CHAPTER III

RESULTS AND DISCUSSION

Hydrogen bonding in a traditional phenolic resin and polybenzoxazines, 44O-a, B-a and B-m, was investigated by an infrared temperature study. Hydrogen bonding in novolac produces an absorption in three different regions of the infrared spectrum. These are the bands at 3520 cm^{-1}, the intramolecular hydrogen bonding at 3470 cm^{-1}, and the intermolecular hydrogen bonding at 3330 cm^{-1}. The band at 3520 cm^{-1} is found in both novolac and benzoxazine model compounds, but the origin of this mode has not yet been determined, and thus in this work it is called "nearly free OH". For polybenzoxazines, four regions are of interest : nearly free OH at 3520 cm^{-1}, intramolecular hydrogen bonding (OH---O) around 3460 cm^{-1}, intermolecular hydrogen bonding (OH---O) around 3380 to 3330 cm^{-1}, and the special intramolecular chelation hydrogen bonding (O---H$^+$---N) around 2700 cm^{-1}.

All of the hydrogen bonding modes are broad and have overlapping bands. In order to solve these problems, curve analysis program was used with baseline correction before curve fitting. The function used for curve fitting was the product of Gaussian and Lorentzian contributions. Our band positions agree well with the previous work for both model compounds [Cairns and Eglinton, 1962, 1965; Kovac and Eglinton, 1969; Dunkers et. al., in press]. No intensity comparisons were made between bands with different frequencies since the specific absorptivities drastically change as a function of the strength of hydrogen bonding. For the intramolecular chelation

hydrogen bonding around 2700 cm^{-1} in polybenzoxazines, curve fitting analysis was difficult. The chelation hydrogen bond vibration has been reported to form multiple combination bands with the lower frequency hydrogen bond vibration in the far infrared region [Joesten and Schaad, 1974]. Thus, it is not possible to use a single line shape to fit these multiple bands, and therefore the total area under the broad complex shaped curve could be 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, Δv ($\Delta v_{free\ OH}$ - $\Delta v_{hydrogen\ bonded}$), an increase in band width at half height, $v_{1/2}$, and an increase in the integrated intensity, B, of the band. The correlation of these factors was established by Huggins and Pimentel (1956) 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 band width change caused by hydrogen bonding is linear and this correlation is applicable in a wide variety of intermolecular hydrogen bonding species, but is inapplicable for intramolecular hydrogen bonded complexes. The intramolecular hydrogen bond is more restricted and displays much narrower band widths than intermolecularly associated species [Tsubomura, 1956].

3.1   Curve Analysis

For the phenolic resin, as shown in Figure 3.1, the linear relationship between Δv and $v_{1/2}$ is obtained. Carins and Eglinton (1962) reported that for

dimer novolac the band around 3470 cm^{-1} was attributed to the intramolecular OH---π bond interaction. However, in the trimer system, the band of intramolecular hydrogen bonding was appeared at lower frequency around 3390 cm^{-1} and this band was assigned to the intramolecular OH---O interaction instead of OH---π bond. Thus, the origin of the band around 3470 cm^{-1} of the phenolic resin is in question. This band lies on the straight line with the other bands that are assigned to be intermolecular hydrogen bonding. Thus, it is likely that the band around 3460 cm^{-1} being to intermolecular mode rather than intramolecular hydrogen mode.
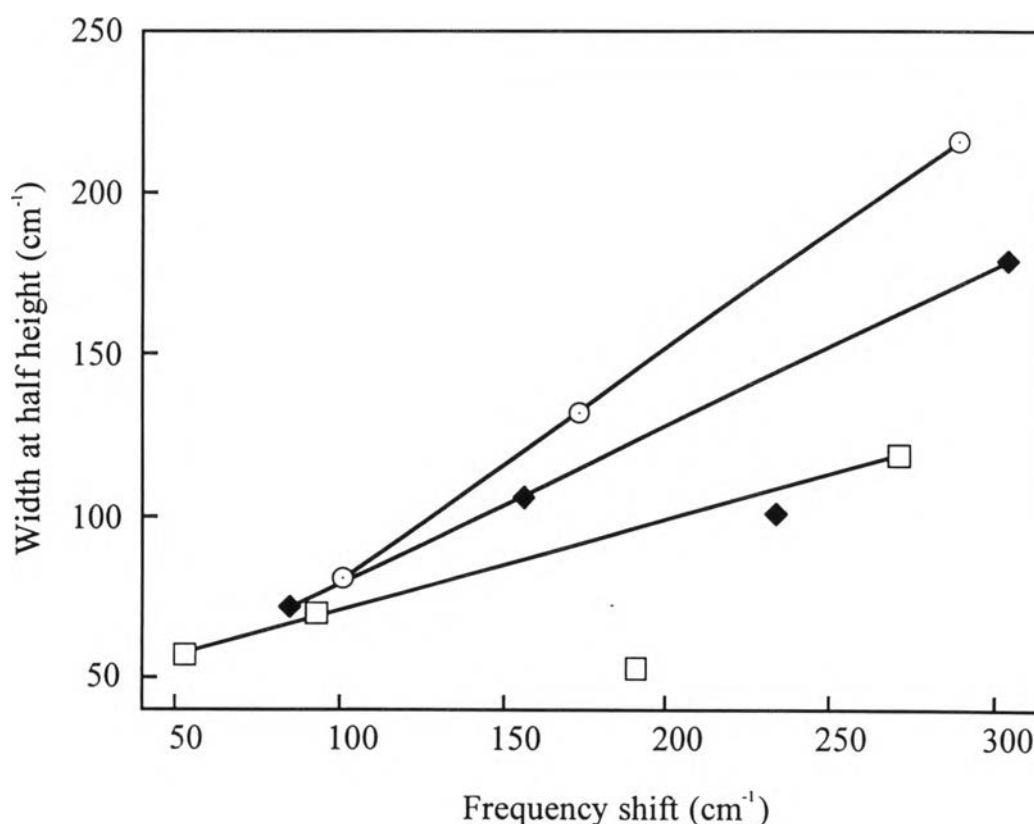

Figure 3.1 Width at half intensity as a function of frequency shift of phenolic resin (⊙), 44O-a (◆), B-a (□).

Similar to novolac, the polybenzoxazines also exhibit a linear relationship except for the bands at 3390 cm^{-1} for 44O-a and 3425 cm^{-1} for B-a. These bands are attributed to intramolecular hydrogen bonding. From these, it can be stated that there are at least two kinds of hydrogen bonding in polybenzoxazines not including chelation hydrogen bonding. Curve analysis provides reasonable results which are consistent with the reported studies on hydrogen bonding.

3.2   Thermal Stability of Materials

To confirm that the material did not degrade over the temperature range of interest, integrated absorbance of the C-H out-of-plane deformation was measured as a function of temperature. By plotting the absorbance of the C-H band versus temperature, as shown in Figure 3.2, the starting point of the sudden decrease is considered to be the final temperature of the study. Sometimes the intensity change in the C-H band is not due to the degradation of the materials. It may be caused by the conformational change or some other factors that resulted in the change in force constants. These phenomena are out of interest of this study. The decrease of the C-H band intensity was arbitrarily set to 5% beyond which the slate was deemed unreliable. The starting temperature for all materials was 50° C. The final temperature for the phenolic resin was 210° C, 350° C for 44O-a, and 190° C for both B-a and B-m, respectively.
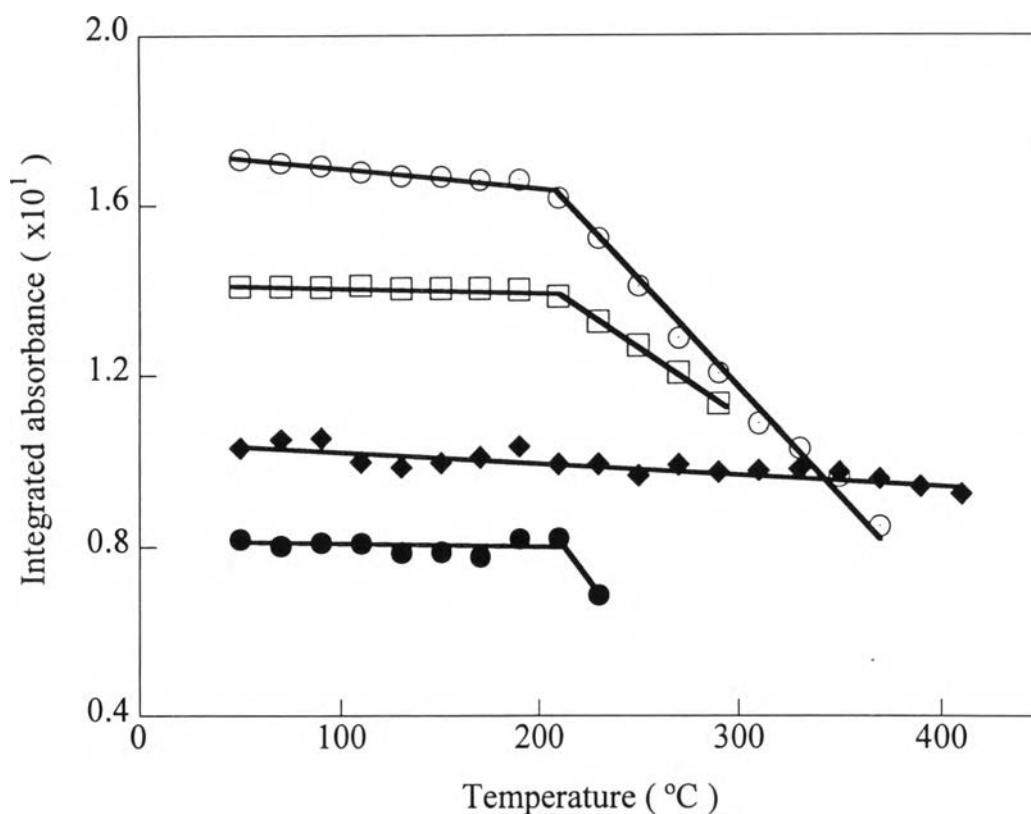
Figure 3.2 Thermal stability of phenolic resin (☉), 44O-a (◆), B-a (□)
and B-m (●).

3.3 Hydrogen Bonding Study as a Function of Temperature of Polybenzoxazine

It has been demonstrated by many authors [Morrow et al, 1976; Volkov et al, 1974; Ugliengo et al, 1990] that water molecules adsorb on free silanol on silica powder. Volkv et al (1974) reported a dramatic reduction in the intensity of the free silanol band in dehydrated silica powder after equilibration with water vapor even at very low relative humidity. Chakonmakos and Gibbs (1986) found that the free silanol favored the water molecule to act as proton acceptor rather than proton donor. From this

From this evidence, it is understandable why polybenzoxazines have low water content even though they have hydroxyl and amine groups which were generally regarded to be the main loci of water interaction [Danieley and Long, 1981; Carfagna et al, 1982]. Figure 3.3 shows the infrared spectra of cured 44O-a, B-a, and B-m. There is no sign of any free hydroxyl groups around 3615 cm^{-1} which was observed in the dilution study of benzoxazine model compounds [Dunkers et al, submitted]. This implies that all of hydroxyl groups of polybenzoxazines are hydrogen bonded in either inter or intramolecular manners.
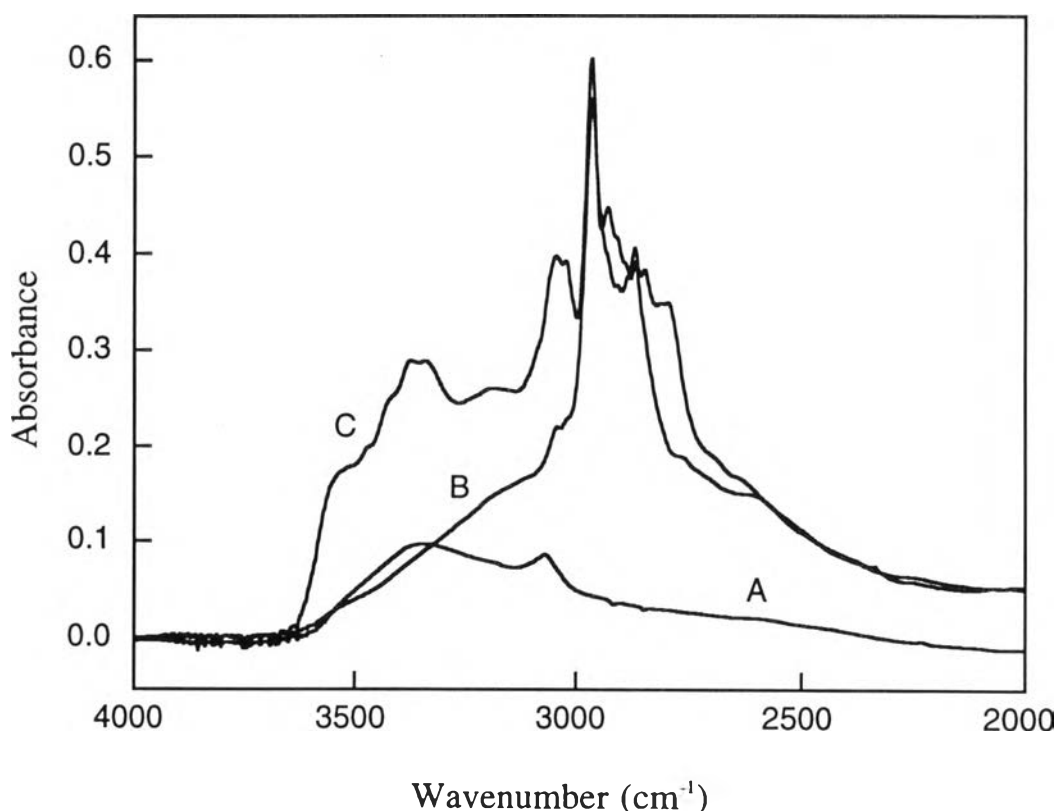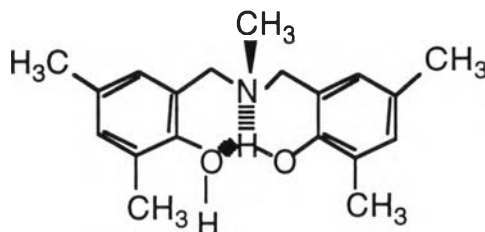

Figure 3.3 Infrared spectra of cured 44O-a (A), B-a (C), B-m (B).

Dunkers et. al. (submitted) also reported that intramolecular hydrogen bonding between hydroxyl and amine groups existed in the benzoxazine

model compound at around 2700 cm^{-1}. They proposed that the most likely conformation of hydrogen bonding is bifurcated hydrogen bonding, as shown below:

An X-ray crystallographic study of the model compound shown above indeed strongly supports this structure .

This band at around 2700 cm^{-1} also appears in the polybenzoxazines. This means that the amine portion of the polybenzoxazine is not available for water molecules to interact. By studying the frequency shift of the hydrogen bonding as a function of temperature, it was found that this hydrogen bonding is unusually strong. The lower the frequency, the stronger the hydrogen bonding. As can be seen in Figure 4, the integrated absorbance of this hydrogen bond is almost constant over the wide temperature ranges from 50° C to 350° C for 440-a, and from 50 to 190° C for B-a and B-m.
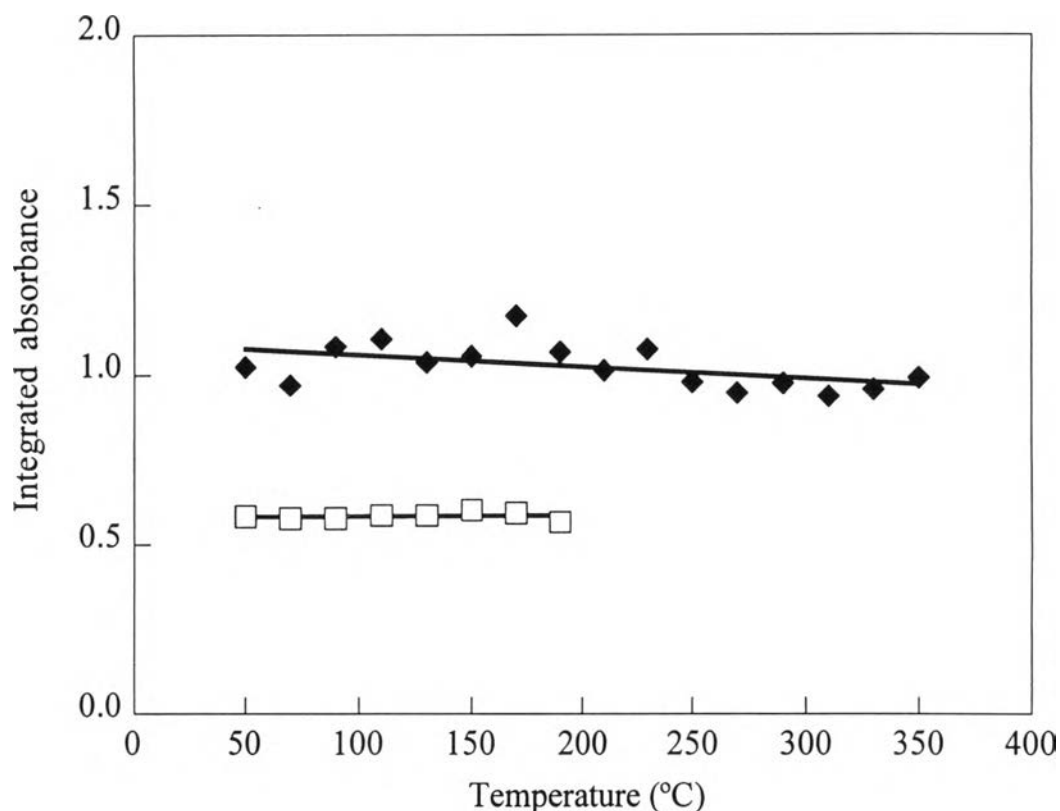
Figure 3.4 Integrated absorbance of chelation hydrogen bonding as a function of temperature of 44O-a (◆), B-a (□).

The strength of chelation hydrogen bonding is dependent on the electronegativity of the amine group attached to the nitrogen atom. It has also been reported that the higher electron density on the nitrogen atom gives the higher concentration of intrasegmental hydrogen bonding which cannot be involved in water bonding [Bellenger et al, 1989]. From this, the methylamine-based benzoxazine should give lower water content than the aniline-based benzoxazine and should have the stronger hydrogen bond as well. The FT-IR spectrum of B-m is nearly the same over the entire temperature range studied, indicating that there is almost no change in hydrogen bonding as the temperature increases.
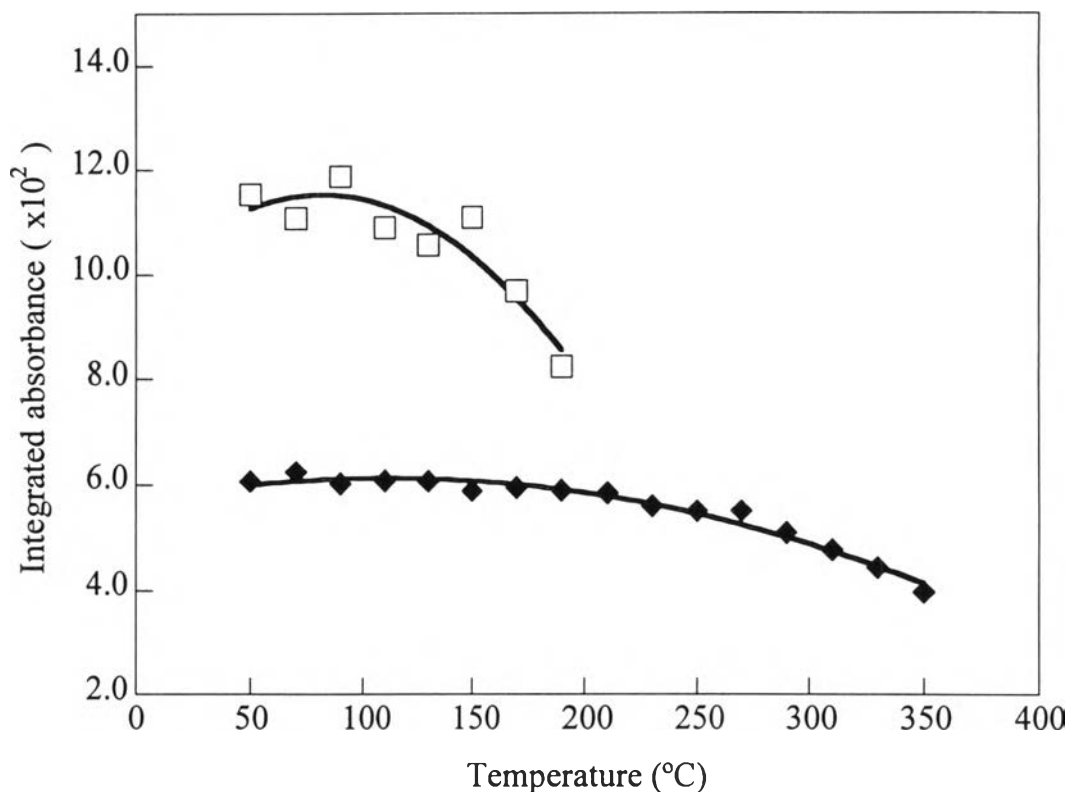
Figure 3.5 Integrated absorbance of intermolecular hydrogen bonding
as a function of temperature of 44O-a (◆), B-a (□).

Intermolecular hydrogen bonding has also been observed at
frequency around 3380 to 3330 cm^{-1}. As shown in Figure 3.5, the integrated
absorbance decreases as the temperature increases for both 44O-a and B-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 B-a
decreases faster. This can be explained by the structures of 44O-a and B-a.
The backbone of 44O-a is benzophenone, which is stiffer than the bisphenol-
A backbone of B-a. Ning and Ishida (1994) have studied the effect of
molecular structure on dynamic mechanical properties of polybenzoxazines.
They found both the γ- and β-transitions of polybenzoxazines are below the

glass transition temperature. They reported that the thermal motion of the pendant groups attached to the nitrogen atom was responsible for the γ-process and independent on the backbone structure. It is believed that the β-transition is caused by the motion of several chemical repeating units of the backbone. The variety of the intermediates that are not incorporated completely into the network are responsible for the breadth of the β-transition. The β-transition of 44O-a, B-a, and B-m are centered around 115, 75, and 60°C, respectively. 44O-a has stiffer backbone chain than B-a and B-m, and therefore has higher β-transition temperature. As temperature increases, hydrogen bonds are disturbed due to the movement of the several units of the backbone.
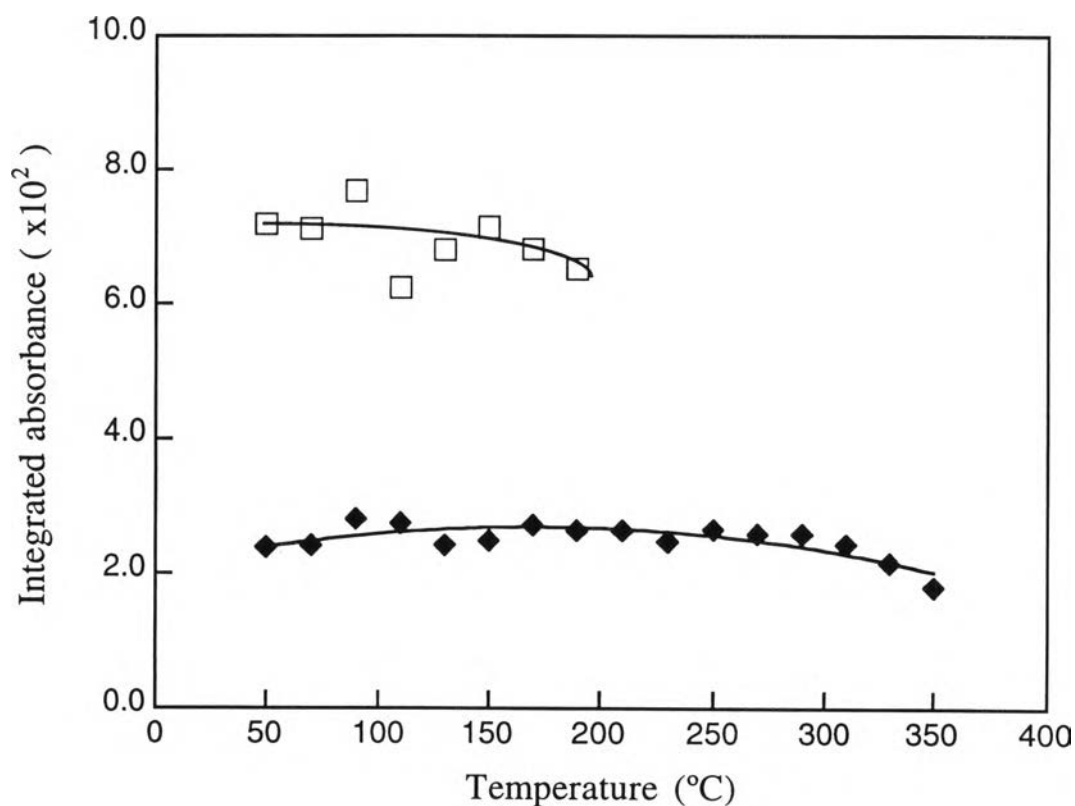

Figure 3.6 Integrated absorbance of intramolecular hydrogen bonding

between OH groups as a function of temperature of 44O-a

(◆), and B-a (□).

The intramolecular hydrogen bondings between hydroxyl groups of polybenzoxazines were also determined as a function of temperature as can be seen in Figure 3.6. These hydrogen bondings of both 44O-a and B-a are slightly decreased when increasing temperature. By comparison intramolecular hydrogen bonding to inter- and chelation hydrogen bonding. It is found that intramolecular hydrogen bonding is more stable than intermolecular hydrogen bonding. The most stable hydrogen bonding is chelation hydrogen bonding. This result is consistent to the theory that the lower the frequency, the higher the hydrogen bond strength.

Upon increasing temperature, hydrogen bonds are broken and yield a greater free OH component as the integrated absorbance of nearly free OH bonds becomes higher as shown in Figure 3.7. The support for the above statement can be seen in this figure where the nearly free OH concentration started increasing well below the Tg of the respective polybenzoxazines. The Tg of 44O-a is 350° C and that of B-a is 180° C. From Figure 3.11, the onset temperature of the increase intensity of the nearly free OH modes are determined to be approximately 110° C for 44O-a and 80° C for B-a, which are closed to the β -transition of these polymers.
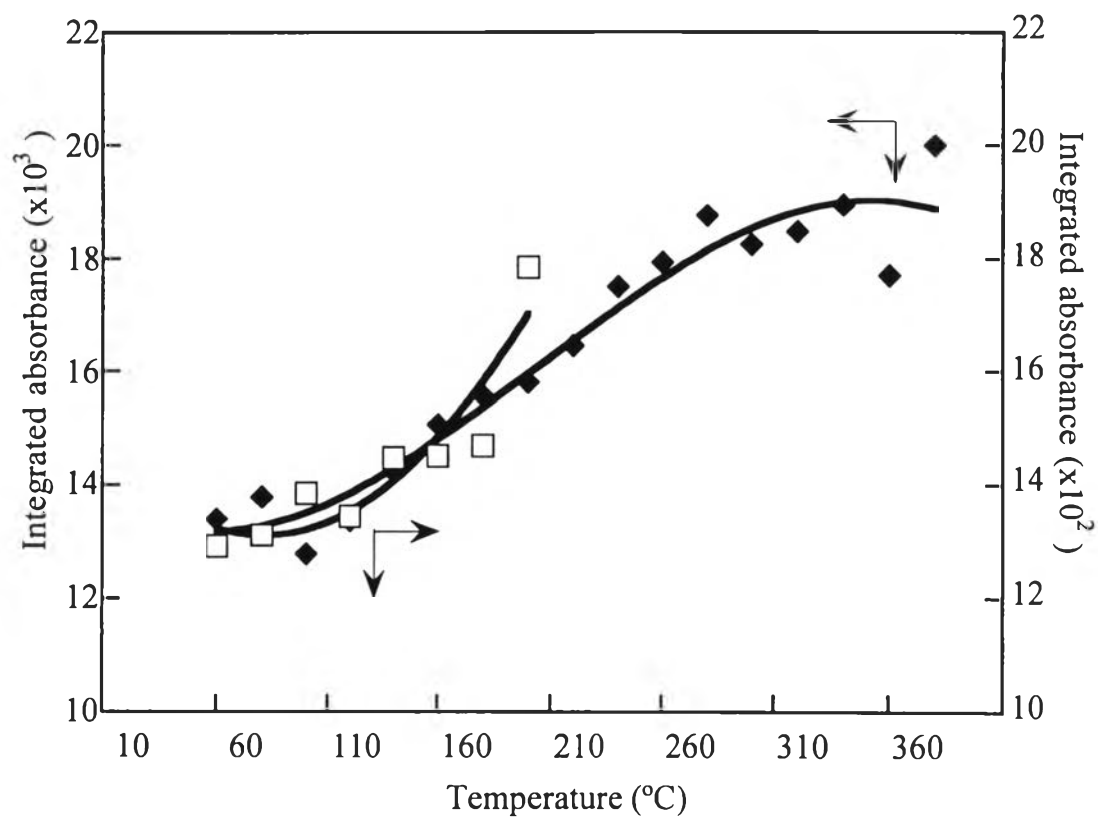
Figure 3.7 Integrated absorbance of nearly free OH as a function of
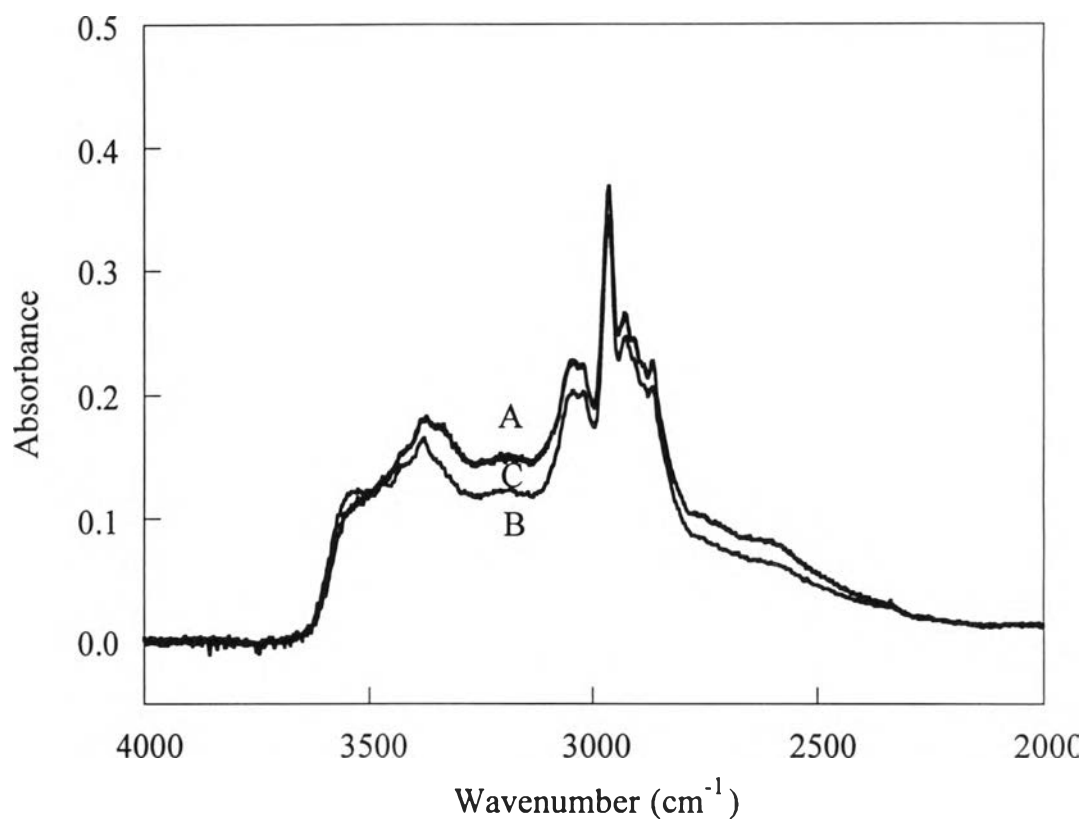temperature of 44O-a (◆), B-a (□).

Figure 3.8 Infrared spectra of hydrogen bond recovery study of B-a;
at room temperature (A), at 190 °C (B), at room temperature
after cooling from 190 °C (C).

3.4   Recovery of Hydrogen Bonding

The recovery of hydrogen bonding after cooling from a certain elevated temperature to room temperature are also studied. The hydrogen bonding of both B-a and B-m recovered instantaneously when cooled back to ambient temperatures, as shown in Figures 3.8 and 3.9, respectively.
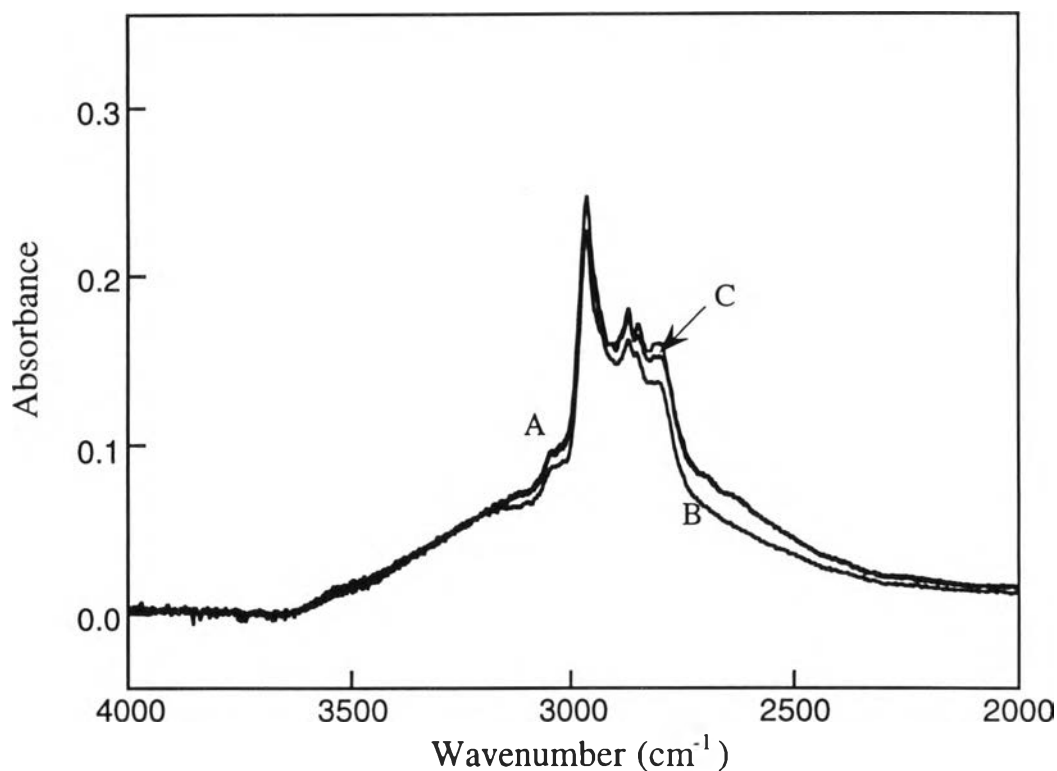
Figure 3.9 Infrared spectra of hydrogen bond recovery study of B-m;
at room temperature (A), at 190 °C (B), at room temperature
after cooling from 190 °C (C).

However, hydrogen bonding of 44O-is recovered only partially after reaching room temperature and remained unchanged even at 11 h later, as can be seen in Figure 3.10. Similarly, the hydrogen bonding of novolac-type phenolic resin is also recovered slowly (Figure 3.11). As mentioned earlier, the β-transition of B-a is close to that of B-m while both compounds have a broad distribution that reaches room temperaure. Upon cooling to room temperature, the main chains of both B-a and B-m still have some mobilities that allows 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. Consequently, hydrogen bond recovery is slower than the other polybenzoxazines. Accordingly, it is proposed that the β-transition plays an important role in the hydrogen bonding break-up as well as recovery. A previous study on the temperature dependence of hydrogen bonding suggested that beyond glass transition temperature, the intensity of the hydrogen bonding mode reduced approximately linearly [Seymour and Cooper, 1973]. To our knowledge, no one has related the β-transition to hydrogen bonding. Only the α-transition is considered to be the point where hydrogen bonding decreases dramatically.
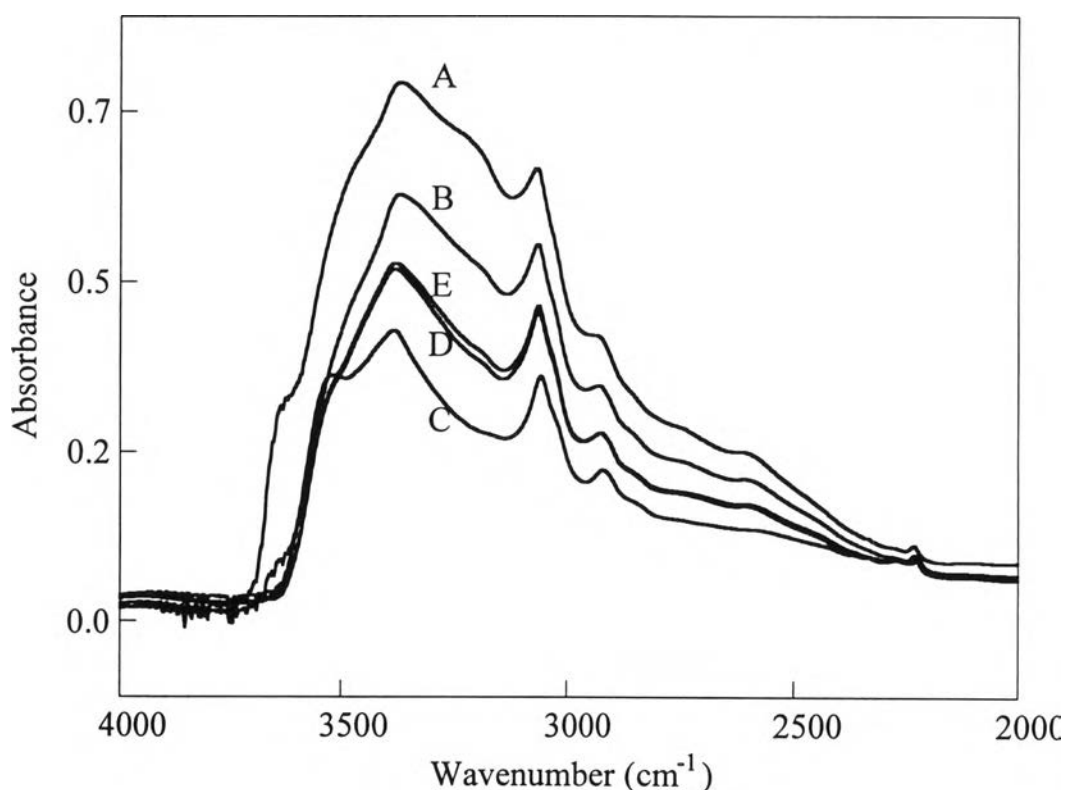

Figure 3.10 Infrared spectra of hydrogen bond recovery study of 44O-a; at

room temperature (A), at 50 °C (B), at 350 °C (C), at room

temperature after cooling from 350 °C (D), and allowing at
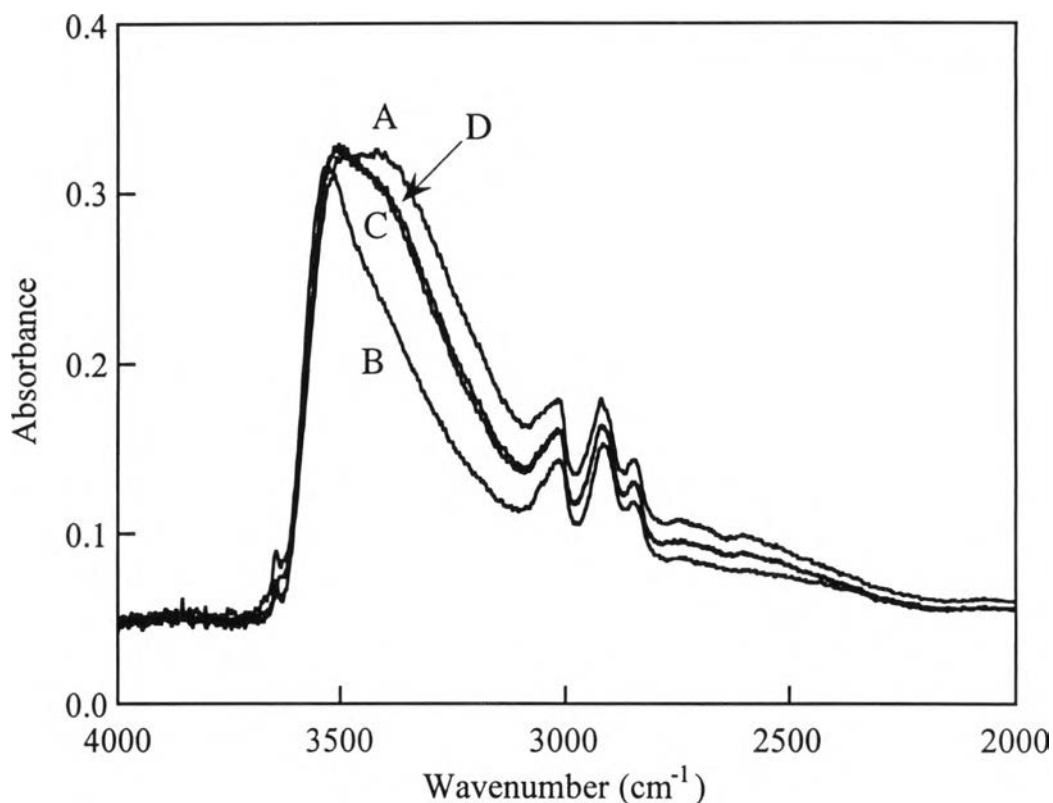
room temperature for 11 h (E).

Figure 3.11 Infrared spectra of hydrogen bond recovery study of
phenolic resin; at room temperature (A), at 210 °C (B), at
room temperature after cooling from 210 °C (C), and
allowing at room temperature for 12 h (D).

3.5 Hydrogen Bonding Study as a Function of Temperature of Phenolic Resin

Figure 3.12 shows infrared spectrum of the novolac-type phenolic resin. It can be observed that there is a band around 3640 cm^{-1} which is attributed to hinder free hydroxyl group. This band was reported by Cairns and Eglinton (1962) that it was found in ortho-di-t-butyl substituted dinuclear novolac. They suggested that the di-ortho-t-butyl substituents

prevent the intermolecular association so intramolecular OH---O bonds could be formed around 3450 cm^{-1}. Crosslinking network structure of phenolic resin is di-ortho substitution which is similar to what was found in dinuclear novolac. However, di-ortho substituents of novolak studied in our work are methylene or ether linkages which have a very weak effect for preventing intermolecular hydrogen bonding. Therefore, intramolecular hydrogen bonding should be rarely formed. Most of hydrogen bondings in phenolic resin are probably intermolecular association.
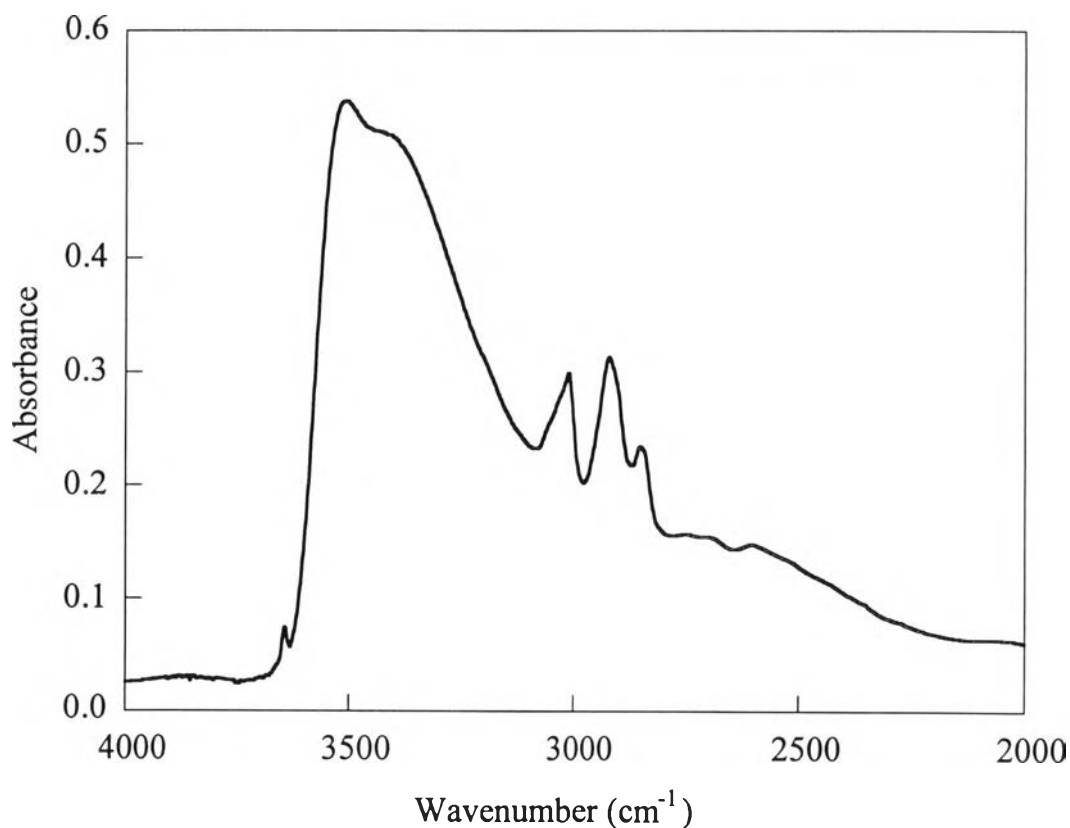

Figure 3.12 Infrared spectrum of cured novolac-type phenolic resin.

The integrated absorbances of hydrogen bonding modes of phenolic resin are shown in Figure 3.13 as a function of temperature. Intermolecular

hydrogen bonding appears to be more sensitive to temperature than intramolecular hydrogen bond. Nonetheless, the intensity reduction of the intermolecular hydrogen bonding of the phenolic resin is low. This may be because the phenolic resin used is highly crosslinked. Any transitions below Tg cannot be observed. Even the Tg (α-transition) is not clear [Ishida and Low, to be published]. Since the network of the phenolic resin is very tight, the temperature below Tg does not have much influence on hydrogen bonding. Upon increasing temperature, more free OH component is observed, as can be demonstrated by the slight increase in absorbance of the nearly free OH band.
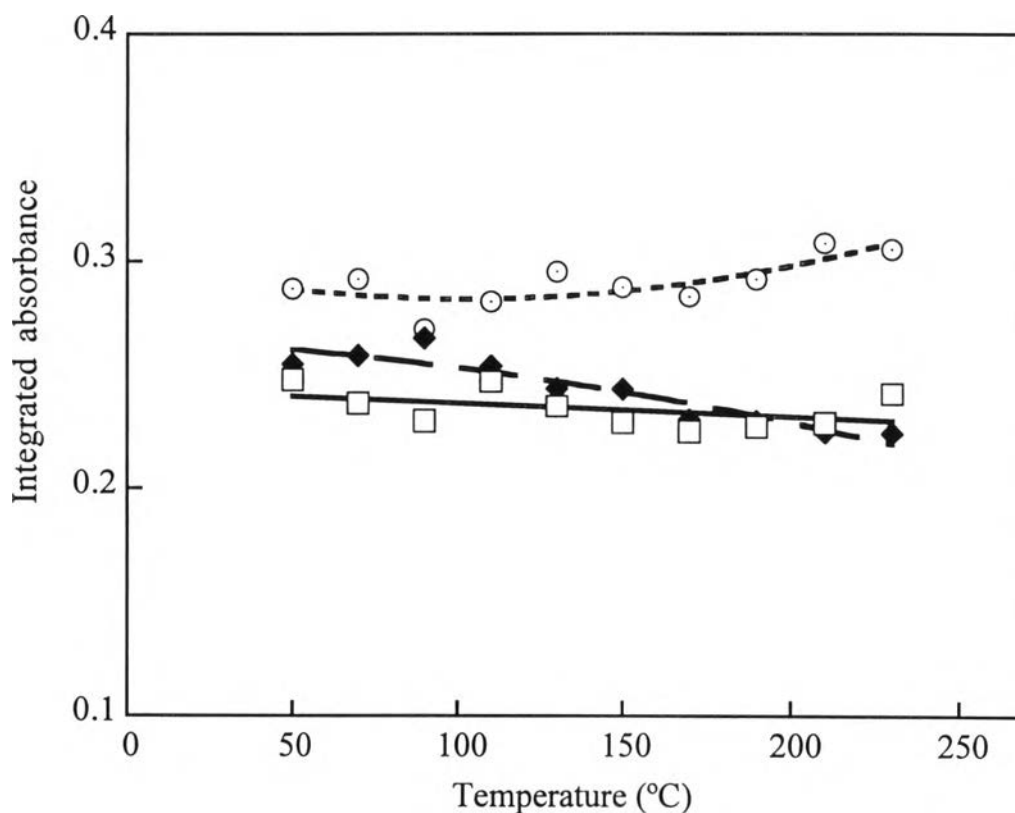

Figure 3.13 Integrated absorbance of nearly free OH (⊙), inter- (◆) and intramolecular hydrogen bonding (□) of phenolic resin.

Polybenzoxazines have an unusually strong hydrogen bonding among those hydroxyl and amine groups which makes them unavailable for water adsorption. Thus, water content is quite low, only 0.11% and 0.17% for B-a and B-m, respectively, under an immersion in water at room temperature for 24 h. These values are compared to the novolac-type phenolic resin which has some free hydroxyl groups which are available for interaction with water molecules. It has water content around 0.23% (1990) at the same condition.

It is possible that the local structure of the polybenzoxazines is a double chain ladder structure, as shown below. In this structure, the covalent bonds comprise one chain and the train of hydrogen bonds forms another chain.
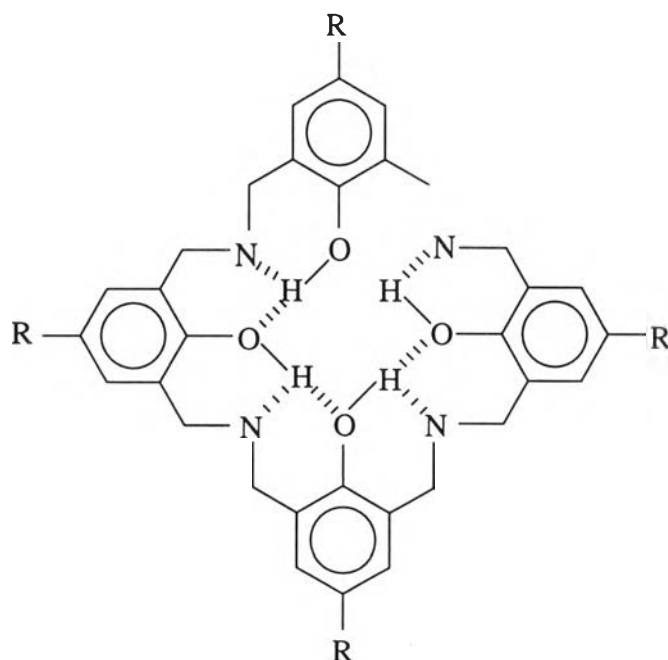
The intramolecular OH---O bond is weaker than the chelated O---H^{+}---N bond. Thus, in the chemical repeating unit, at least one six-

membered ring involving the OH and N may be preserved while the intramolecular OH---O bond is disturbed, allowing the b-process to take place by providing the main chain some freedom for rotation. Indeed, the chelation intramolecular hydrogen bonds, O---H$^+$---N, as shown in Figure 3.4 are more stable as a function of temperature than the intramolecular OH---O bonds which is shown in Figure 3.6. Since not all OH---O bonds need to be broken for a chain to rotate at the β-transition temperature, the fraction of broken intramolecular OH---O bonds could be low. This is also reflected in the mild temperature sensitivity, see Figure 3.6.

The aforementioned double chain ladder structure would lead to local cyclic structure with several chemical repeating units before the helical turn experiences steric hindrance. While the polybenzoxazines are crosslinked polymers and as such an amorphous structure is envisaged, local order has been observed by wide angle x-ray diffraction where local order on the order of a few nanometers has been observed [Dunkers et al, submitted]. Further support of the local cyclic structure is obtained by the model compounds of a polybenzoxazine. The size exclusion chromatogram indicated that the hydrodynamic volume of the tetramer was much smaller than what would be expected from the sizes of the dimer and trimer. Furthermore, the UV-visible absorption spectra of the model compound showed a hyperchromic effect as the number of benzene groups increased from two to four [Ishida and Krus, 1995], reflecting the train of hydrogen bonded groups. In other words, the terminal phenolic OH group of the tetramer is more acidic than the dimer or trimer. These finding is also consistent with results reported on the model compounds of novolak resin [Bellenger and Dhaoui, 1988].

Ishida and Allen (in press) reported that polybenzoxazines have low crosslink densities but high Tg'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 temperature. This can be explained by the existence of an unusually strong intramolecular hydrogen bonding in the polybenzoxazines. As discussed in the previous section that the polybenzoxazines display many kinds of hydrogen bonding, especially intramolecular hydrogen bonding between the hydroxyl and amine groups, that are very stable over a wide temperature range. The strength of both inter- and intramolecular hydrogen bonding may contribute to the stiffness of the chain and obstruct the mobility of the chain. Also, the double chain ladder structure mentioned above will certainly stiffen the main chain. Hence, despite the low degree of crosslinking, hydrogen bonding contributes to the stiffness of the system and leads to high Tg and high modulus.

Unlike other thermosetting resins, polybenzoxazines exhibit volumetric expansion upon polymerization. It has been mentioned that in epoxy networks, hydrogen bonding increases at the same time as crosslink density [Bellenger and Dhaoui, 1988]. They also reported that the density increases with the crosslink density. These can be implied that the more hydrogen bonding, the higher the density which may due to better packing in the network. However, it has been reported that the stiffness of the chain is also responsible for the change in volume [Won et al, 1991]. In our case, the polybenzoxazines have many benzene rings in their structure that make the chain become stiff to some extent. Furthermore, they have many kinds of hydrogen bonds which may restrict the motion of the chain and further

stiffer the chains, leading to poor molecular packing. This factor may result in high free volume which is known to be one of many factors of expansion.