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The chemistry of novolac resins—VI. Reactions between benzoxazine intermediates and model phenols

Xiaoqing Zhang and David H. Solomon*
Polymer Science Group, Department of Chemical Engineering, The University of Melbourne, Parkville, VIC 3052, Australia
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The reaction between 3-(,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3,-benzoxazine and either 2,4-xylenol or 2,6-xylenol was studied by ^{13}C n.m.r. techniques, to model the reactions between benzoxazine intermediates and free *ortho*- and *para*-phenolic sites in the curing of novolac resins with hexamethylenetetramine (HMTA). The results indicate that 2,4-xylenol can directly react with benzoxazine intermediate at low temperature via several pathways to form methylene linkages between phenolic rings. 2,2′-Methylene-4,4′,6,6′-tetramethyldiphenol is the dominant product after heating benzoxazine and 2,4-xylenol to 205°C. However, no reaction occurs between the benzoxazine and 2,6-xylenol before the decomposition of the benzoxazine structure. At higher temperatures, 2,6-xylenol reacts with the decomposition species of the benzoxazine to form *para–para* and *ortho–para* methylene linkages between phenolic rings, together with *ortho–ortho* methylene linkages generated from the decomposition of the benzoxazine. Minor amounts of nitrogen-containing structures, such as amines, amides and imines, were also formed. The results when applied to novolac/HMTA systems provide possible reaction mechanisms and pathways from the benzoxazine intermediates and vacant *ortho*- and *para*-phenolic reactive sites leading to the final cross-linking network. © 1997 Elsevier Science Ltd.

(Keywords: novolac resins; hexamethylenetetramine; benzoxazine intermediates)

INTRODUCTION

Substituted benzoxazines and benzylamines are the major first-formed intermediates produced in the curing of novolac resins with hexamethylenetetramine (HMTA), and further reaction of these intermediates leads to a highly cross-linked network[1–6]. The thermal decomposition of 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,-4-dihydro-(2H)-1,3-benzoxazine, as a model of benzoxazine intermediates, has been reported in the previous paper[7], providing reaction pathways from benzoxazine intermediates to the methylene linkages and various side-products. When a low amount of HMTA is used in the curing of novolac resins, the first-formed intermediates, e.g. benzoxazine, may react with vacant *ortho*- and *para*-phenolic positions of novolac resins[6], and the reaction may be competitive with the thermal decomposition. As a continuation of the systematic investigation of the curing chemistry of novolac resins, this paper will report the reactions between 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine and the model phenols, 2,4-xylenol and 2,6-xylenol. The reaction mechanisms and pathways are suggested on the basis of the structural changes, and the relevance of the pathways to curing in novolac/HMTA system is discussed.

* To whom correspondence should be addressed

EXPERIMENTAL

Samples

3-(3,5-Dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine was prepared by the method reported previously[4,6]. The compound was heated with 2,4- or 2,6-xylenol, respectively, in a ratio of 1:1 by wt% in a Eurotherm 902 oven under the same conditions used to cure novolac resins with HMTA[6] and the benzoxazine model system[7]. The samples were heated at 90°C for 6 h, then the temperature was increased at a rate of 3.7°C h^{-1} until 135°C, thereafter, 12°C h^{-1} until 205°C, and finally at 205°C for 4 h. In order to follow the structural changes in the process, the samples were taken after curing to 90°C for 6 h, at 105, 120, 135, 160, 185, 205°C, and finally after heating at 205°C for 4 h.

n.m.r. Experiments. solution ^{13}C n.m.r. spectra were recorded on a JEOL JNM-GX400 spectrometer at resonance frequency of 100 MHz with $CDCl_3$ (99.8%) as a solvent. ^{13}C DEPT spectra were observed by the normal DEPT pulse sequence with $\theta = 135°$. The $\tau = (1/2J_{CH})$ was 3.7 ms, and 90° pulse for ^1H and ^{13}C were 24.6 and 10 μs, respectively. Tetramethylsilane (TMS) was used as an internal chemical shift reference.

RESULTS AND DISCUSSION

Reactions between benzoxazine and 2,4-xylenol

^{13}C spectra of 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine (**1**) heated with 2,4-xylenol to various temperatures are shown in

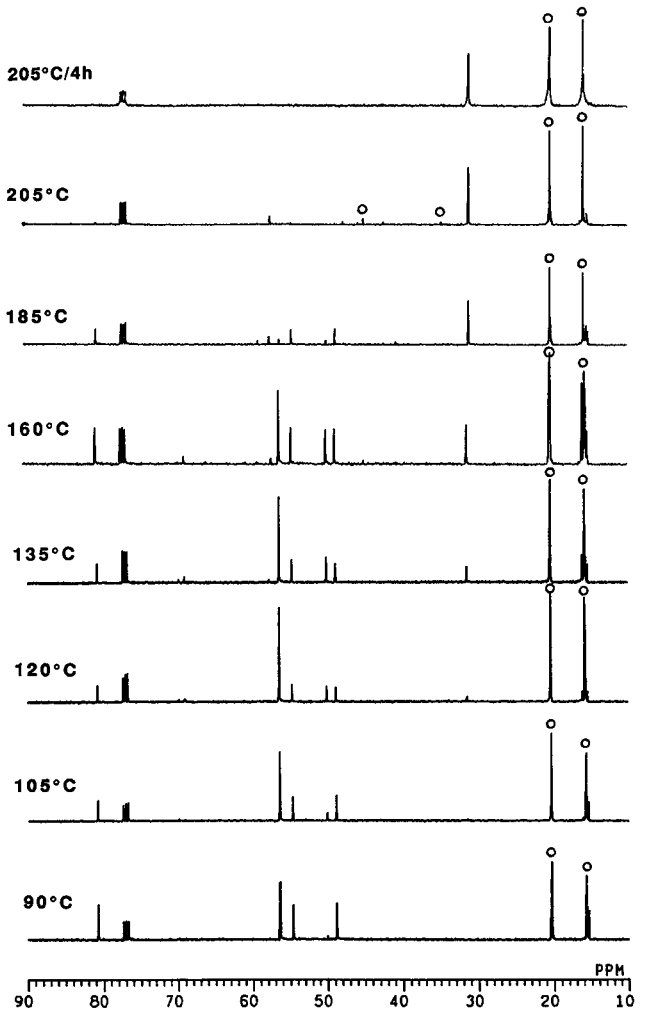


Figure 1 ^{13}C n.m.r. spectra (10–90 ppm range) of the benzoxazine/2,4-xylenol after heating to 90°C for 6 h, 105, 120, 135, 160, 185, 205°C, and 205°C for 4 h. The (O) peaks appear negative relative to $-CH_2-$ resonances in DEPT spectra

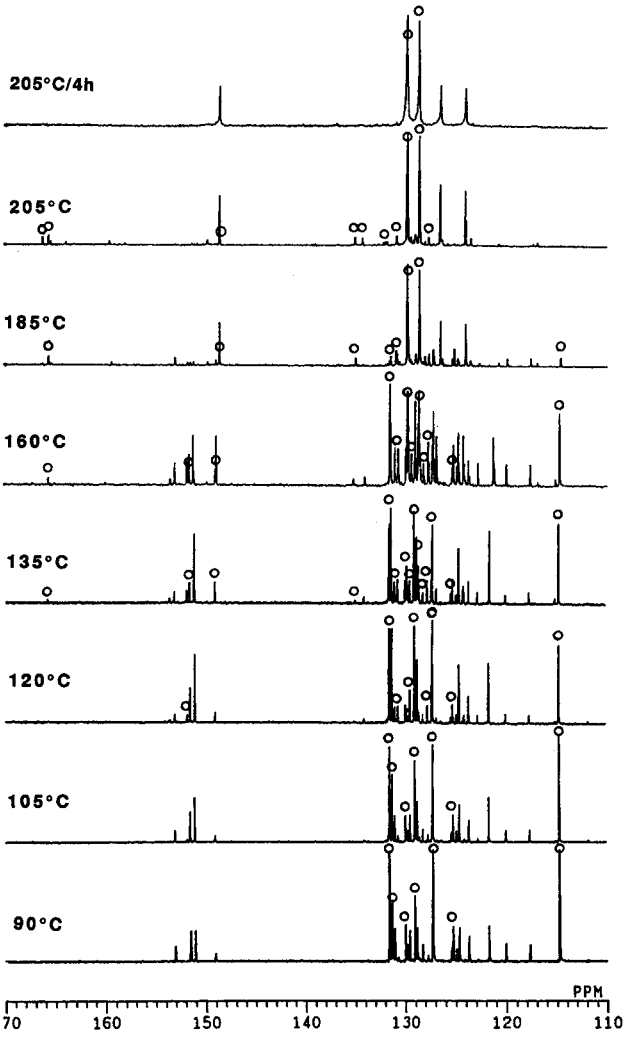
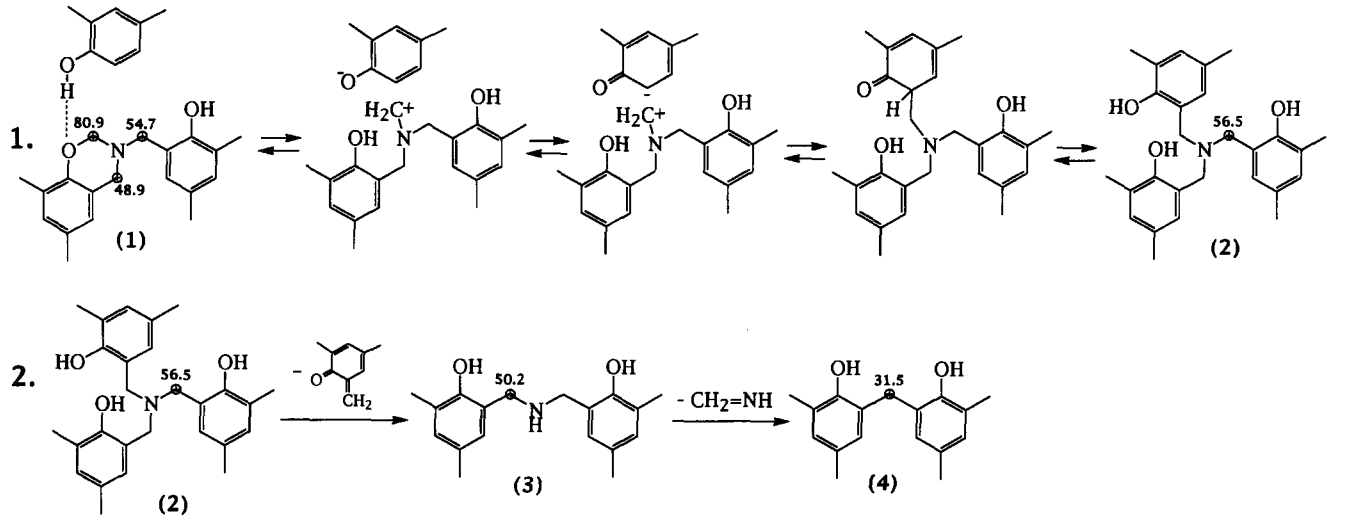


Figure 2 ^{13}C n.m.r. spectra (110–170 ppm range) of the benzoxazine/2,4-xylenol after heating to 90°C for 6 h, 105, 120, 135, 160, 185, 205°C, and 205°C for 4 h. The (O) peaks appear negative relative to $-VH_2-$ resonances, while the rest peaks disappear in DEPT spectra

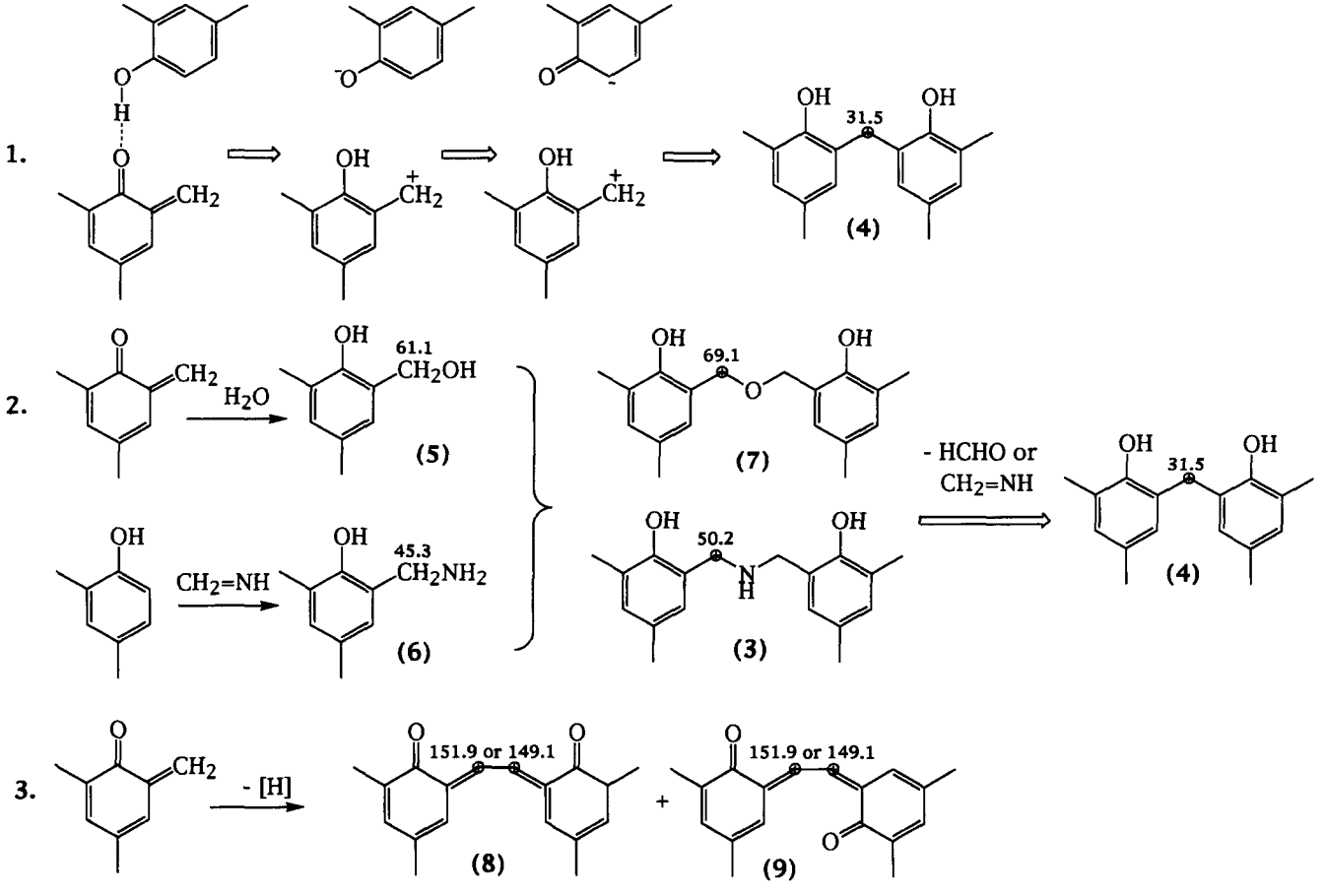
Figures 1 and 2. In the ^{13}C spectra of low chemical shift range (10–100 ppm), the peaks with open circles are either CH or CH_3, while the rest are CH_2 carbons. In the high chemical shift range (100–200 ppm) the peaks marked by open circles are due to CH and the rest are quaternary carbons, as detected by the DEPT technique. The three strong ^{13}C resonances at 80.9, 54.7 and 49.0 ppm are the signals indicative of the benzoxazine (**1**)[5]. The 114.7 ppm peak is due to the *ortho*-unsubstituted phenolic carbon of 2,4-xylenol[5,8]. The resonances indicative of *ortho*-methyl groups appear at 15.5–15.9 ppm while those of the *para* methyl groups are located at 20.3 ppm. The intensity of *para* phenolic methyl carbons (at 20.3 ppm) does not change during the heating process, and thus, can be taken as an internal reference. Less attention has been paid to the aromatic resonances in the range of 124–135 ppm in the systems.

It has been shown that the benzoxazine (**1**) is relatively stable and no apparent decomposition occurred until 160°C[7]. However, reactions occurred at relatively low temperatures between (**1**) and 2,4-xylenol. After heating (**1**) with 2,4-xylenol to 90°C for 6 h, a strong resonance at 56.5 ppm and a minor peak at 50.2 ppm were observed, due to the $Ar-CH_2-N<$ carbons in tris- and bis(2-hydroxy-3,5-dimethylbenzyl)amine [(**2**) and (**3**)], respectively[5]. Above 120°C, the 31.5 ppm peak was detected corresponding to the formation of 2,2′-methylene-4,4′,6,6′-tetramethyldiphenol (**4**) (hereafter called the *ortho–ortho* dimer). As the heating temperature increased, the intensities at 56.5 and 50.2 ppm [(**2**) and (**3**)] increased, together with an increase of the *ortho–ortho* dimer (**4**), while the signals of (**1**) decreased relative to the *para*-CH_3 peak at 20.3 ppm. The results indicate that the initial and the major reaction in the system occurs between the benzoxazine (**1**) and 2,4-xylenol, and gives tris(2-hydroxy-3,5-dimethylbenzyl)amine (**2**) first, and then, bis(2-hydroxy-3,5-dimethylbenzyl)amine (**3**), which thereafter produced the *ortho–ortho* dimer (**4**) through loss of a CH_2=NH unit (*Scheme 1*).

Some other related side-reactions may also occur as shown in *Scheme 2*. The benzoquinone methide unit liberated from the decomposition of (**2**) could react with 2,4-xylenol to produce the *ortho–ortho* dimer (**4**). The benzoquinone methide could also react with H_2O (present as an impurity) to form 2-hydroxy-3,5-dimethylbenzyl alcohol (**5**) ($Ar-CH_2-OH$, 61.1 ppm)[8] while 2,4-xylenol might react with $HN=CH_2$ unit to form 2-hydroxy, 3,5-dimethylbenzylamine (**6**) ($Ar-CH_2-NH_2$, 45.3 ppm)[6]. The formation of bis(2-hydroxy-3,5-dimethylbenzyl)ether (**7**) and (**3**) may be through condensation reactions of (**5**) and (**6**),



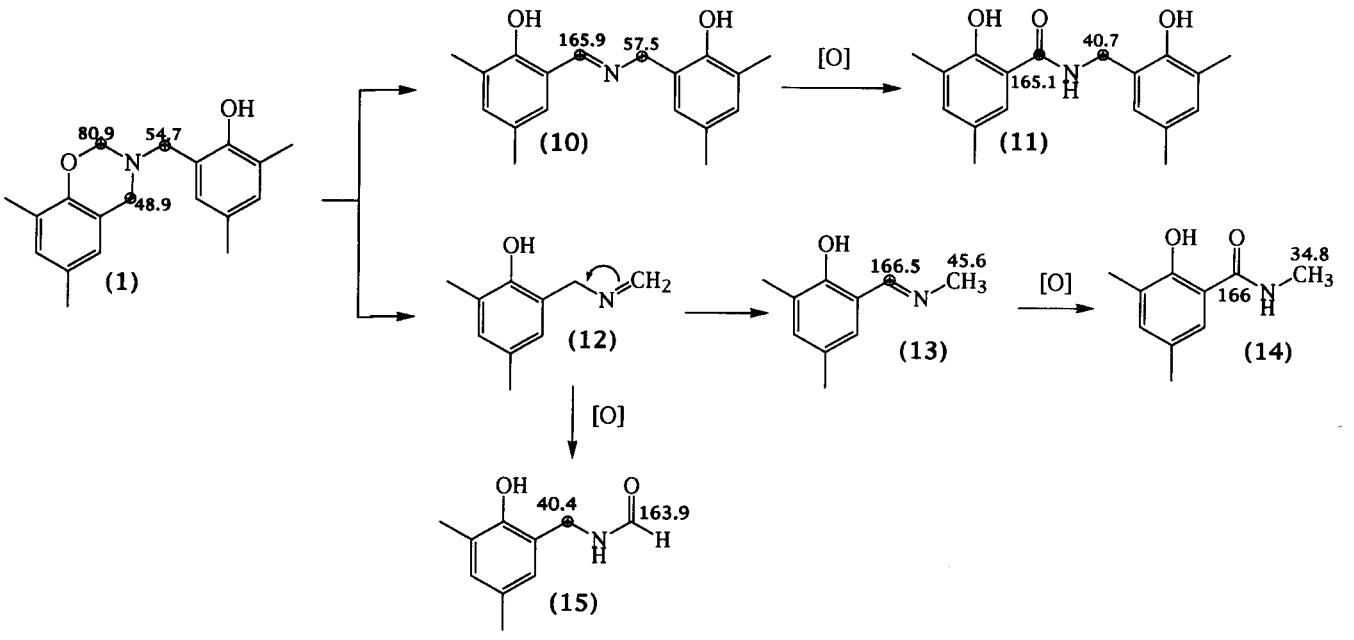
Scheme 1



Scheme 2

respectively. The resonance at 69.1 ppm which appeared at 120–160°C is consistent with the formation of (**7**)[6,8]. The minor signals of (**5**) and (**6**) are possibly due to their low concentration in the system and their fast conversion to (**7**) and (**3**). Both (**3**) and (**7**) could produce the dimer (**4**) by losing either a $HN{=}CH_2$ or HCHO unit. On the other hand, dimerization of benzoquinone methide could also occur as suggested in *Scheme 2* and *Scheme 3*. The –CH= resonances observed around 150 ppm at 120–205°C are consistent with the existence of structures (**8**) and (**9**), but the *ortho–ortho* ethylene-linked dimer was not detected during the reactions.

Other side-products found during the reactions are shown in *Scheme 2*. After heating to 135°C, two resonances at 165.9 and 57.5 ppm appeared simultaneously and were assigned to the imine structure (**10**). This structure could



Scheme 3

originate from the decomposition of (**1**) and remained in the system until 205°C. At 185°C, two minor resonances due to amide (**11**)[9] were detected at 165.1 and 40.6 ppm. Decomposition of (**1**) at 205°C also resulted in imine (**13**) (the Ar–CH=N– at 166.5 ppm and the =N–CH_3 at 45.6 ppm)[7], amide (**14**) (the Ar–CO–N< at 166.0 and the –NH–CH_3 at 34.8 ppm)[7,10] and amide (**15**) (the Ar–CH_2–N< at 40.4 ppm and the –CHO at 163.9 ppm)[7,9].

On further heating, 2,4-xylenol disappeared at 185°C since the *ortho* vacant phenolic CH resonance of 2,4-xylenol at 114.7 ppm could no longer be detected, and the signals of (**1**), (**2**) and (**3**) all disappeared at 205°C. Above 185°C, the *ortho–ortho* dimer (**4**) became dominant together with a minor amount of side-products. After heating the system to 205°C for 4 h, the dimer (**4**) became the only product obtained. This study indicates that the reaction between the benzoxazine (**1**) and 2,4-xylenol can cleanly produce methylene linkages between phenol. The weight loss of the system was 24% after heating to 205°C for 4 h. Bearing in mind that the amount of 2,4-xylenol was 50% before reaction and the thermal decomposition of the benzoxazine itself can lead to 13% weight loss due to volatilization of NH_3[7], it can be concluded that more than 60% of 2,4-xylenol reacted with benzoxazine after heating to 205°C for 4 h.

Reactions between benzoxazine and 2,6-xylenol

The ^{13}C spectra of 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine (**1**) heated with 2,6-xylenol to various temperatures are shown in *Figures 3 and 4*. The CH resonance at 120.0 ppm is due to the *para*-unsubstituted phenolic carbon of 2,6-xylenol which is indicative of 2,6-xylenol in the system. Compared to the system with 2,4-xylenol, the benzoxazine/2,6-xylenol system was relatively stable and no apparent reactions occurred until 135°C. Above 160°C, the intensities of (**1**) (80.9, 54.7 and 48.9 ppm) and 2,6-xylenol (120.0 ppm) decreased, while 2,2′-methylene-4,4′,6,6′-tetramethyl diphenol, 2,4′-methylene-4,2′,6,6′-tetramethyl diphenol

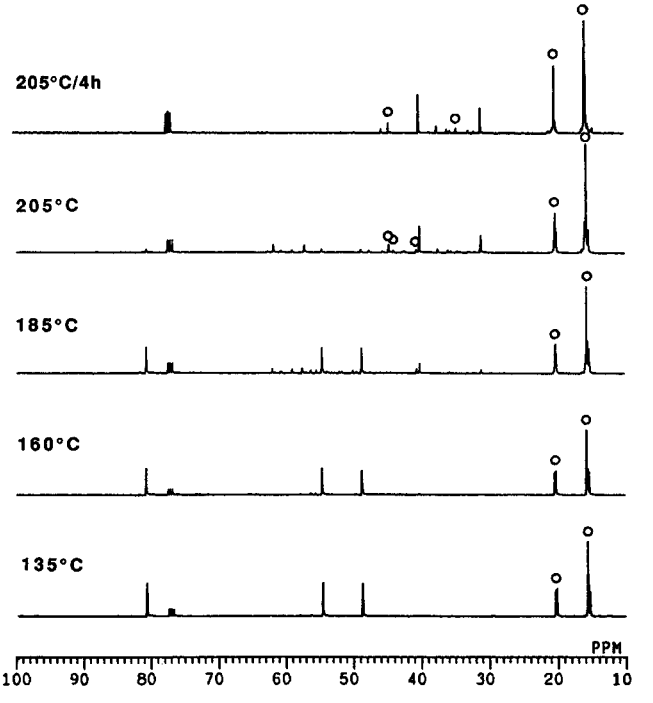


Figure 3 ^{13}C n.m.r. spectra (10–100 ppm range) of the benzoxazine/2,6-xylenol after heating to 135, 160, 185, 205°C, and 205°C for 4 h. The (O) peaks appear negative relative to –CH_2– resonances in DEPT spectra

and 4,4′-methylene-2,2′,6,6′-tetramethyl diphenol (termed the *ortho–ortho*, *ortho–para* and *para–para* dimers, with methylenes at 31.5, 35.8 and 40.3 ppm, respectively) appeared. Their intensities increased with increase of the temperature. Note that the *para--para* dimer appeared first and its relative intensity was always higher than the other two dimers, while the intensity of the *ortho–para* dimer was always very weak. After heating to 205°C for 4 h, the signals of benzoxazine (**1**) and 2,6-xylenol, and most of the resonances of the side-products had disappeared. The dominant products were the *para--para* and *ortho–ortho*

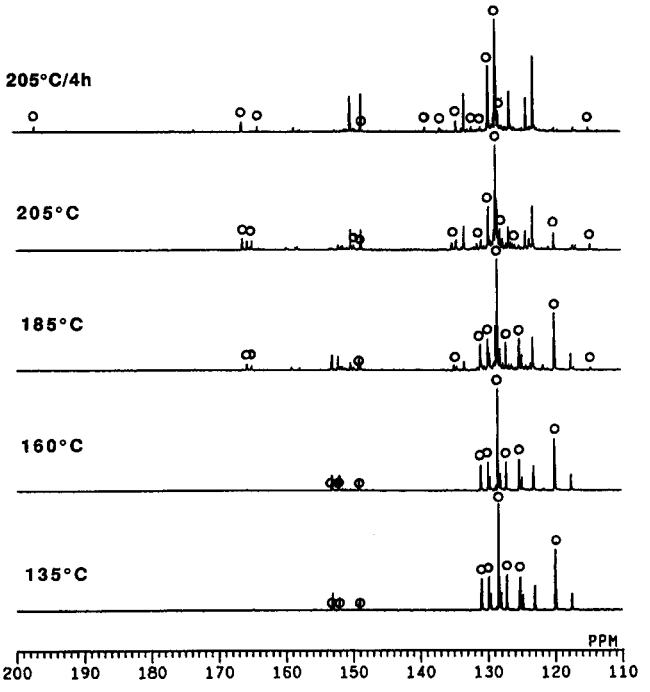


Figure 4 ^{13}C n.m.r. spectra (110–200 ppm range) of the benzoxazine/2,6-xylenol after heating to 135, 160, 185, 205°C, and 205°C for 4 h. The (O) peaks appear negative relative to $-CH_2-$ resonances, while the rest peaks disappear in DEPT spectra

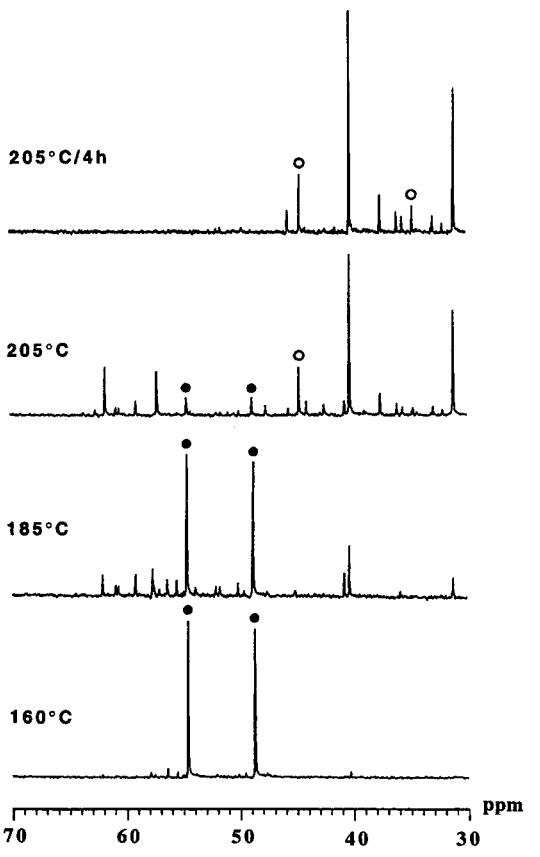
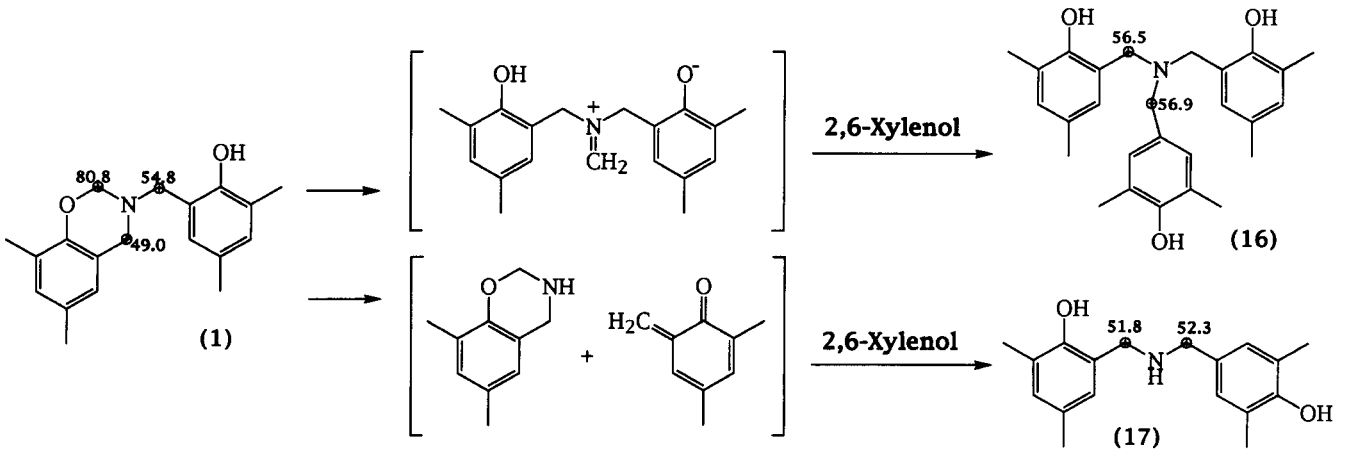


Figure 5 ^{13}C n.m.r. spectra (30–70 ppm range) of the benzoxazine/2,6-xylenol after heating to 160, 185, 205°C, and 205°C for 4 h. The (O) peaks appear negative relative to $-CH_2-$ resonances in DEPT spectra

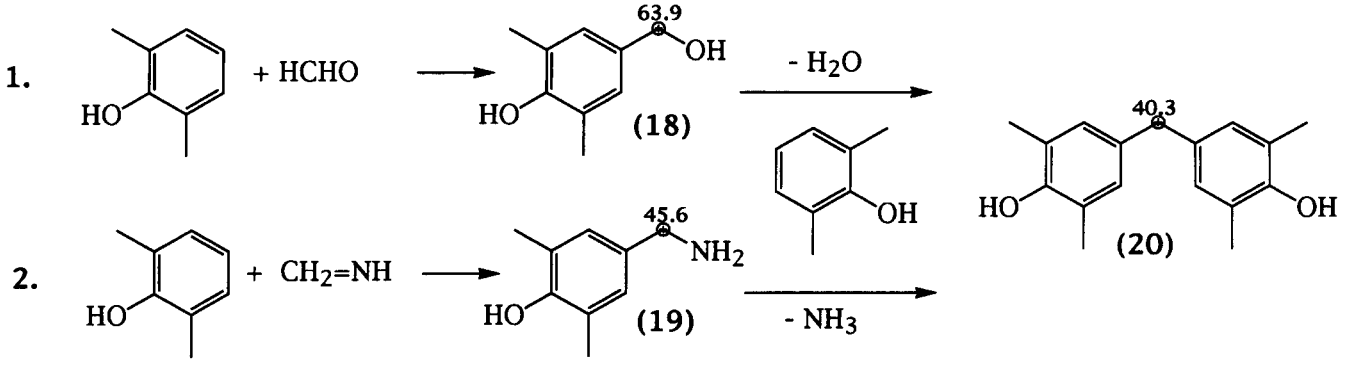
dimers. The result indicates that heating 2,6-xylenol and benzoxazine (**1**) can produce not only *ortho–ortho* methylene linkages, but also *para–para* methylene linkages and *ortho–para* methylene linkages. No *para*-linked product would have formed if 2,6-xylenol was not involved in the reactions. The weight loss of this system is 28% after heating to 205°C for 4 h, which indicates that about 50% of 2,6-xylenol reacted to produce dimers.

The enlarged ^{13}C n.m.r. spectra in the range of 30–70 ppm for the sample heated up to 205°C for 4 h are shown in *Figure 5*. A detailed examination of the ^{13}C spectra provides possible reaction pathways for the benzoxazine/2,6-xylenol system. At 160°C, mixed tris(hydroxybenzyl)amines (**16**) (the methylenes at 57.0 and 56.6 ppm)[5] and bis(hydroxybenzyl) amine (**17**) (the methylenes around 52 ppm and at 50.2 ppm, respectively)[5] appeared first. The reactions between the decomposition species of the benzoxazine and 2,6-xylenol could form these compounds as shown in *Scheme 4*. The resonances at 165.5 ppm (>CH–) and 57.5 ppm ($-CH_2-$) are due to an imine structure (**10**) derived from the decomposition of the benzoxazine as reported before[7]. Note that the *para–para* dimer (40.3 ppm) also appeared at the same time. In order to form this dimer, 2,6-xylenol must gain a methylene linkage from the decomposition of the benzoxazine compound. Two possible pathways are suggested in *Scheme 5*. The decomposition species HCHO and/or CH_2=NH could react with 2,6-xylenol to form 4-hydroxy-3,5-dimethylbenzyl alcohol (**18**) and/or 4-hydroxy-3,5-dimethylbenzylamine (**19**), and then generate the *para–para* dimer (**20**). The signal indicative of 4-hydroxy-3,5-dimethylbenzyl amine (**19**) at 45.6 ppm was observed above 185°C. However, no methylene resonance around 65 ppm due to (**18**) was detected. Possibly (**18**), if formed, reacted with 2,6-xylenol immediately because of a large amount of 2,6-xylenol in the system at that time, or the second pathway was dominate. On the other hand, a group of three peaks with minor intensities was observed at 82.1, 55.2 and 49.5 ppm above 160°C, which can be assigned to 3-(5,5-dimethyl-4-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(-2H)-1,3,-benzoxazine (**21**) formed via the possible pathways shown in *Scheme 6*. The resonances disappeared after heating to 205°C due to the decomposition and/or further reactions similar to (**1**) as previously reported[7].

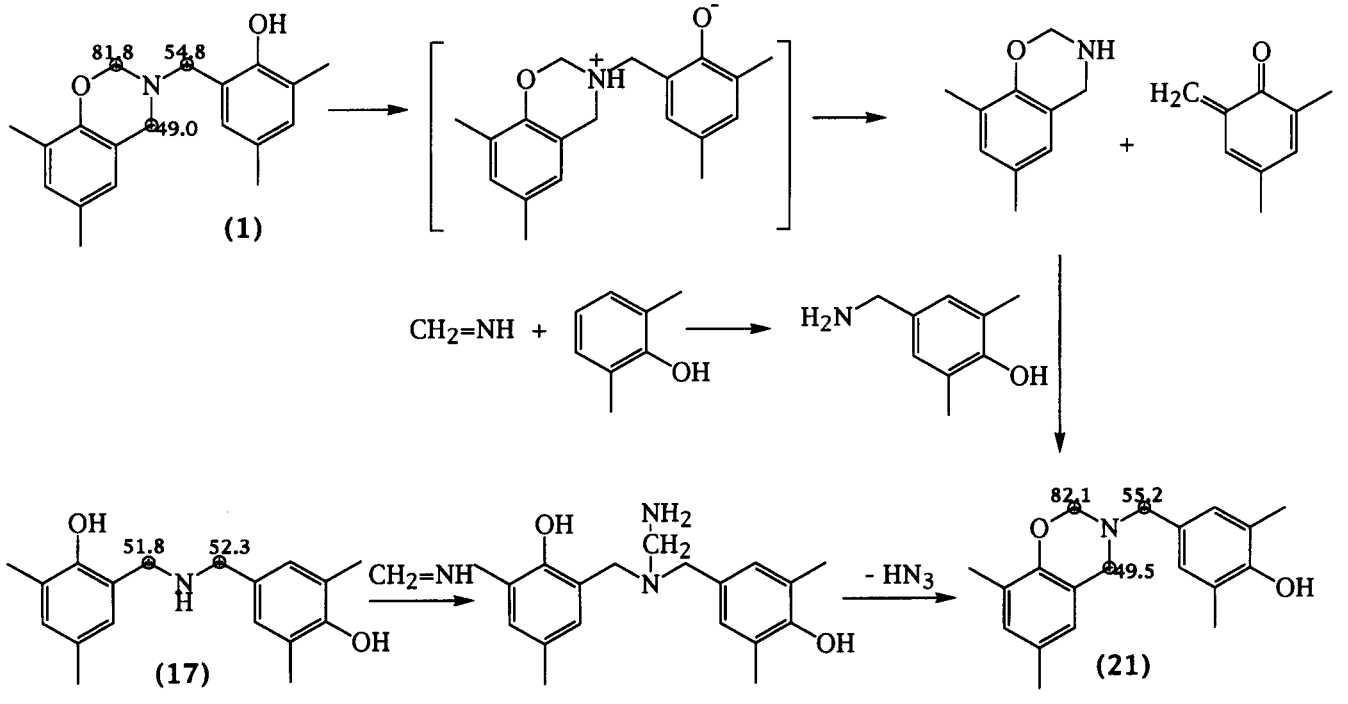
Numerous resonances were observed at a large chemical shift range after heating samples to 185°C. Most of the products observed at 160°C still existed or even increased in intensity at 185°C, while the intensities of the benzoxazine (**1**) and 2,6-xylenol decreased. The *ortho–ortho* dimer (the $-CH_2-$ at 31.5 ppm) could be generated from the decomposition of (**1**), while the *ortho–para* (the $-CH_2-$ at 35.8 ppm) dimer could be formed by the decomposition of the mixed tris- and bis(hydroxybenzyl)amines (**16**) and (**17**) and/or the reaction between *ortho*-benzoquinone methide and 2,6-xylenol. Some other minor resonances can be assigned to amide (**11**) (>C=O, 165.1 ppm, $-CH_2-$ at 40.6 ppm)[8], 2-hydroxy-3,5-dimethylbenzyl alcohol (**5**) ($-CH_2OH$ at 61.9 ppm)[8], and 4-hydroxy-3,5-dimethylbenzyl amine (**19**) ($-CH_2NH_2$ at 45.6 ppm). After heating to 205°C, the intensity of (**1**) decreased considerably while the intensities of *ortho–ortho* and *para–para* dimers (at 31.5 and 40.3 ppm) became dominant in the spectra. Note that no further increase of the intensity of the *ortho–para* dimer (at 35.8 ppm) was observed as compared to that at 185°C. At that time, the intensities of all bis- and tris(hydroxybenzyl)amines decreased to a large extent. Other products were 2-hydroxy-3,5-dimethylbenzyl alcohol (**5**) (61.9 ppm), imine (**10**) (165.9 and 57.5 ppm) and (**22**) (165.9 and 62.5 ppm), imine (**13**) (the –CH=N at 166.5 ppm and the $=N-CH_3$ at



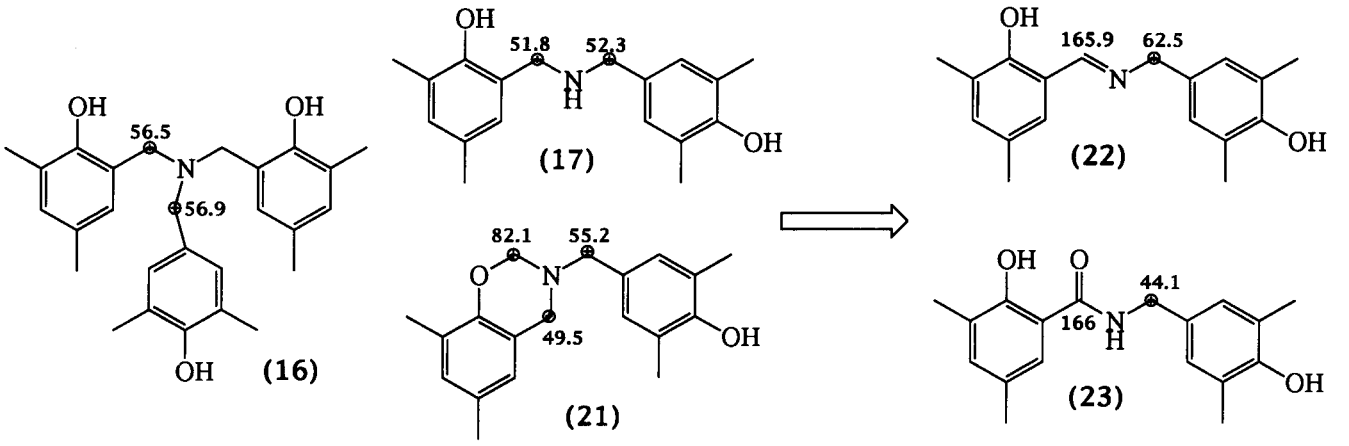
Scheme 4



Scheme 5



Scheme 6



Scheme 7

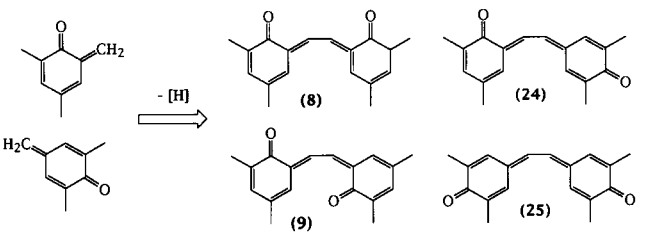
44.8 ppm), amides (**11**) (165.1 and 40.7 ppm), (**14**) (165.9, 34.8 ppm), (**15**) (163.9 and 40.4 ppm) and (**22**) (166 and 44.1 ppm). The imines (**10**), (**13**) and amides (**11**), (**14**), (**15**) could be formed via the decomposition of the benzoxazine (**1**) as suggested previously[7]. The decomposition of (**16**), (**17**) and (**21**) could produce the imine (**22**) and amide (**23**) as shown in *Scheme 7*. The *para–para* ethylene-linked dimer was also obtained as shown by the resonance at 37.8 ppm. After heating the system to 205°C for 4 h, most of the side-products disappeared and the dominant products were the *para–para* and the *ortho–ortho* dimers, together with imine (**13**), amides (**14**) and (**15**), 4-hydroxy-3,5-dimethylbenzylamine (**19**), the *para–para* ethylene-linked dimer and the *ortho–para* dimer. A minor amount of 4-hydroxy-3,5-dimethylbenzaldehyde (196.9 ppm) and 4-hydroxy-3,5-dimethylbenzoic acid (173.2 ppm) originating from oxidation was also detected. Note that most of the side-products (amides and imines) at high temperatures were *ortho*-linked, probably because the intramolecular hydrogen bonding in *ortho*-linked amides and imines stabilizes the structures[6]. The *para*-linked amides and imines are less stable and they decompose at relatively lower temperatures to form *para*-linked dimers. This also explains why the intensity of the *para--para* dimer is always higher than those of the other two dimers.

A few CH resonances at 149–154 ppm were found above 160°C and remained until heating at 205°C for 4 h, possibly due to the formation of Ar=CH–CH=Ar structures as shown in *Scheme 7*. The *ortho*-benzoquinone methide could originate from the decomposition of (**1**) (*Scheme 5*) while the *para*-benzoquinone methide could be formed from either 4-hydroxy-3,5-dimethylbenzyl alcohol or 4-hydroxy-3,5-dimethylbenzylamine through loss of water or NH_3, respectively. Certainly the concentration of these benzoquinone methides was very low, and thus the amount of the Ar=CH–CH–Ar structures was also very small. Note that at low temperatures, three CH resonances were observed at 153.1, 152.2 and 149.1 ppm, possibly corresponding to structures (**24**), (**25**), and (**8**) or/and (**9**). However, we did not observe any *ortho*-linked Ar=CH–CH=Ar structures (**8**) or/and (**9**) in the decomposition of the benzoxazine[7], although in that case the concentration of the *ortho*-benzoquinone methide should be higher than that in the system with xylenols[7]. It seems that the lower pH of the system is necessary for the formation of these structures, which is consistent with the results obtained in novolac/HMTA curing systems[6].

CONCLUSION

The ^{13}C n.m.r. study provides direct evidence about the formation of methylene linkages between phenol rings from reactions of 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine and 2,4- or 2,6-xylenols. Various amines, amides and imines were also obtained during the reaction process, but the diphenylmethanes (dimers) are the predominant products in both systems. However, the reaction pathways of the two systems are different. The benzoxazine can react with 2,4-xylenol at low temperatures (even 90°C), but the reaction with 2,6-xylenol only occurs above 135°C. In addition, 2,4-xylenol can react with the benzoxazine directly and the product is the *ortho–ortho* dimer, while 2,6-xylenol actually reacts with the decomposition species of benzoxazine to form *ortho–ortho*, *ortho–para* and *para–para* dimers. Reaction mechanisms are postulated on the basis of the structural changes observed by ^{13}C n.m.r. studies. The results provide valuable information of the reaction pathways for curing novolac resins with HMTA, which are important for understanding the curing chemistry.

The distinct pathways taken by the *ortho* and *para* vacant sites emphasize the importance of novolac structure in determining the pathways and products of reactions with HMTA. The amount of HMTA is critical for the reaction course and the chemical structure of the cures resins. If conventional novolac resins (containing a high ratio of *ortho*-reactive sites) are cured with a high amount of HMTA, the methylene linkages are formed mainly from the thermal decomposition of benzoxazine intermediates, and they appear at relatively high temperatures, together with the formation of various *ortho*-linked nitrogen-containing products in the resins. If the amount of HMTA is low, the methylene linkages are predominantly derived from the reactions of first-formed intermediates and the vacant sites



Scheme 8

of the resins at relatively low temperatures. The nitrogen content in the cured resins is also low. The results also indicate that the cross-linking density is not simply determined by the amount of HMTA used in the curing. When curing novolac resins to a low temperature (e.g. 150–180°C), using a low level of HMTA, a network linked by methylene linkages (one $-CH_2-$ for one cross-linking bridge) is produced. While in the network obtained using a high level of HMTA, nitrogen-containing structures, such as benzoxazines, benzylamines, amides, imides and imines, also act as linkages, and at least two methylenes will be consumed for one cross-linking bridge. Excess amount of HMTA could inhibit the curing reactivity, increase the nitrogen-retention in the cured resins and increase volatile (containing nitrogen and excess $-CH_2-$ structures) released at high temperatures. The difference of the chemical structures of the cured resins will consequently influence their properties, and the understanding of the curing chemistry will enable us to modify the properties of the resins or extend their application by controlling the curing conditions.

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REFERENCES

1. Kopf, P.W. and Wagner, E.R., *Journal of Polymer Science and Polymer Chemistry*, 1973, **11**, 939.
2. Sojka, S.A., Wolfe, R.A. and Guenther, G.D., *Macromolecules*, 1981, **14**, 1539.
3. Kostyuchenko, V.M., *Kauchuk i Rezina*, 1984, **6**, 14.
4. Hatfield, G.R. and Maciel, G.E., *Macromolecules*, 1987, **20**, 608.
5. Dargaville, T., de Bruyn, P.J., Lim, A.S.C., Looney, M.G., Potter, A.C., Solomon, D.H. and Zhang, X., *Journal of Polymer Science and Polymer Chemistry*, 1997, **35**, 1389.
6. Zhang, X., Looney, M.G., Solomon, D.H. and Whittaker, A.K., *Polymer*, 1997, (in press).
7. Zhang, X., Potter, A.C. and Solomon, D.H., *Polymer*, 1998, **39**, 399–404.
8. Values taken from The Sadtler Standard Carbon-13 n.m.r. Spectra, Sadtler Research Laboratories, Philadelphia, PA, 1977.
9. Tomita, B. and Matsuzaki, T., *Industrial Engineering and Chemical Production. Research and Development*, 1985, **24**, 1.
10. Levy, G. C., Lichter, R. L. and Nelson, G. L., *Carbon-13 Magnetic Resonance Spectroscopy*. Wiley, New York, 1980.