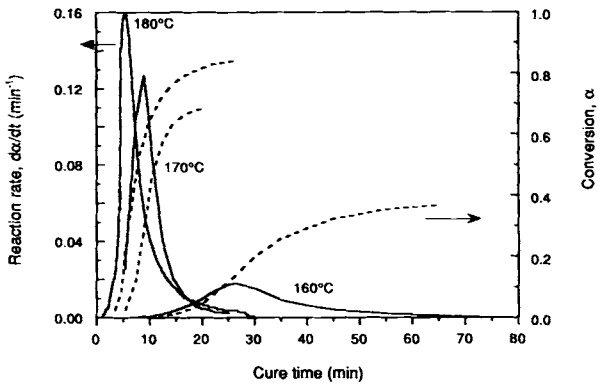


**Figure 4** (---) Conversion and (—) reaction rate as a function of time for the as-synthesized precursor at different isothermal cure temperatures. From left to right: 180, 170, and 160°C.

tilization in sample pans that can affect the reaction kinetics or reaction exotherm. Thus, it is feasible to relate the area under the exotherm curves to the heat of reaction.

From the curves of reaction rate and conversion versus time shown in Figure 4, it is evident that the curing reaction for the as-synthesized precursor is autocatalyzed. The rate of reaction does not have a maximum at time zero. In addition, the conversion curves have an inflection point when plotted against cure time.[8] Conversion rate, induction time, and final conversion were expected to change with cure temperature.

According to other authors, the autocatalytic nature of the reaction kinetics of these resins can be explained by the generation of free phenol groups while the benzoxazine ring starts to open. These groups can actually accelerate further ring opening.[1,4]

Furthermore, Figure 4 shows that the maximum reaction rate occurs at 14% of conversion for 160°C and at 27% for 170 and 180°C. These values are fairly close to what is typically found for autocatalyzed reactions (maximum reaction rate between 20 and 40% conversion).[8-10] However, the fact that the maximum reaction rate does not always occur at the same conversion for all cure temperatures may indicate that certain structural rearrangements are occurring at higher temperature, as was suggested for the purified monomer.

Comparison of the conversion and reaction rate of the purified monomer[6] and the as-synthesized precursor under isothermal conditions is illustrated on Figure 5. The conversion of the precursor at all times and the final conversion is greater than that of the purified monomer. That is due to the presence of phenolic structures with a free *ortho* position that can act as catalysts for the ring-opening reaction.

Sourour and Kamal[7] showed that by extrapolating a semilogarithmic plot of $1 - \alpha_{iso}$ (where $\alpha_{iso}$ is the maximum isothermal conversion) against isothermal cure temperature, the temperature below which curing of the unreacted resin must take place in the glassy state, $T_{c0}$, can be obtained. Figure 6 shows this plot and the extrapolation to an isothermal conversion equal to unity. The value obtained for $T_{c0}$ is 153°C, which coincides with the value obtained for the monomer data.[6] Because no significant reaction will occur below this temperature, $T_{c0}$ is an important value to set a temperature limit for storage and processing purposes.[7,8]

Most of the methods to quantify kinetic parameters require prior knowledge of the reaction mech-

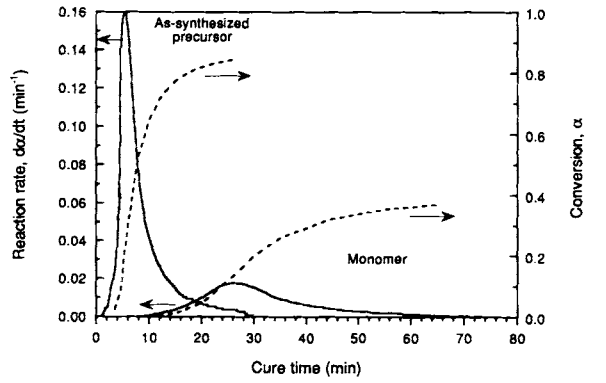


**Figure 5** Comparison of the (---) conversion and (—) reaction rate as a function of time for the benzoxazine monomer[6] and as-synthesized precursor (isothermal cure temperature = 180°C).

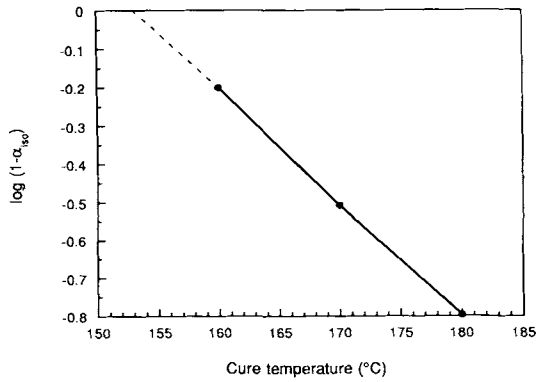


**Figure 6** Unreacted fraction of the as-synthesized precursor after isothermal experiments as a function of isothermal cure temperature.

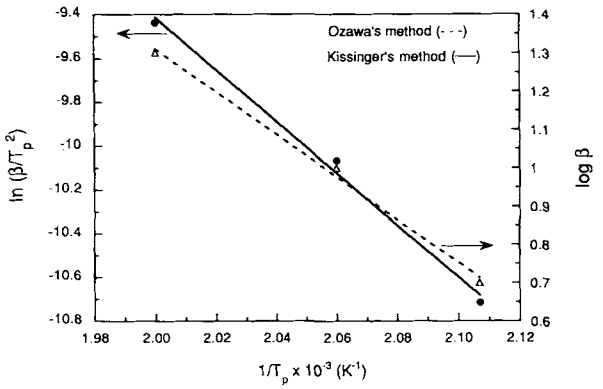


**Figure 8** Representation of the Ozawa[12] and Kissinger[13] methods to calculate activation energy from nonisothermal data of the as-synthesized precursor ($T_p$ = temperature at maximum reaction rate; $\beta$ = scanning rate).

anism,[8,11] but this information is not yet available for the benzoxazine resins. Nevertheless, there are some methods that can be used to calculate kinetic parameters, such as activation energy, without involving any mechanistic knowledge of the system. For that purpose, nonisothermal DSC experiments at various heating rates were performed and their results are presented in Figure 7. By using this data according to the methods of Ozawa[12] and Kissinger,[13] the activation energy, $E_a$, can be calculated without any consideration of the reaction mechanism. The plots are shown in Figure 8. The $E_a$ values obtained were similar: 107 kJ/mol (Ozawa) and 99 kJ/mol (Kissinger).

Table I shows the differences between the total heat of reaction, $\Delta H_{RXN}$, calculated from nonisothermal experiments at different heating rates. The results for the monomer[6] are included for comparison purposes. For the as-synthesized precursor, the $\Delta H_{RXN}$ averaged from experiments at 5, 10, and 20°C/min is 281 J/g. This is the value used for the calculations of conversion. The average of $\Delta H_{RXN}$ from isothermal tests (calculated by adding the values of $\Delta H_{iso}$ and $\Delta H_{resid}$) is 261 J/g, which is fairly close to the average of the nonisothermal experiments.

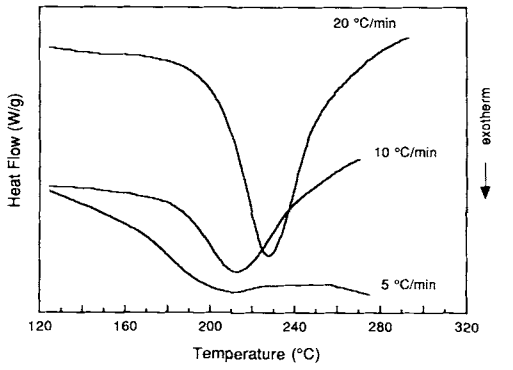


**Figure 7** Nonisothermal DSC curves for the as-synthesized precursor at various heating rates.

It is important to mention here that the accuracy of the kinetic information obtained through isothermal and nonisothermal DSC depends on the reliability of the value of $\Delta H_{RXN}$. Theoretically, $\Delta H_{RXN}$ is the total heat liberated for a material when it is taken from an uncured state to a complete cure; thus, it is expected to be constant for each thermoset. However, it is recommended that this value be calculated from nonisothermal tests at different heating rates, preferably 2–20°C/min.[8,14] For isothermal experiments, there is a risk of unrecorded heat evolving at the beginning of the tests or falling within the detection limit of the calorimeter at very slow reaction rates. In any circumstance, accurate measurements of $\Delta H$ by scanning tests require that a baseline can be drawn between a discernible onset and end of the cure reaction, which is the case for these experiments.

Furthermore, if $\Delta H_{RXN}$ cannot be confirmed by another complementary technique, it is uncertain that the actual ultimate heat of reaction is being measured.[15] Even with postcure resulting in no residual exotherm, some systems never reach 100% conversion. This is because a certain mobility in the network is required to obtain total conversion, and the system cannot achieve full conversion in spite of the increased temperature.[16]

Having established that the system under study is autocatalytic, it was assumed that the reaction can be described by the following general expression for autocatalyzed systems:

**Table I Summary of Results Obtained from Nonisothermal Experiments**

| | Catalyst Added | Scanning Rate (°C/min) | Exotherm Peak (°C) | Onset Exotherm (°C) | $\Delta H$ (J/g) |
|---|---|---|---|---|---|
| Monomer[6] | None | 5 | 226 | 188 | 313 |
| | | 10 | 241 | 176 | 321 |
| | | 20 | 255 | 209 | 313 |
| | 6 mol % adipic acid | 5 | 188 | 150 | 322 |
| | 20 mol % adipic acid | 5 | 182 | 149 | 204 |
| | 30 mol % adipic acid | 5 | 176 | 144 | 203 |
| | 6 mol % sebacic acid | 5 | 203 | 154 | 352 |
| | 6 mol % 2,2′-dihydroxybiphenyl | 5 | 209 | 155 | 328 |
| Precursor | None | 5 | 202 | 142 | 309 |
| | | 10 | 212 | 125 | 237 |
| | | 20 | 228 | 145 | 298 |

$$d\alpha/dt = k(1 - \alpha)^n(\alpha)^m \quad (1)$$

where $\alpha$ is the fractional conversion, $k$ is the kinetic rate constant, and $m + n$ is the overall reaction order. In general, it can be assumed that the specific heat is constant or that it has a linear variation with the scanning temperature in order to generate kinetic data from nonisothermal experiments.[11] In addition, the reaction rate was considered to have an Arrhenius temperature dependence. Thus, the following expression can be written:

$$d\alpha/dt = A \cdot \exp(-E_a/RT)(1 - \alpha)^n\alpha^m \quad (2)$$

where $A$ is the preexponential or frequency factor.

By expressing the scanning rate as $\beta = dT/dt$ and taking the natural logarithm of both sides of eq. (2), we obtain:

$$\ln(\beta d\alpha/dT) = \ln(A) - (E_a/RT) + [n \cdot (1 - \alpha)] + (m \cdot \alpha) \quad (3)$$

By a multilinear regression the values of $A$, $E_a$, $m$, and $n$ for the as-synthesized precursor can be obtained. Those values are presented in Table II. The values of $E_a$ agree with the results obtained by Ozawa and Kissinger.

From the plots of $d\alpha/dt$ versus $(1 - \alpha)^n\alpha^m$ for the as-synthesized precursor at different isothermal temperatures (the values of $m$ and $n$ were obtained through the multilinear regression of the nonisothermal data and they were assumed constants with temperature), the vitrification times can be obtained.[8] They are presented in Table III. These values are considerably smaller than those for the purified monomer.[6] Thus, as for the purified monomer, the model proposed is valid for the earlier stages of cure. The behavior deviates from the model when the reaction is diffusion controlled.

## Effect of Potential Catalysts by Solubility and DSC Tests

In the preliminary tests performed to choose a suitable catalyst for the curing, monomer samples were heated at 200°C for several controlled periods of time with different concentrations of the potential cat-

**Table II Values Obtained from Multilinear Regression with Nonisothermal Data**

| System | Scanning Rate (°C/min) | Activation Energy (kJ/mol) | $n$ | $m$ |
|---|---|---|---|---|
| Monomer[6] | 5 | 93 | 1.6 | 1.0 |
| | 10 | 80 | 1.2 | 0.8 |
| | 20 | 57 | 1.3 | 1.1 |
| As-synthesized precursor | 5 | 113 | 1.6 | 0.2 |
| | 10 | 109 | 1.1 | 0.2 |
| | 20 | 100 | 1.0 | 1.0 |

**Table III Vitrification Times of Monomer[6] and As-Synthesized Precursor Obtained from Isothermal Experiments**

| Temperature (°C) | Vitrification Times for (min) | |
|---|---|---|
| | Monomer[6] | Precursor |
| 160 | 75 | 26 |
| 170 | 46 | 9 |
| 180 | 26 | 5 |
| 190 | 18 | — |
| 200 | 10 | — |
| 210 | 7 | — |

alysts. Three main behaviors were observed upon immersion of these samples in THF. The first phenomenon noticed was the total dissolution of the sample, which indicates that no chemical network was formed within the experimental conditions. That was the case for potential catalysts such as bisphenol-A, 2,2′-dihydroxybenzophenone, 2,7-dihydroxynaphthalene, poly(*p*-hydroxystyrene), and benzoic acid. The second behavior was characterized by the curing and degradation of the sample, evidenced by the dark color of the cured samples and their poor mechanical integrity. Potential catalysts that resulted in this behavior were: $BF_3(OC_2H_5)_2$, sulfuric acid, acetic acid, sodium hydroxide, and the mixture of *p*-toluenesulfonic acid, and *o*-phosphoric acid. It is possible that the mixing and curing conditions adopted (suitable for processing) may have been too severe for these potential catalysts. The third set of results corresponded to the tests that produced cured samples with no or minimal dissolution after immersion in THF; those were samples cured with adipic acid, sebacic acid, 2,2′-dihydroxy biphenyl, and 2,6-di-*tert*-butyl-*p*-cresol. From these, adipic acid was chosen to be the most suitable catalyst because it has a very low dissociation constant; therefore, it is unlikely to be corrosive when in contact with processing machines and other instruments. Also, it has a relatively low melting point (153°C), it is inexpensive, nontoxic, and readily available.

Isothermal experiments were performed on uncured samples of benzoxazine monomer with 6 mol % of adipic acid as catalyst. For experiments at temperatures higher than 160°C, the reaction could not be monitored because the cure exotherm had already appeared when data acquisition was to begin. For the cases at 200 and 210°C, the reaction rate was in its decay (diffusion-controlled stage) by the time that the experiment began, which means that it started

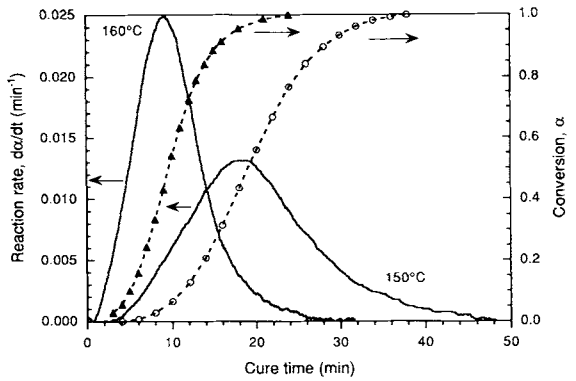


**Figure 9** Comparison of the (---) conversion and (—) reaction rate as functions of time for samples of monomer with 6 mol % adipic acid at two different isothermal cure temperatures: (○) 150 and (▲) 160°C.

and reached its maximum rate within the first 100 s of heating.

Figure 9 shows the isothermal reaction rate and conversion curves for monomer samples with 6 mol % of adipic acid at 150 and 160°C. As expected, both the onset and the maximum of the exotherm occur sooner at 160°C; in addition, the area under the curve is larger in this case, indicating that the conversion is also greater (assuming that all the heat generated comes from the curing reaction and the catalyst's contribution is negligible).

The effect of the addition of the catalyst can be observed in Figure 10, where the reaction rate curves for the pure monomer[6] and the monomer with 6 mol % adipic acid are shown. For the sample with adipic acid, the maximum of the exotherm appears 1 h prior to that for the pure monomer. The onset of the exotherm also occurs about 10 min sooner.

The results from isothermal experiments regard-

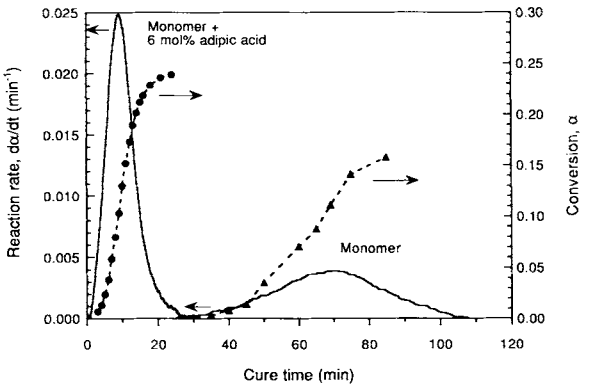


**Figure 10** Effect of the addition of adipic acid on the (---) conversion and (—) reaction rate of the benzoxazine monomer (isothermal cure temperature = 160°C).

ing the dependence of reaction rate with time and conversion for samples with adipic acid is indicative of an autocatalytic system. That implies that the presence of the catalyst is just contributing to the ring-opening process, and the species that produce autoacceleration are still being formed.

Figure 11 shows the conversion as a function of temperature for the purified benzoxazine monomer,[6] several catalysts, and the as-synthesized precursor. The presence of structures with free *ortho* positions reduces the induction time of the curing reaction at levels comparable with the addition of 6 mol % adipic acid. However, the rate (slope) is lower for the as-synthesized precursor than for the purified monomer with catalysts and even for the purified monomer without a catalyst. This is likely due to the higher acidity of the adipic acid over the phenolic structures and diffusion problems caused by the higher viscosity of the as-synthesized precursor.

The results obtained from nonisothermal tests for the purified monomer with different concentrations of catalysts are summarized in Table I (see also Fig. 12). As expected, the onset and the maximum temperature of the exotherm, and the heat of reaction are smaller when the catalyst is present. The larger the amount of catalyst present, the more pronounced is the effect. Figure 13 depicts the effect of catalyst concentration on the conversion. The efficiency of the adipic acid over sebacic acid and 2,2-dihydroxybiphenyl as catalyst is also shown in Table I and Figure 11.

For some of the systems with catalysts, the precise determination of the area under the DSC curve was difficult because the curves did not level off at the initial heat value once the reaction was no longer detected (e.g., Fig. 12). The presence of water (all

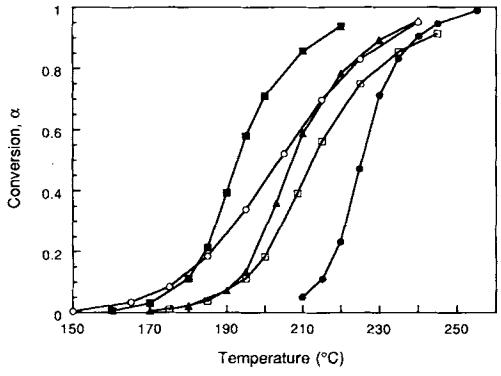


**Figure 11** Comparison of the conversion as a function of temperature for the (○) as-synthesized precursor, (●) purified monomer, and the monomer with three different catalysts at 6 mol %: (■) adipic acid, (▲) sebacic acid, and (□) 2,2'-dihydroxybiphenyl.

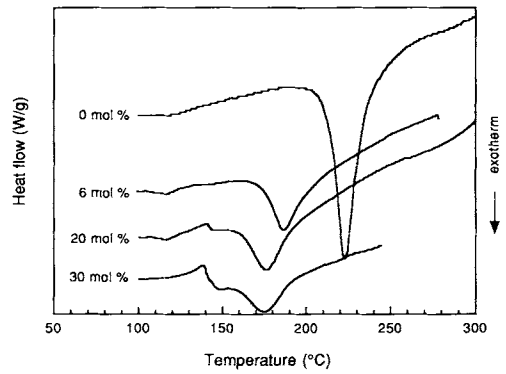


**Figure 12** Nonisothermal DSC curves of the benzoxazine monomer at different concentrations of adipic acid.

three catalysts tested absorb moisture rapidly) or residual solvent can contribute to it.

Usually corrections must be made to account for the heat of catalyst decomposition, but in this case the catalyst does not decompose. The only precaution taken was to ensure that the melting peak of the catalyst did not overlap with the reaction exotherm. In the cases when the catalyst melting peak falls within the range of the exotherm, caution was taken to check that the peak area was negligible with respect to the area of the cure exotherms.

Some non-isothermal DSC tests have been done with small amounts of $BF_3(OC_2H_5)_2$ (<2 mol %) and the exotherm maximum was lowered to 124°C; however, the conversion appears to be lower than for other catalysts. Further work needs to be done based on these promising results.

## Effect of Catalyst by FTIR

The FTIR spectra of the benzoxazine monomer and as-synthesized precursor are presented in Figure 14.

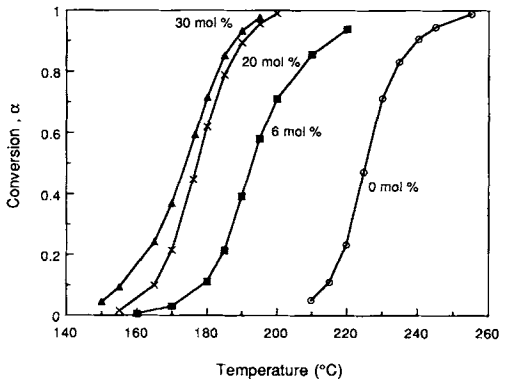


**Figure 13** Conversion as a function of temperature of the benzoxazine monomer with different concentrations of adipic acid.

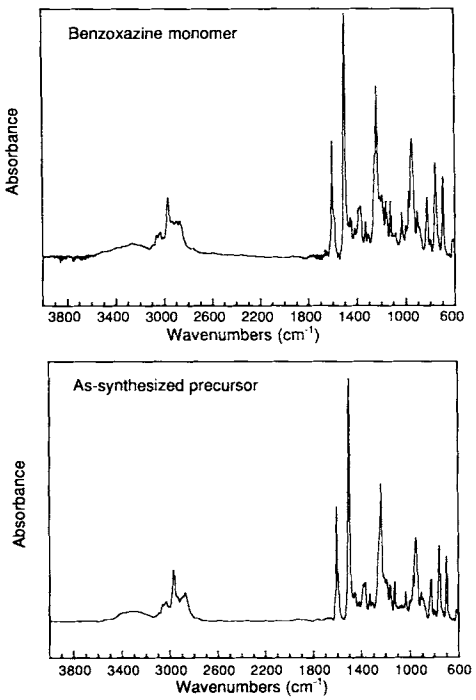


**Figure 14** FTIR spectra of the benzoxazine monomer and the as-synthesized precursor.

Work has been done on the complicated peak assignments.[17]

If the curing reaction is followed by taking consecutive FTIR spectra at a certain time interval, we can determine the spectral features that change upon curing. For example, by looking at the region between 1545 and 1340 $cm^{-1}$, it is observed that the band at 1498 $cm^{-1}$, which corresponds to the in-plane carbon–carbon stretching of the trisubstituted benzene ring, decreases upon reaction. The band at 1478 $cm^{-1}$, the in-plane carbon–carbon stretching of the tetrasubstituted benzene ring, is expected to increase with curing time as the methylene bridges

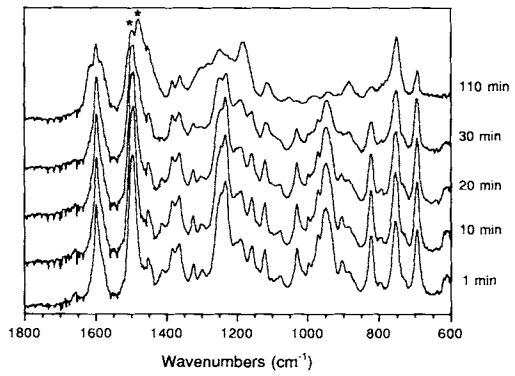


**Figure 15** FTIR spectra of the benzoxazine monomer during isothermal curing at 180°C.

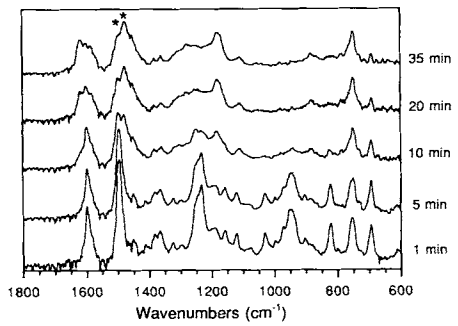


**Figure 16** FTIR spectra of the benzoxazine monomer during isothermal curing at 210°C.

form in the free *ortho* positions of the phenolic structures. Because the thickness of the sample in the IR beam keeps decreasing during the reaction due to the low viscosity of the monomer, an internal reference band is needed for quantitative analysis. The carbon–hydrogen symmetric deformation at 1383 $cm^{-1}$, assigned to the methyl group of the bisphenol-A, can be used for that purpose, as this group is sufficiently removed from the reacting groups.

Calculations of the areas under those peaks were intended to quantify kinetic parameters, but the overlapping becomes more pronounced as the curing proceeds. Figures 15 and 16 qualitatively illustrate the effect of temperature on the reaction. The top spectrum shown in each case is the spectrum after which no more changes are detected. Notice the dramatic difference in the curing behavior of both cases. At 10 min, the reaction at 180°C has not begun; but at 210°C, the peak at 1478 $cm^{-1}$ (tetrasubstituted benzene ring) has grown considerably. At 20 min, the reaction at 210°C is almost in the last stage; but at 180°C a small shoulder at 1478 $cm^{-1}$ is starting to appear, indicating the onset of the network formation.

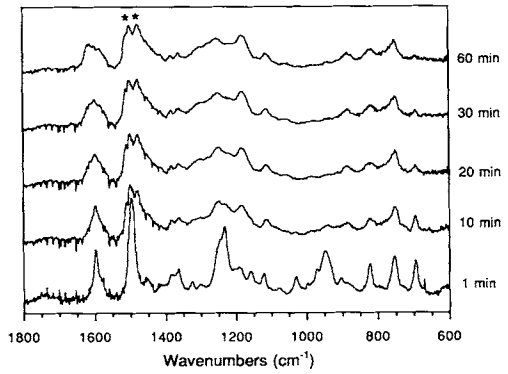


**Figure 17** FTIR spectra of the benzoxazine monomer with 6 mol % of adipic acid during isothermal curing at 180°C.

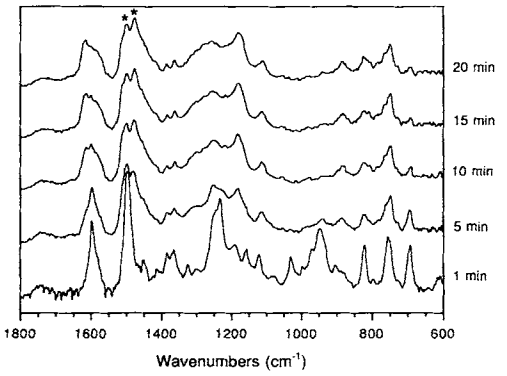


**Figure 18** FTIR spectra of the benzoxazine monomer with 6 mol % of adipic acid during isothermal curing at 210°C.

Figures 17 and 18 show two sets of spectra taken at two different isothermal cure temperatures that illustrate the effect of adipic acid on the reaction kinetics. As seen for the purified monomer, the curing is accompanied by a reduction of the peak at 1498 $cm^{-1}$ and the appearance and growth of the peak at 1478 $cm^{-1}$. As expected, these changes occur faster in the presence of the catalyst.

Comparing the last spectra from Figure 16 and Figure 18, it seems that the reaction did not go to completion when catalyst was present, based on the changes of the bands at 1498 and 1478 $cm^{-1}$. The same feature can be recognized from the last spectra of Figures 15 and 17. It could be that the acid catalyst is inducing side reactions that are hindering the crosslinking. The presence of water in the catalyst may also produce this effect by blocking reactive intermediates during the curing.[3]

## CONCLUSIONS

The curing behavior of the as-synthesized benzoxazine precursor studied is autocatalytic and very similar to that of the purified monomer. The autocatalyzed model proposed for the curing is valid up to the diffusion-controlled stage. The activation energy values are between 99 and 107 kJ/mol, and the overall reaction order is approximately 2. The presence of the phenol structures with free *ortho* positions in the as-synthesized precursor have a catalytic effect on the curing reaction; that is, it reduces the reaction induction time and increases the reaction rate.

The curing of the benzoxazine precursors with catalysts can effectively decrease the induction time for curing and increase the reaction rate. Among the catalysts tested, adipic acid shows the best performance within the time–temperature range of interest for processing with weak acidity. Sebacic acid and 2,2′-dihydroxybiphenyl can also be used as catalysts.

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