Molecular Origin of Unusual Physical and Mechanical Properties in Novel Phenolic Materials Based on Benzoxazine Chemistry

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ABSTRACT: The effect of temperature on hydrogen bonding was investigated by measuring the integrated infrared absorbance of various hydrogen-bonding modes as a function of temperature. It was found that conformationally preferred hydrogen-bonding modes maintain constant intensities over the wide temperature ranges studied for both polybenzoxazines and a novolac-type phenolic resin. In particular, the O— — —H— — —N hydrogen bond shows strong bonding that does not change over the temperature range. On the other hand, statistically distributed hydrogen bonding is more sensitive to the temperature change and its infrared intensities start decreasing around the β-transition of polybenzoxazines. The unusual physical and mechanical properties of polybenzoxazines, including volumetric expansion upon polymerization, high moduli, and high glass transition temperatures, are explained based on the complex hydrogen bonding. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1299–1306, 1998

Key words: polybenzoxazine; phenolic resin; hydrogen bonding; infrared spectroscopy

INTRODUCTION

The formation of a hydrogen bond in a compound modifies a great many physical and chemical properties as described by Pimentel and McClellan.[1] Many researchers have studied hydrogen bonding in phenolic compounds.[2–4] Recently, benzoxazines, a new class of phenolic materials, were synthesized in our laboratory and unusual properties were observed.[5] Benzoxazine resins have been found to exhibit a near-zero shrinkage or volumetric expansion upon curing,[5,6] which is attractive for many applications.[7] It was also found that some polybenzoxazines have high glass transition temperatures even though they have low crosslink densities. A dilution study of hydrogen bonding in model benzoxazine compounds by Dunkers et al. provided evidence of the existence of hydrogen bonding.[8]

The purpose of this work was to study the temperature dependency of various hydrogen-bonding infrared modes to further the fundamental understanding of the hydrogen-bonded structure in the polybenzoxazine molecules. It is of special significance since several unusual physical and mechanical properties of polybenzoxazines are hypothesized to be strongly linked to hydrogen bonding.

EXPERIMENTAL

Paraformaldehyde, aniline (99.5%), and bisphenol-A (polycarbonate grade) were purchased from Aldrich Chemical Co. 6,6′-Bis(2,3-dihydro-3-phenyl-4H-1,3-benzoxazinyl)ketone and aniline, and bisphenol-A and methylamine or aniline-based benzoxazine were synthesized. The chemical structures and their abbreviated names are shown below:
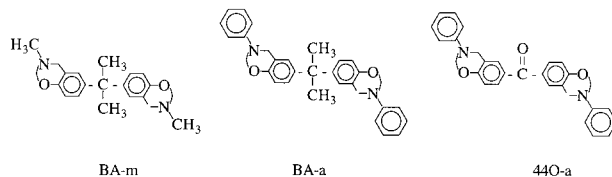
A detailed description of the synthesis procedures was presented elsewhere.[9,10] The as-synthesized 44O-a was cured at 290°C in air for 4 h. BA-m, BA-a, and the novolac-based phenolic resin were cured in air at 180°C for 3, 3, and 4 h, respectively.

Infrared spectra were recorded on a Fourier transform infrared spectrometer (Bomem Michelson MB 110) which is equipped with a narrow band pass mercury–cadmium–telluride (MCT) detector with specific detectivity, W^*, of 1×10^{10} $cmHz^{1/2} W^{-1}$. The spectra were recorded at a resolution of $4 cm^{-1}$ and were obtained by placing each sample in a variable temperature hot cell. The spectra were collected at 20°C increments with an equilibrium time of 15 min at each temperature. Heavily overlapped bands were curve-resolved using a mixed Lorentzian–Gaussian
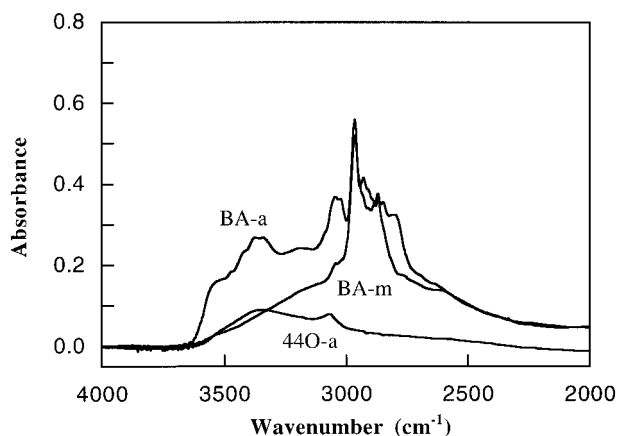

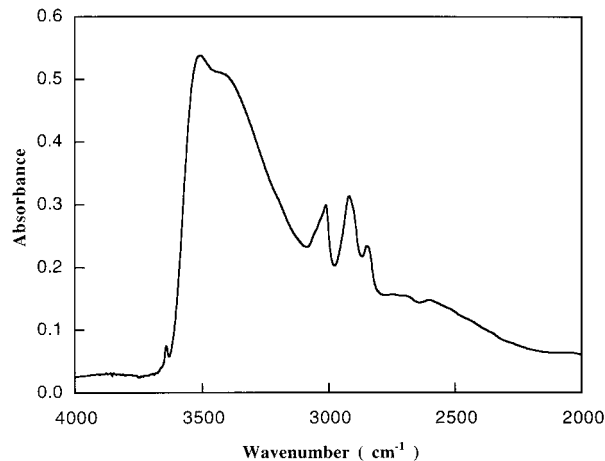**Figure 1** Infrared spectra of cured 44O-a, BA-a, and BA-m.

Figure 2 Infrared spectrum of cured novolac-type phenolic resin.

function. Calculation was continued until the least-squares curve fitting converged. Reproducibility of the curve resolving was excellent for the bands other than the band termed the chelated hydrogen bond near $2700 cm^{-1}$. Since these chelated hydrogen-bonded OH bands are believed to be the combination bands with a lower-frequency band, the ordinary Lorentzian–Gaussian band shape is believed to be inapplicable.

RESULTS AND DISCUSSION

Hydrogen bonding in a traditional phenolic resin and polybenzoxazines, 44O-a, BA-m, and BA-a, was investigated by an infrared temperature study. All the hydrogen-bonding modes of the polybenzoxazines, shown in Figure 1, are broad and heavily overlapped compared with the infrared spectrum of a polymerized novolac-type phenolic resin shown in Figure 2. A curve analysis program was used on a baseline-corrected spectrum to resolve these overlapped bands. Thus, the frequencies cited in this article are those of the curve-resolved spectra. Hydrogen bonding in novolac produces an absorption in three different regions of the infrared spectrum. These regions include the bands at 3539, 3467, and $3351 cm^{-1}$. For polybenzoxazines, five regions around 3562, 3530–3522, 3459, 3344–3311, and $2700 cm^{-1}$ are of interest.

Our band positions agree well with the previous work for model compounds.[2–4,8] No intensity comparisons were made between bands with different frequencies since extinction coefficients of

the OH stretching modes vary dramatically between bands with different frequencies. Hydrogen bonding of the type, O— — —H— — —N, sometimes called chelated hydrogen bonding, has been reported to form multiple combination bands with the lower-frequency hydrogen-bond vibration in the far-infrared region.[11] Thus, it is not possible to use a single lineshape to fit these multiple bands and, therefore, the total area under the broad complex-shaped curve was determined.

It is known that when a compound, R—X—H, forms a hydrogen bond, R—X—H— — —Y, the absorption band due to the X—H stretching mode usually shows a frequency shift, $\Delta \nu$ ($\nu_{\text{free OH}} - \nu_{\text{hydrogen-bonded}}$), an increase in bandwidth at half-height, $\nu_{1/2}$, and an increase in the integrated intensity, B, of the band. A correlation of these factors was established by Huggins and Pimentel[12] by a systematic study of the spectral changes accompanying hydrogen bonding in various solutions. They discussed two systems of hydrogen bonding: hydrogen-bonded complexes and hydrogen-bonded polymers. For both systems, the relationship between the frequency shift and bandwidth change caused by hydrogen bonding is linear. This correlation is applicable in a wide variety of hydrogen-bonded species, but is inapplicable for intramolecularly hydrogen-bonded complexes which are more restricted and display much narrower bandwidths than those of intermolecularly associated species.[12]

A technical difficulty arises as to how inter- and intramolecular hydrogen bonding can be distinguished in thermosetting resins, since no intermolecular hydrogen bonds can exist for infinite molecular weight polymers. However, when the local structure of these hydrogen bonds are examined, there can be roughly two types of hydrogen bonds: One is the hydrogen bonds that are favored by a low-energy conformation with a narrow structural distribution, such as the six-membered ring structure shown below. In this structure, the OH group is strongly hydrogen-bonded to the nitrogen atom of the Mannich base:
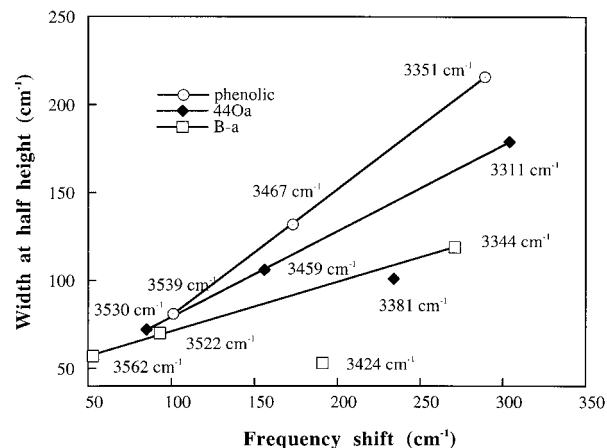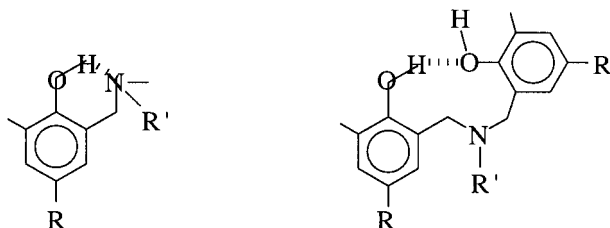

Figure 3 Width at half-intensity as a function of frequency shift of (○) novolac-type phenolic resin, (◆) 44O-a, and (□) BA-a.

These structures are *conformationally preferred hydrogen bonds*. To avoid confusion between these two types of hydrogen bonds, the six-membered ring structure is called the chelated hydrogen bond.

The other type is more opportunistic and the structure of these hydrogen bonds are more statistically distributed and should have a wider absorbance band. This type of hydrogen bond will be called a *statistically distributed hydrogen bond*. The designation of inter- and intramolecular hydrogen bonds will be used only for noncrosslinked systems.

For the phenolic resin (Fig. 3), a linear relationship between $\Delta \nu$ and $\nu_{1/2}$ is obtained, indicating that these bands are of similar origin. However, Carins and Eglinton[2] reported that, for the dimer novolac, the band around 3470 cm^{-1} and, for the trimer system, the band around 3390 cm^{-1} were assigned to the intramolecular hydrogen bonds. This band at 3467 cm^{-1} of the phenolic resin lies on the straight line with the other bands that are assigned to be statistically distributed hydrogen bonding.

Similar to novolac phenolic resin, the polybenzoxazines also exhibit a linear relationship as shown in Figure 3 except for the bands at 3381 cm^{-1} for 44Oa and 3424 cm^{-1} for BA-a. These bands are attributed to conformationally preferred hydrogen bonding. Thus, there are at least two kinds of hydrogen bonding in polybenzoxazines not including chelated hydrogen bonding.

To verify that the material did not degrade over the temperature range of interest, the integrated absorbance of the C—H out-of-plane defor-
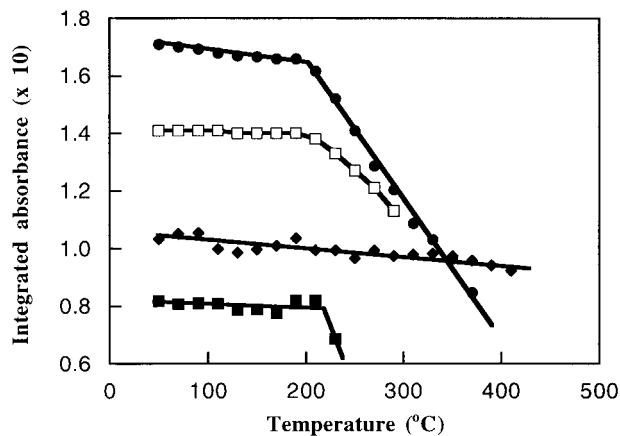
Figure 4 Integrated absorbance of the C—H out-of-plane deformation of (●) phenolic resin, (◆) 44O-a, (■) BA-m, and (□) BA-a.

Figure 5 Integrated absorbance as a function of temperature of chelated hydrogen bonding of (◆) 44O-a and (□) BA-a.

mation was measured as a function of temperature. The study in this article was limited to the temperature range below the sudden change of the integrated intensity as shown in Figure 4. The intensity change in the C—H band may be due to the degradation of the material or may also be the result of a change in the force constant caused by conformational changes. These phenomena are beyond the interest of this study; however, the majority of the intensity lost is recovered upon cooling, implying that the sudden intensity changes in this temperature range are not due to degradation. The starting temperature of the study for all materials was 50°C. The final temperature for the phenolic resin was 210 and 350°C for 44O-a and 190°C for both BA-a and BA-m. These temperatures are very close to the glass transition temperatures of the respective materials, and, thus, this study is restricted mostly to the phenomena in the glassy region where it is unlikely that these materials degrade.

Dunkers et al. found that chelated hydrogen bonding between hydroxyl and amine groups exists in benzoxazine model compounds and produced an IR band around 2700 cm^{-1}.[8] Their X-ray crystallographic study of the model benzoxazine dimer indeed strongly supports the possibility of intramolecular hydrogen bonding. The band around 2700 cm^{-1} also appears in the polymeric form of benzoxazine. The integrated absorbance of this hydrogen bond is almost constant over a wide temperature range from 50 to 350°C for 44O-a and from 50 to 190°C for BA-a, as shown in Figure 5. It is important not to overinterpret the
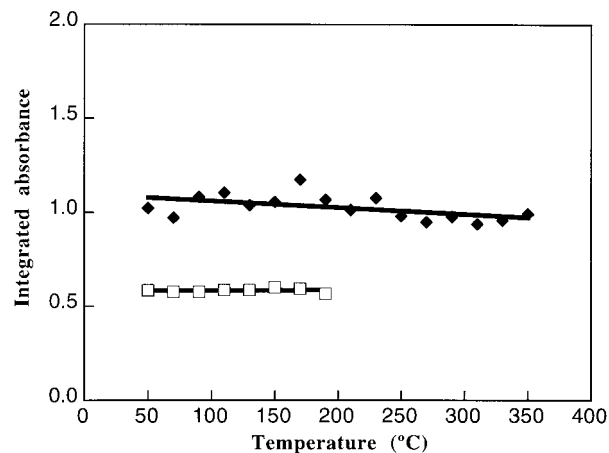
intensity change as a function of temperature since the extinction coefficient of the infrared band could change as a function of temperature without a change in concentration.

The integrated intensity of the conformationally favored, six-membered hydrogen bonding other than the chelated hydrogen bonding described above is shown in Figure 6. The intensity of this hydrogen-bonding mode is not as stable as is the chelated hydrogen bonding as a function of temperature.

Statistically distributed hydrogen bonding has also been observed in the polybenzoxazines at frequencies around 3344–3311 cm^{-1}. As shown in
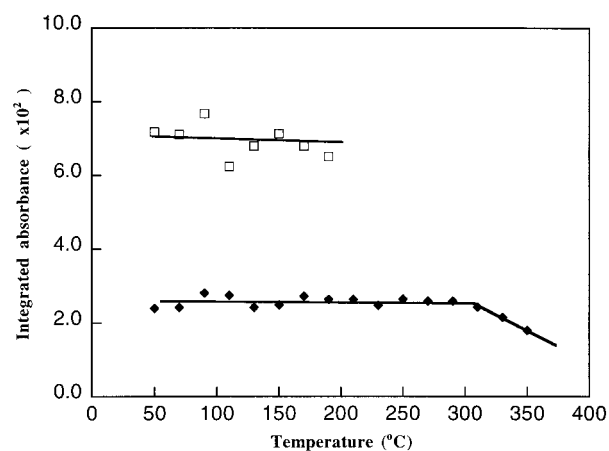

Figure 6 Integrated absorbance of conformationally preferred hydrogen bonding as a function of temperature of (◆) 44O-a and (□) BA-a.
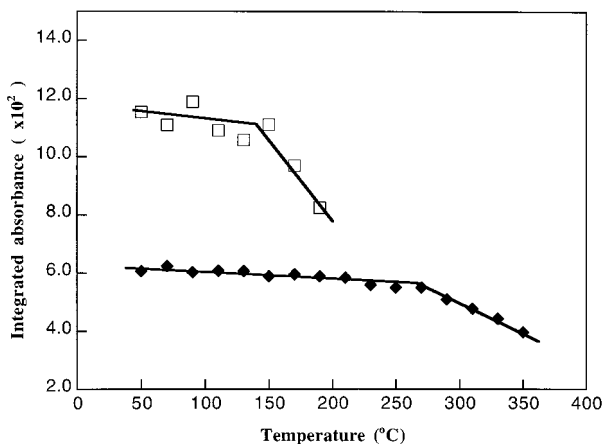
Figure 7 Integrated absorbance of statistically distributed hydrogen bonding as a function of temperature of (◆) 44O-a and (□) BA-a.

Figure 8 Integrated absorbance of nearly free OH as a function of temperature of (◆) 44O-a and (□) BA-a.

Figure 7, the integrated absorbance decreases as the temperature increases for both 44O-a and BA-a. The integrated absorbance of 44O-a is almost constant up to 250°C and then decreases beyond 250°C. Compared to 44O-a, the hydrogen bonding of BA-a decreases faster. This can be explained by the stiffer backbone of 44O-a than that of the bisphenol-A backbone of BA-a. Ning and Ishida[13] studied the effect of molecular structure on the dynamic mechanical properties of polybenzoxazines and the β-transitions of 44O-a, BA-a, and BA-m are centered around 115, 75, and 60°C, respectively. As the temperature increases, the hydrogen bonds are disturbed due to the short movement of the backbone. 44O-a has a stiffer backbone chain than has BA-a or BA-m and, therefore, has a higher β-transition temperature and thus a greater stability of the hydrogen bonds. These β-transitions are observed in wide temperature ranges; the sudden intensity changes occur close to the higher end of the transitions.

Upon increasing temperature, hydrogen bonds are broken and yield a greater free OH component as the integrated absorbance of nearly free OH bonds increases as shown in Figure 8. The T_g of 44O-a is 350°C and that of BA-a is 170°C. From Figure 8, the intensity increase of the nearly free OH modes occurs at temperatures that are well below the glass transition temperatures of the respective polymers and are in the range of the β-transition of these polymers. This supports the importance of the β-transition on hydrogen bonding.
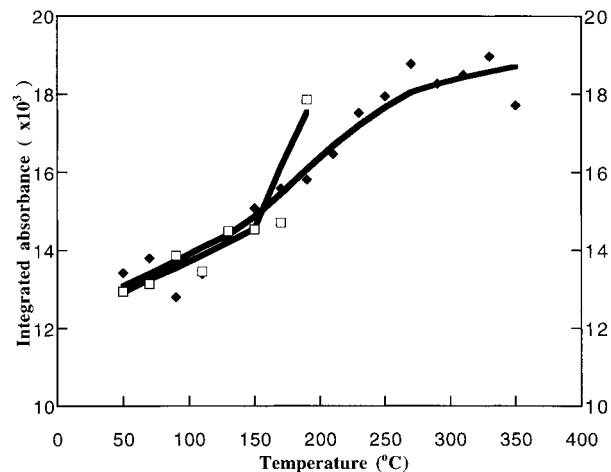
The integrated absorbances of the hydrogen-bonding modes of phenolic resin are shown in Figure 9 as a function of temperature. The intensity reduction of the statistically distributed hydrogen bonding of the phenolic resin is low, probably due to a highly crosslinked structure. Any transitions below the T_g cannot be easily observed. Upon increasing temperature, a slight increase in absorbance of the nearly free OH band can be observed. Interestingly, the band at 3467 cm^{-1} (the maximum is observed at 3450 cm^{-1}) behaves similar to other bands as
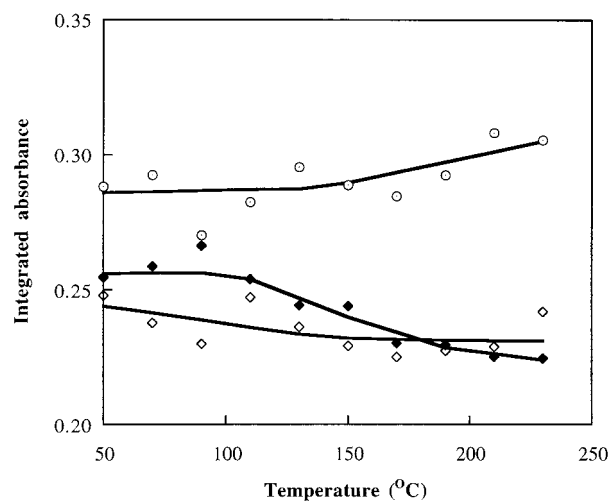

Figure 9 Integrated absorbance of (○) nearly free OH, (◆) statistically distributed hydrogen bonding, and (◇) conformationally preferred hydrogen bonding of novolac-type phenolic resin as a function of temperature.
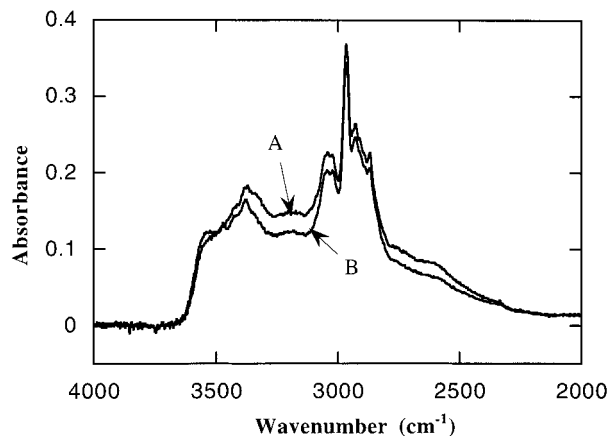
Figure 10 Infrared spectra of recovery study of BA-a: (A) room temperature; (B) 190°C, cooled to room temperature (A). The two spectra at room temperature before and after the heating are practically indistinguishable.
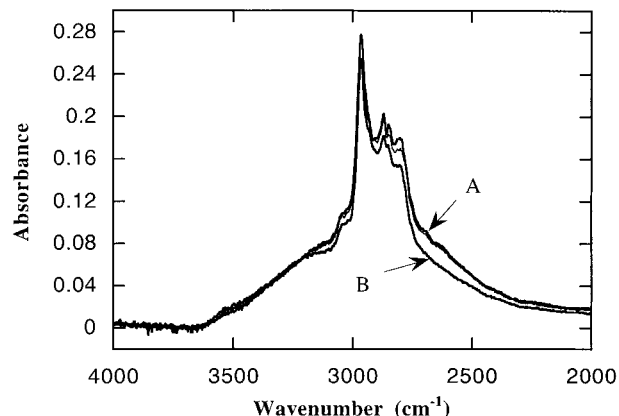

Figure 11 Infrared spectra of recovery study of BA-m: (A) room temperature; (B) 190°C, cooled to room temperature (A). The two spectra at room temperature before and after the heating are practically indistinguishable.

shown in Figure 3 in terms of the bandwidth. However, the temperature dependence of this 3467 cm^{-1} mode is quite weak. While the insensitivity to temperature variation is expected from conformationally preferred hydrogen bonds, the peak-width–frequency-shift correlation is normally demonstrated only by statistically distributed hydrogen bonds. A highly crosslinked network of the novolac phenolic resin may explain this discrepancy. Further study is needed to resolve this question.

The room-temperature recovery of hydrogen bonding after cooling from elevated temperatures was also studied. The hydrogen bonding of both BA-a and BA-m recovered instantaneously when cooled to ambient temperatures as shown in Figures 10 and 11, respectively. However, 44O-a recovered only partially after reaching room temperature and remained unchanged even after 11 h as can be seen in Figure 12. Similarly, the hydrogen bonding of novolac-type phenolic resin also recovered slowly (Fig. 13). As mentioned earlier, the β-transitions of both BA-a and BA-m have a broad distribution that extends to room temperature. Upon cooling to room temperature, the main chains of both BA-a and BA-m still have some mobility that may allow hydrogen bonds to be reformed. The 44O-a material has a higher β-transition temperature so that the main-chain motion at room temperature is restricted. Thus, hydrogen-bond recovery is slower than that of the other polybenzoxazines. Accordingly, it is proposed that the β-transition plays an important

role in the hydrogen-bonding breakup as well as in recovery. A previous study on the temperature dependence of hydrogen bonding suggested that beyond the glass transition temperature the intensity of the hydrogen-bonding mode was reduced approximately linearly.[14] Few articles have dealt with the effect of β-transition on hydrogen bonding.

Ishida and Allen[5] reported that polybenzoxazines have low crosslink densities but high T_g's and high moduli when compared with epoxy resin. This phenomenon is somewhat unexpected, since, in general, the higher the degree of crosslinking, the higher the glass transition tem-
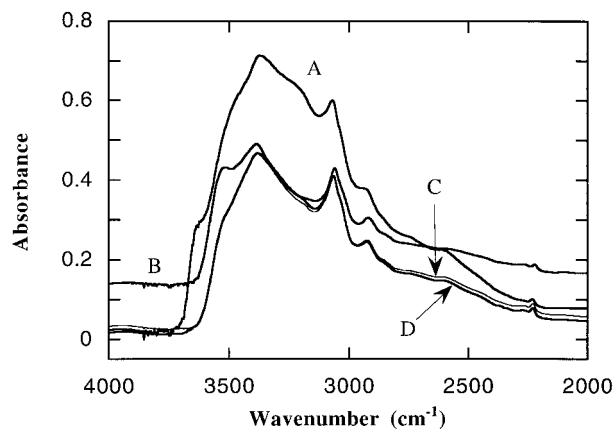

Figure 12 Infrared spectra of recovery study of 44O-a: (A) room temperature; (B) 360°C; (C) cooled to room temperature; (D) after reaching room temperature for 11 h.
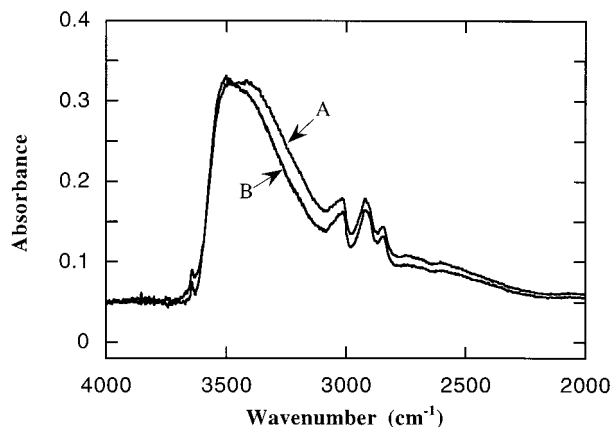
Figure 13   Infrared spectra of recovery study of phenolic resin: (A) room temperature; (B) 210°C and 12 h after cooling to room temperature (B).

perature. Both statistically distributed and conformationally preferred hydrogen bonding in the polybenzoxazines may contribute to the stiffness of the chain. Hence, despite the low degree of crosslinking, hydrogen bonding contributes to the stiffness of the system and leads to a high T_g and high modulus.

Despite the abundance of hydrophilic phenolic and tertiary amine groups in each chemical repeat unit, polybenzoxazines do not absorb water as much as do phenolic or epoxy resins. The saturation water content of BA-a was 1.9% by weight, and of BA-m, 1.3% by weight, after 600 days in water at room temperature. At a shorter immersion time of 24 h at room temperature, the water uptake was 0.11 and 0.17% for BA-a and BA-m, respectively, which compares with novolac-type phenolic resins of 0.23% at the same condition.[15] The low water uptake can be explained by the strong hydrogen bonding of the phenol and the nitrogen atom of the Mannich base. This conformationally preferred acid–base interaction competes favorably with the water and reduces the water absorption.

Unlike other thermosetting resins, polybenzoxazines exhibit volumetric expansion upon polymerization. This volumetric expansion is observed from a quenched amorphous monomer to an amorphous polybenzoxazine. Greater expansion can be observed if the volume comparison is compared from a crystalline monomer to an amorphous polymer. Polybenzoxazines have various hydrogen bonds that may restrict the freedom of the chain and further stiffen the chains, leading to poor molecular packing. This

factor may result in a high free volume which is known to be one of many factors of expansion.[6] The effect of hydrogen bonding on the conformation of the polybenzoxazine main chain is also observed by the model compound study. Size-exclusion chromatography indicated that the hydrodynamic volume of the tetramer is considerably smaller than is the size predicted from the dimer and trimer if a linear conformation is assumed. Furthermore, the UV-visible absorption spectra of the model compounds showed a hyperchromic effect as the number of benzene groups increased from two to four, reflecting the train of hydrogen-bonded groups.[16] Together, this implies that the main chain of polybenzoxazine is curled and is difficult to pack tightly. This is consistent with the observation of volumetric expansion.

CONCLUSIONS

It is found that temperature influences statistically distributed hydrogen bonding but has little effect on conformationally preferred hydrogen bonding below the glass transition temperature. The breakup of statistically distributed hydrogen bonding is influenced by the β-transition. Both statistically distributed and conformationally preferred hydrogen bonds can be used to explain the unusual properties of polybenzoxazines.

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