# The chemistry of novolac resins: 9. Reaction pathways studied via model systems of *ortho*-hydroxybenzylamine intermediates and phenols

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Studies on the reaction pathways involved in the curing of novolac resins with hexamethylenetetramine (HMTA) have been further extended by a [13]C n.m.r. examination of the thermal decomposition of tris(2-hydroxy-3,5-dimethylbenzyl)amine and its reactions with 2,4- and 2,6-xylenol. Both the thermal decomposition and reactions with the xylenols lead to methylene-bridged phenolic structures (for chain extension and crosslinking in curing novolac resins). Other pathways lead to minor amounts of products, and some of which remain in the systems up to 205°C. The results taken in conjunction with our previous studies allow us to draw general conclusions on the overall novolac/HMTA reactions as deduced from the model studies. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

In previous papers of this series[1–8] we have reported on the use of small-molecular models to study the reaction pathways of the novolac/(HMTA) hexamethylenetetramine system[2,4–7]. Benzoxazine and hydroxybenzylamine have been identified as key initially formed intermediates in the curing reaction sequences[2]. The conversion from benzoxazine and *para*-hydroxybenzylamine intermediates to methylene-linked structures in further reactions has been investigated[4–7], but no studies of the equally important *ortho*-hydroxybenzylamine intermediates have been reported.

In this paper, the thermal decomposition of *ortho*-hydroxybenzylamine intermediates and their reactions with phenols are studied by taking tris(2-hydroxy-3,5-dimethylbenzyl)amine, 2,4- and 2,6-xylenols as model compounds. This study, taken in conjunction with previous work on reactions of benzoxazine and *para*-hydroxybenzylamine[4–7], completes the model reactions necessary for the postulation of the curing chemistry of the novolac/HMTA system.

## EXPERIMENTAL

### Samples

2,4-Xylenol, 2,6-xylenol and hexamethylenetetramine (HMTA) used in this study are the same as reported previously[2,4–8]. A mixture of 2,4-xylenol, HMTA and 35.5% formaldehyde (aq.) in mole ratio of 12:1:4.3 was refluxed for 48 h, and the product tris(2-hydroxy-3,5-dimethylbenzyl)amine was isolated by medium-pressure

liquid chromatography (MPLC) using $CH_2Cl_2$ and then $CH_2Cl_2$:EtOH (95:5) as solvents. The structure and purity of the compound was confirmed by ^{1}H and [13]C n.m.r. spectroscopy. Tris(2-hydroxy-3,5-dimethylbenzyl)amine and its 1:1 (w/w) mixtures with 2,4- or 2,6-xylenol were heated in a Eurotherm 902 oven with the same heating cycle as was used to cure novolac resins with HMTA and other model systems[3–8]. In order to follow the structural changes during the heating process, samples were taken after heating to 90, 105, 120, 135, 160, 185 and 205°C for 6 h and finally after heating to 205°C for 4 h.

### N.m.r. experiments

Solution [13]C n.m.r. spectra were recorded immediately after dissolving the samples in $CDCl_3$ (99.8%) solvent on a Varian400 Unity + or a JEOL JNM-GX400 spectrometer at a resonance frequency of 100 MHz for carbon-13. [13]C DEPT spectra were observed by the normal DEPT pulse sequence with $\theta = 135°$ and $\tau = (1/2J_{CH})$ of 3.7 ms. $CDCl_3$ at 77.0 ppm (relative to TMS) was used as an internal chemical shift reference.

## RESULTS AND DISCUSSION

The [13]C n.m.r. assignments of tris(2-hydroxy-3,5-dimethylbenzyl)amine are shown in structure (**1**) in *Scheme 1*. The resonance at 56.5 ppm is due to the $CH_2$ between a phenolic ring and nitrogen of tris(2-hydroxy-3,5-dimethylbenzyl)amine, while the *ortho*- and *para*-methyl substituent carbons appear at 15.5–15.9 and 20.3 ppm, respectively. For 2,4- or 2,6-xylenol, the *ortho*- or *para*-unsubstituted phenolic carbon appears at 114.7 or 120.1 ppm[2,4,5]. In this study, the resonances at 56.5, 114.7 and 120.1 ppm were taken as indicative for tris(2-hydroxy-3,5-dimethylbenzyl)-amine (**1**), 2,4-xylenol and 2,6-xylenol, respectively. The intensity of *para*-phenolic methyl carbons at 20.3 ppm in
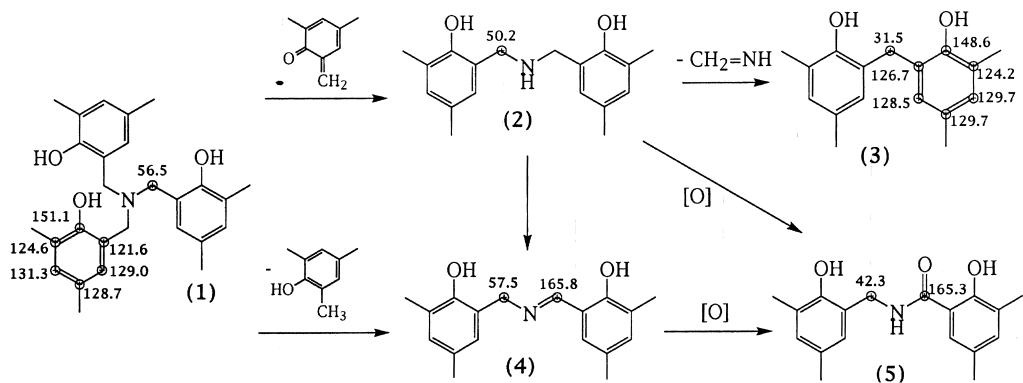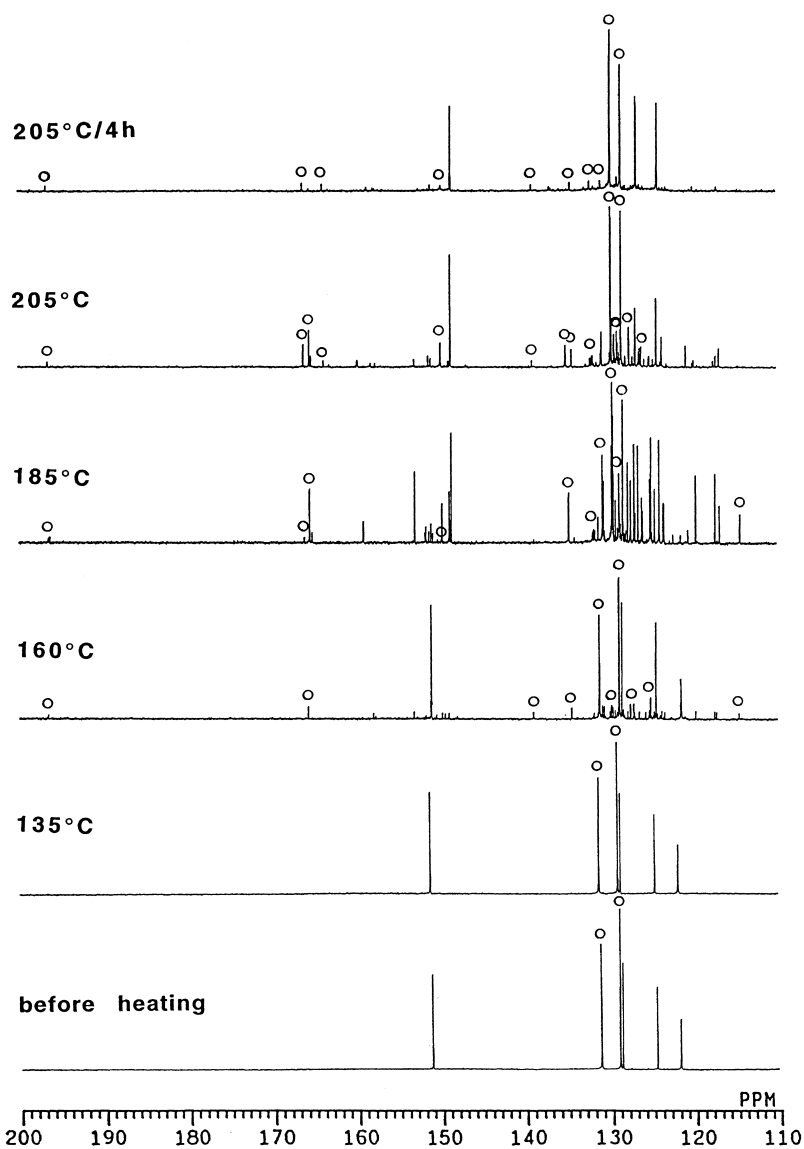
**Scheme 1**



**Figure 1** $^{13}$C n.m.r. spectra (110–200 ppm) of tris(2-hydroxy-3,5-dimethylbenzyl) amine after heating

the systems was taken as an internal reference since its intensity did not change during the reactions.

*Thermal decomposition of tris(2-hydroxy-3,5-dimethylbenzyl)amine*

The $^{13}$C n.m.r. spectra of tris(2-hydroxy-3,5-dimethyl-benzyl)amine after heating are shown in *Figures 1* and *2*.

The peaks marked with circles in *Figure 1* are due to CH and the rest are due to quaternary carbons, whereas in *Figure 2* the marked peaks are either CH or CH$_3$, and the rest are CH$_2$, as detected by DEPT spectra. Note that tris(2-hydroxy-3,5-dimethylbenzyl)amine (**1**) is relatively stable and no significant decomposition was detected until 135°C. After heating to 160°C, the intensity of (**1**) decreased while
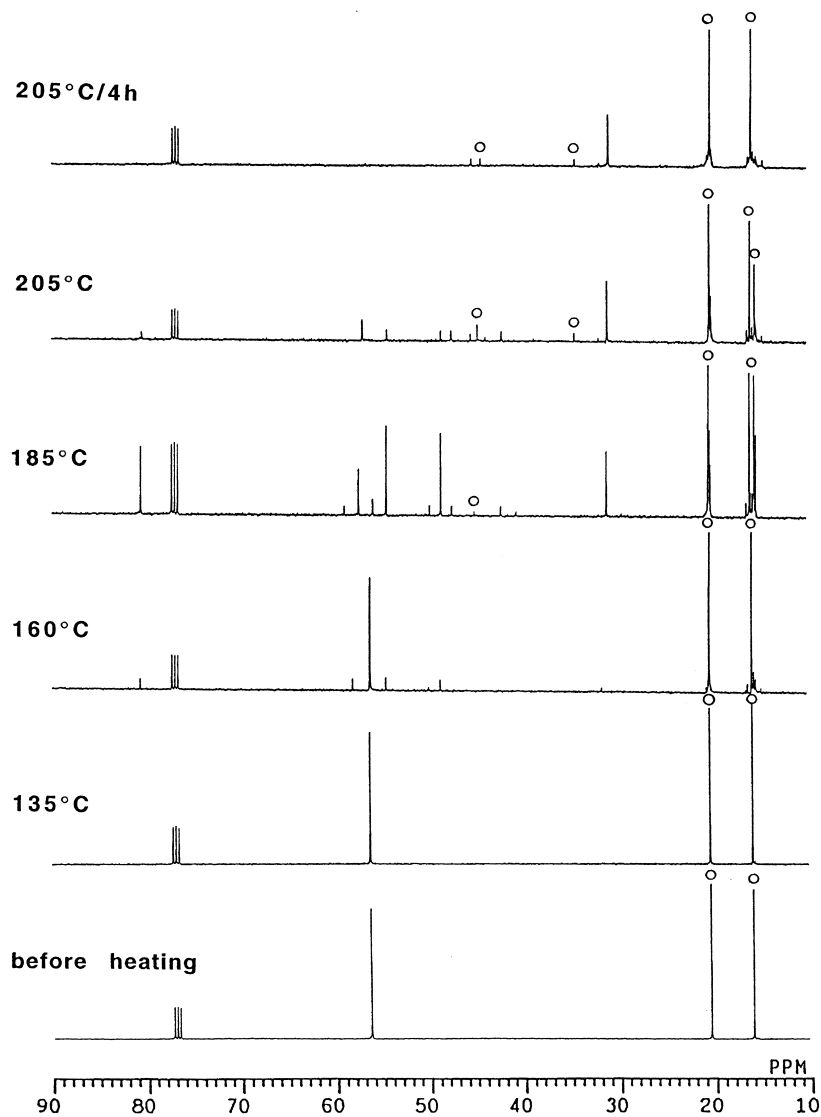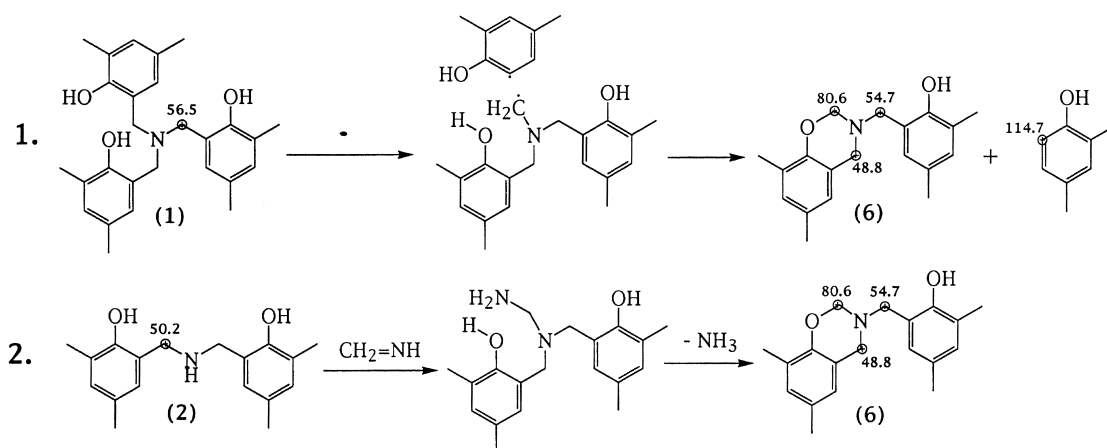
**Figure 2** $^{13}C$ n.m.r. spectra (10–90 ppm) of tris(2-hydroxy-3,5-dimethylbenzyl) amine after heating
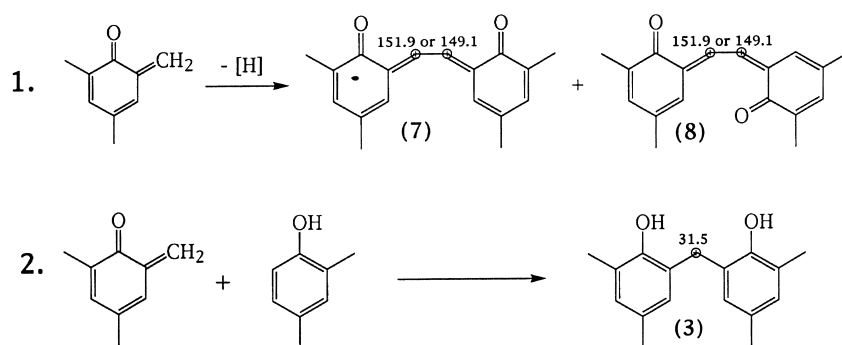


**Scheme 2**

new resonances were observed at 196.7, 165.8, 114.7, 80.6, 58.2, 54.7, 50.2, 48.8 and 31.5 ppm, in conjunction with various aromatic resonances in the range 117–156 ppm. The 50.2 ppm peak was assigned to the $CH_2$ between a phenol ring and a nitrogen of bis(2-hydroxy-3,5-dimethylbenzyl)

amine $(2)^{2-7}$, while the 31.5 ppm peak is attributed to the methylene linkage in 2,2′-methylene-4,4′,6,6′-tetramethyl-diphenol (hereafter called the *ortho–ortho* dimer $(3)^{2-7}$. This suggests that tris(4-hydroxy-3,5-dimethyl-benzyl)amine can decompose to the *ortho–ortho* dimer
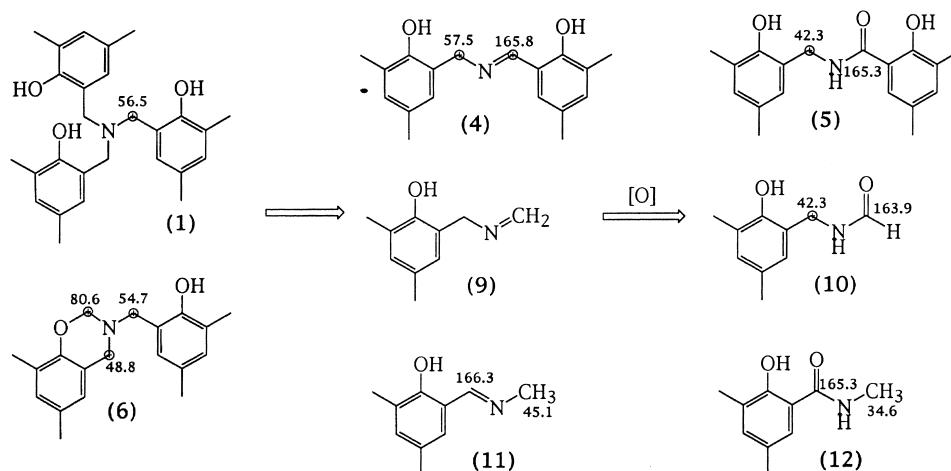
via bis(4-hydroxy-3,5-dimethylbenzyl)amine (*Scheme 1*) by loss of a benzoquinone methide and then a $CH_2=NH$ molecule. This is a similar reaction sequence to that noted on heating tris(4-hydroxy-3,5-dimethylbenzyl)amine[6,7]. The peaks at 165.8 and 57.5 ppm were assigned to an imine (**4**), which could arise by loss of a 2,4,6-trimethyl-phenol unit from (**1**) and/or dehydrogenation of (**2**)[4-7]. 2-Hydroxy-3,5-dimethylbenzaldehyde was also formed (seen at 196.7 ppm, the –CHO carbon) as noted in previous reports[4-7]. A quaternary carbon resonance at 165.3 ppm and a –CH$_2$– at 42.3 ppm could be due to amide (**5**) which might originate from the oxidation of imine (**4**) and/or amine (**2**) (*Scheme 1*)[4,5].

The triple peaks with equal intensity at 80.6, 54.7 and 48.8 ppm were observed at 160°C which are characteristic of another important intermediate in the curing of novolac resins[3,9-11], 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine (**6**)[2-5]. It was possibly formed by loss of a 2,4-xylenol from (**1**) (*Scheme 2*-1). In support of this, we did observe the simultaneous appearance of a resonance at 114.7 ppm due to *ortho*-unsubstituted phenolic CH of 2,4-xylenol. The reactions between (**2**) and the $CH_2=NH$ unit liberated during the decomposition could also produce (**6**) (*Scheme 2*-2). The intensity of (**6**) increased with temperature, and then decreased above 185°C due to thermal decomposition or

further reactions. Our previous results indicated that the decomposition of benzoxazine (**6**) also produced the *ortho–ortho* dimer, and a number of side-products[4,5]. Two CH resonances were observed around 149.1 ppm at 160 and 185°C, and then 151.9 ppm at 205°C, which may be attributed to the stilbenequinone structures (**7**) and (**8**) arising from the self-coupling of the benzoquinone methide (*Scheme 3*-1)[4-7]. The benzoquinone methide unit formed during the decomposition could also react with 2,4-xylenol (formed in the decomposition shown in *Scheme 2*-1) to generate the *ortho–ortho* dimer (**3**) (*Scheme 3*-2). The intensity of dimer (**3**) became predominant after heating to 205°C whereas the intensity of (**1**) disappeared. Note that the intensities of benzoxazine (**6**) and 2,4-xylenol at 114.7 ppm also became very weak at 205°C due to further reactions[4,5]. The other products present at that time were imine (**4**) (–CH=N– 165.8 ppm, –CH$_2$–N= 57.5 ppm), (**11**) (–CH=N– 166.3 ppm, =N–CH$_3$ 44.8 ppm) and amide (**5**) (–CO–N< 165.3 ppm, –CH$_2$–N< 42.3 ppm), (**10**) (–NH–CHO 163.9 ppm, –CH$_2$–NH– 42.3 ppm) and (**12**) (–CO–NH– 165.3 ppm, –NH–CH$_3$ 34.6 ppm), as shown in *Scheme 4*. After heating at 205°C for 4 h, the *ortho–ortho* dimer was the major product (148.6, 129.7, 128.5, 126.7, 124.2 and 31.5 ppm) and other products, such as imine (**11**), amide (**12**) and 2-hydroxy-3,5-dimethylbenzaldehyde, were only present in minor amount.



**Scheme 3**



**Scheme 4**

In summary, the thermal decomposition of tris(2-hydroxy-3,5-dimethylbenzyl)amine can produce the *ortho–ortho* dimer via similar reaction pathways to those postulated for tris(4-hydroxy-3,5-dimethylbenzyl)amine intermediates[6]. Benzoxazine structures were also formed during the reaction, and they decomposed to dimers at high temperatures. Similar to the thermal decomposition of *para*-hydroxybenzylamine[6] and benzoxazine[4] intermediates, the imine and amide products were produced during the reaction and some of these decomposed to form dimers at higher temperatures. Among the three types of first-formed intermediates, tris(*ortho*-hydroxybenzyl)amines are more thermally stable than tris(*para*-hydroxybenzyl)amines, but less stable than benzoxazine intermediates.

*Reactions of tris(2-hydroxy-3,5-dimethylbenzyl)amine with xylenol*

The $^{13}$C n.m.r. spectra of the tris(2-hydroxy-3,5-dimethyl

benzyl)amine (1) and 2,4-xylenol or 2,6-xylenol after heating are shown in *Figures 3–6*, respectively. As in *Figures 1* and *2*, the peaks marked with circles in *Figures 3* and *5* are due to CH and the rest are quaternary C, while those in *Figures 4* and *6* are either CH or CH$_3$ and the rest are CH$_2$, as detected by DEPT spectra.

In the presence of 2,4-xylenol, the decomposition of (1) and/or its reactions with 2,4-xylenol occurred at lower temperatures, as products such as (2) (50.2 ppm) and *ortho–ortho* dimer (3) (31.5 ppm) could be detected after heating to 90°C for 6 h. With increasing temperature, the intensity of (1) decreased while that of (2) increased and then decreased above 160°C. Consequently, the intensity of *ortho–ortho* dimer (3) increased as the temperature increased. The reaction pathway from tris(2-hydroxy-3,5-dimethylbenzyl)-amine and 2,4-xylenol to the *ortho–ortho* dimer could be via a hydrogen-bonding mechanism, similar to tris(4-hydroxy-3,5-dimethylbenzyl)amine/2,4-xylenol (*Scheme 5*-1)[7]. The
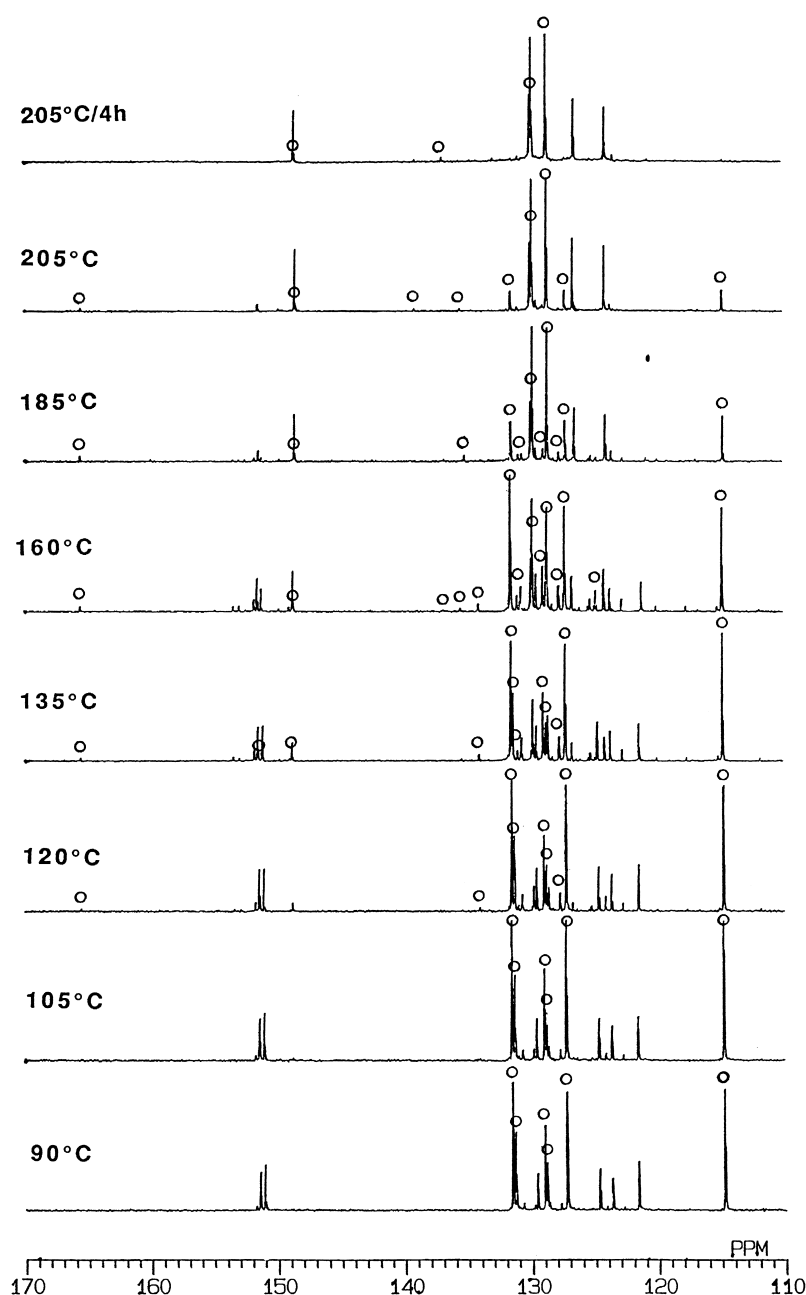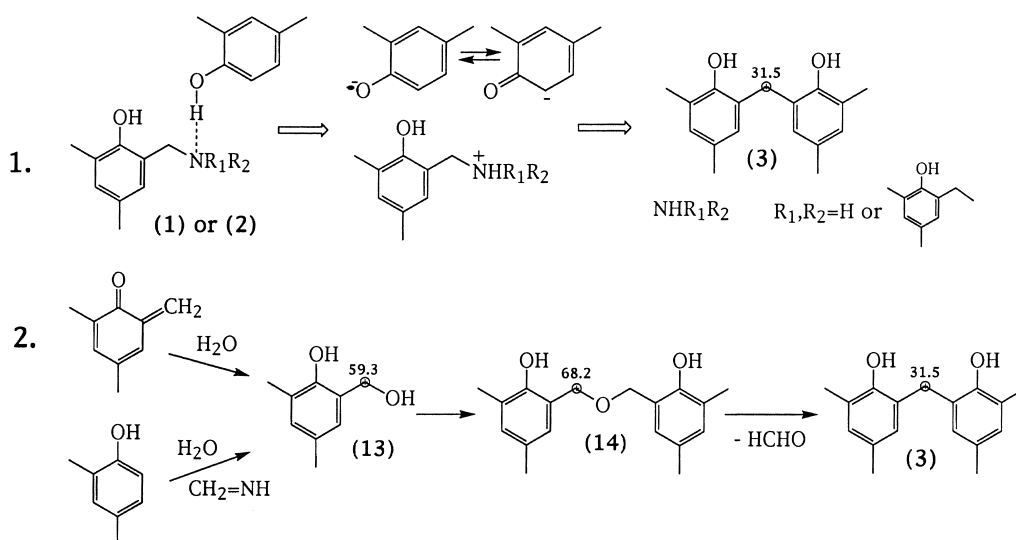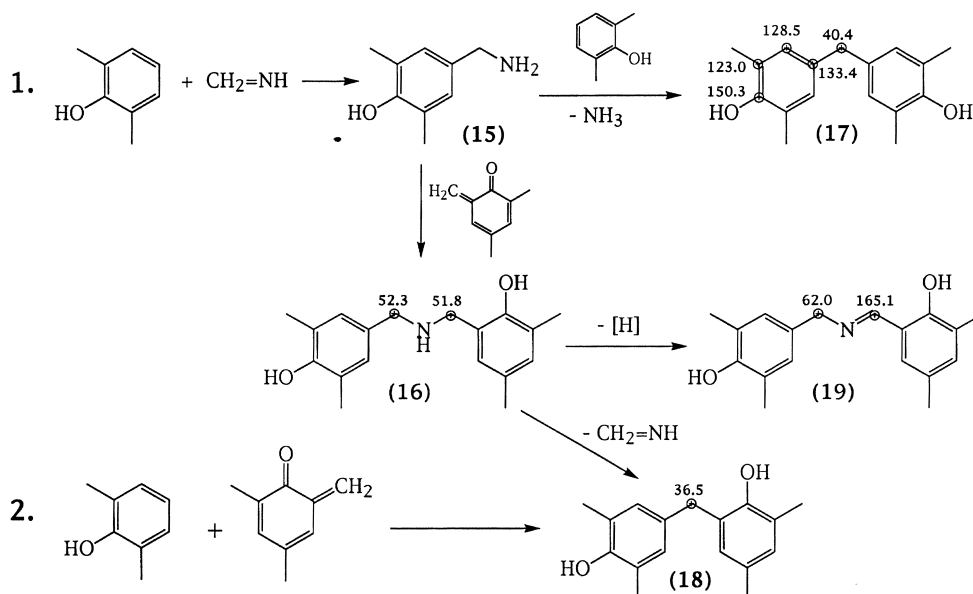


**Figure 3** $^{13}$C n.m.r. spectra (110–170 ppm) of the mixture of tris(2-hydroxy-3,5-dimethylbenzyl)amine and 2,4-xylenol after heating

**Scheme 5**



**Scheme 6**

presence of 2,4-xylenol also reduced the pH of the system, and thus caused the decomposition of (1) (*Scheme 1*) to occur at a relatively low temperature. On the other hand, resonances around 69 ppm observed at 120–185°C are consistent with an ether structure (14) which could be formed via a pathway shown in *Scheme 5*-2. The 2-hydroxy-3,5-dimethylbenzyl alcohol (13) might originate from the reaction with water present as by-product. Since no ether structure was observed for the system without 2,4-xylenol, it seems that this reaction is favoured by a low pH. No significant signal was observed for (13) at 59.3 ppm, and we thus conclude that the conversion to ether is fast. This ether structure (14) could decompose at high temperatures to produce *ortho–ortho* dimer (3). The structures (7) and (8) were also formed in this system as seen by the CH resonances around 150 ppm.

During the process, the three peaks of benzoxazine (6) at 80.9, 54.8 and 49.0 ppm were also observed at 120–185°C. Compared to the system of pure tris(2-hydroxy-3,5-

dimethylbenzyl)amine, the presence of 2,4-xylenol in the system caused (6) to appear and then to decompose at relatively lower temperatures. This reactivity is probably attributed to the low pH caused by 2,4-xylenol. The decomposition of (6) and the reaction with 2,4-xylenol exhausted the benzoxazine (6) at a lower temperature to produce the *ortho–ortho* dimer[5]. In this system, the only nitrogen-containing product was imine (4) (165.8 and 57.5 ppm) and no other imine and amide structures were observed. After heating to 205°C, the *ortho–ortho* dimer (3) became the dominant product, and some extra 2,4-xylenol (114.7 ppm) still remained but evaporated completely after heating at 205°C for 4 h. The result suggests that reactions between tris(2-hydroxy-3,5-dimethylbenzyl)amine and 2,4-xylenol can readily produce the *ortho–ortho* dimer.

In contrast to the system with 2,4-xylenol, the tris(2-hydroxy-3,5-dimethylbenzyl)amine/2,6-xylenol system is relatively stable and no apparent reactions occurred below 120°C. Above 120°C, the intensities of (1) (at 56.5 ppm)
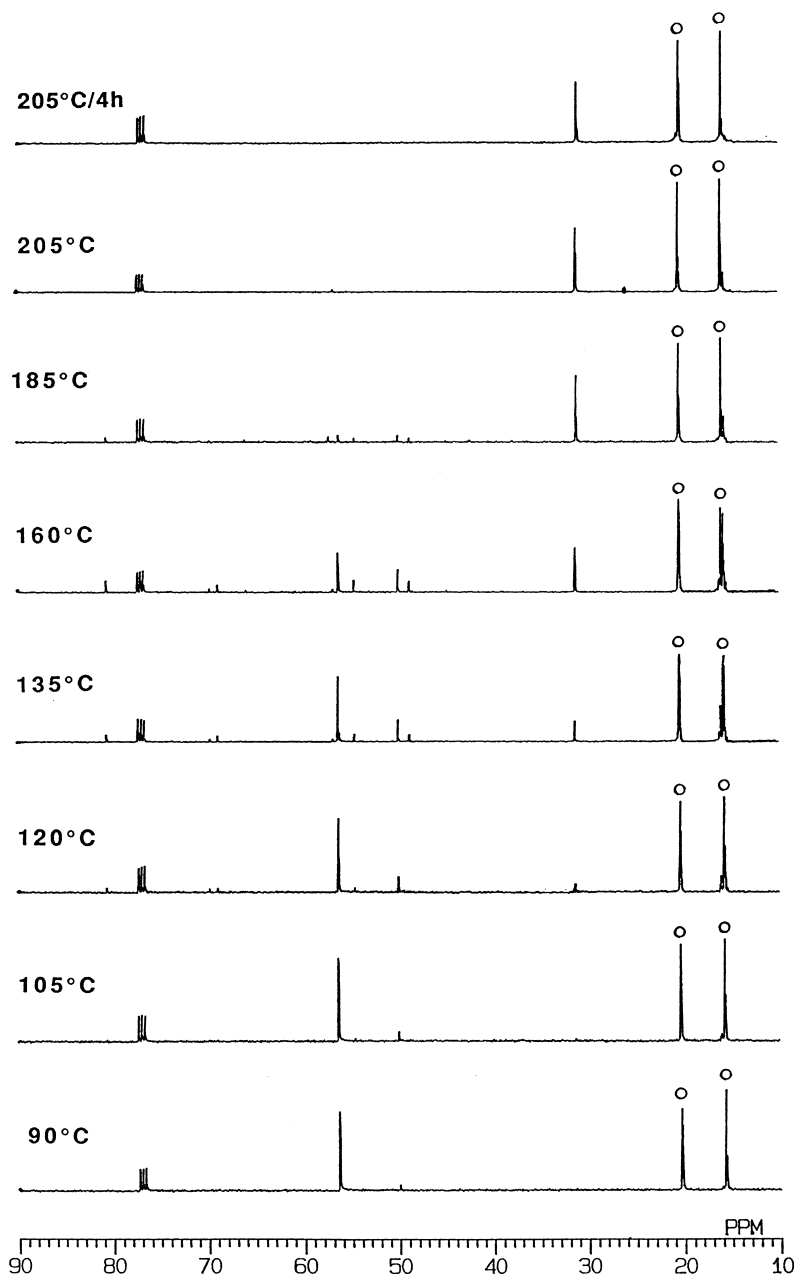
**Figure 4** $^{13}$C n.m.r. spectra (10–90 ppm) of the mixture of tris(2-hydroxy-3,5-dimethylbenzyl)amine and 2,4-xylenol after heating

started to decrease, while the signals of (2) (at 50.2 ppm) and (6) (at 80.7, 54.8 and 48.9 ppm) could be observed in conjunction with 2,4-xylenol (at 114.6 ppm). The ether structure at 69.1 ppm was also observed at 120–160°C. Above 135°C, the *ortho–ortho* dimer (3) at 31.5 ppm was detected, and its intensity increased as the temperature increased. Note that the *para–para* dimer (17) was also observed at 40.4 ppm at 185°C, and further heating even caused the formation of a minor amount of *ortho–para* dimer (18) at 36.1 ppm[2–7]. After heating to 205°C for 4 h, the initial tris(2-hydroxy-3,5-dimethylbenzyl)amine, 2,6-xylenol and most of the other intermediates disappeared, and the dominant products were *ortho–ortho* and *para–para* dimers.

These results indicate that 2,6-xylenol can be involved in the reactions with tris(2-hydroxy-3,5-dimethylbenzyl)-amine, and produce not only *ortho–ortho* methylene linkages, but also *para–para* methylene linkages together with a minor amount of *ortho–para* methylene linkages. If

2,6-xylenol was not involved in the reactions, there should not have been any *para*-linked products. Based on the weight loss and the structures of the products, it can be calculated that 14% of 2,6-xylenol has been converted to the *para–para* or the *ortho–para* dimer. The *para–para* dimer (17) might originate from the reactions of 2,6-xylenol with some decomposition species as shown in *Scheme 6*-1. The 4-hydroxy-3,5-dimethylbenzylamine (15) could further react with 2,6-xylenol to form *para–para* dimer (17) at high temperatures. The reaction between (15) and 2-benzoquinone methide could generate an amine (16) (52.3 and 51.8 ppm at 185°C)[7] and the decomposition of (16) would give the *ortho–para* dimer (18) (36.1 ppm at 205°C). The other products at 205°C were imine (4) (–CH=N⟨ 165.8 ppm and ⟩N–CH$_2$– 57.7 ppm), imine (11) (–CH=N⟨ 166.3 ppm, ⟩N–CH$_3$ 45.1 ppm) and amide (5) (–CO–NH– 165.3 ppm, –NH–CH$_2$– 42.3 ppm). The resonances at 165.1 ppm (–CH=N–) and 62.0 ppm (–NH–CH$_2$–) might be due to an imine (19) (*Scheme 6*-1)[7].
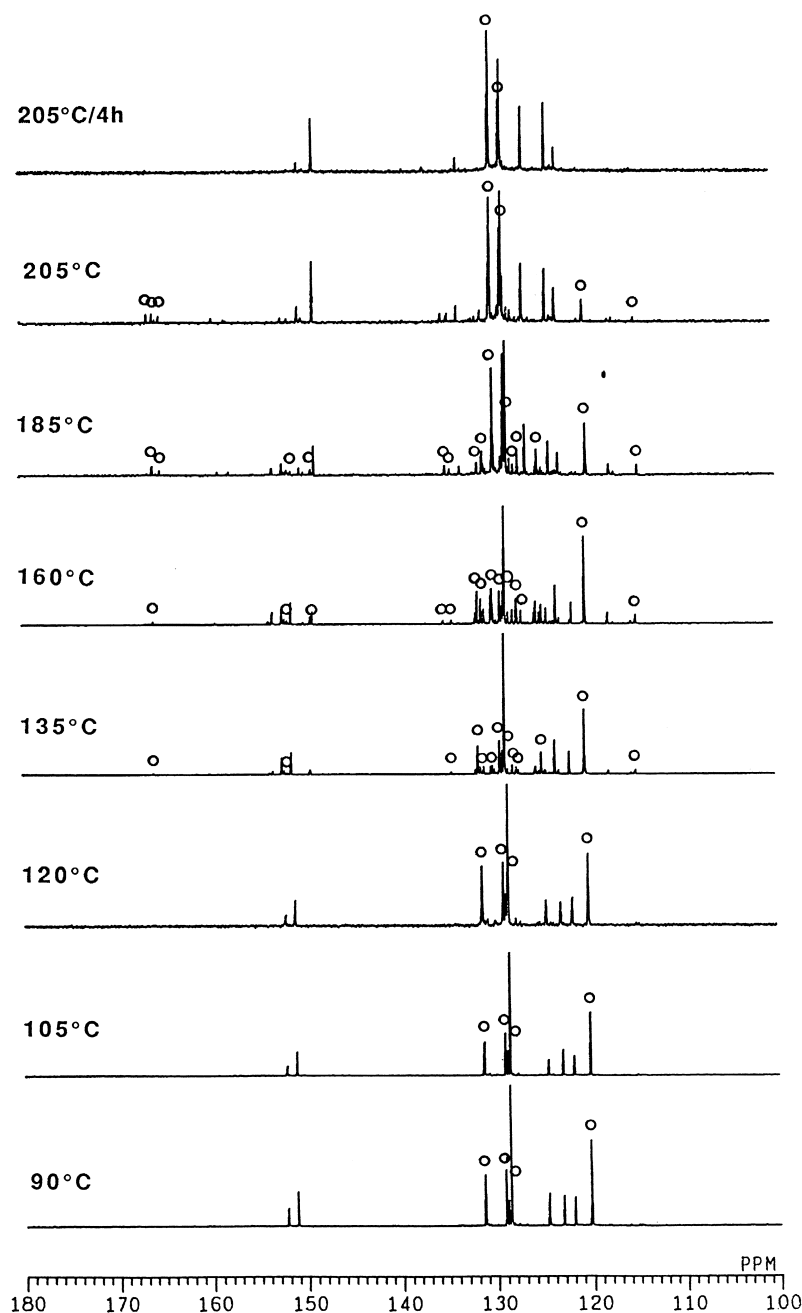
**Figure 5** $^{13}$C n.m.r. spectra (100–180 ppm) of the mixture of tris(2-hydroxy-3,5-dimethylbenzyl)amine and 2,6-xylenol after heating

After heating to 205°C for 4 h, all the 2,6-xylenol had reacted or evaporated, and the products were mainly *ortho–ortho* dimer (**3**), *para–para* dimer (**17**) and a minor amount of *ortho–para* dimer (**18**).

It can be concluded that the presence of xylenols decreases the decomposition temperature of tris(2-hydroxy-3,5-dimethylbenzyl)amine (**1**) possibly due to a low pH effect. In addition, 2,4-xylenol can react with (**1**) at relatively lower temperatures to produce an *ortho–ortho* dimer, but 2,6–xylenol reacts with the decomposition products from (**1**). The reactions produce not only the *ortho–ortho* dimer, but also *para–para* and *ortho–para* dimers. The amount of other products, such as benzoxazine, ethers, imines and amides in the systems with xylenols, is much lower compared with the self-decomposition. These products can also be decomposed or further react with xylenols to produce methylene-linked dimers at high temperatures.

*Reaction mechanisms of curing novolac resins with HMTA*

This study of the chemistry of curing model phenols with HMTA[2,4–7] has provided detailed information which can be applied to the more complex novolac/HMTA systems[3]. The reaction pathways can be summarized below and related to the novolac system:

(1) Curing novolac resins with HMTA starts with reactions between novolac and HMTA to form initial curing intermediates, mainly substituted benzoxazines, hydroxybenzylamines, and a small amount of triazine and diamine intermediates. With the existence of a trace amount of water as an impurity, benzyl alcohols and ether intermediates may also possibly form. These initially formed intermediates can be either *ortho–*
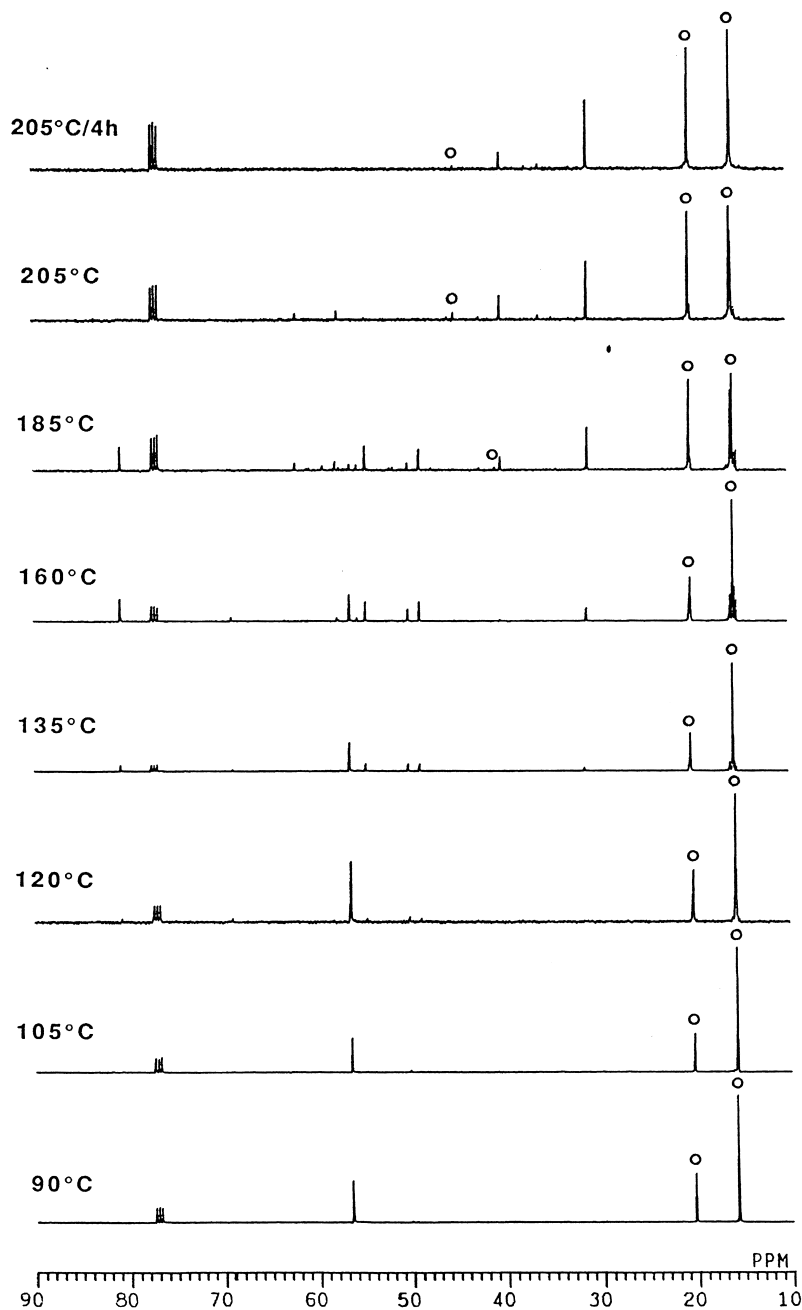
**Figure 6** $^{13}$C n.m.r. spectra (10–90 ppm) of the mixture of tris(2-hydroxy-3,5-dimethylbenzyl)amine and 2,6-xylenol after heating

linked or *para*-linked; the *ortho*-linked structures are more stable than the *para*-linked ones possibly due to the formation of intramolecular hydrogen-bonding with a six-membered ring structure in those nitrogen- and oxygen-containing species. The benzoxazine structure is the most stable intermediate. Among the *ortho*-linked intermediates, the ratio of benzoxazine/hydroxybenzyl-amine depends on the ratio of novolac/HMTA. A large amount of HMTA will result in benzoxazine intermediates as the major products while hydroxybenzylamines are mainly formed if the HMTA ratio is low.

(2) With increase of temperature, these initially formed intermediates are thermally decomposed to produce methylene linkages between phenolic rings of novolac for chain extension and crosslinking. A higher novolac/HMTA ratio reduces the decomposition temperature which is related to the lower pH of the system. Vacant *ortho*- or *para*-phenolic CH of novolacs can

also react with the initially formed intermediates if the polymer chains have sufficient mobility to form the methylene linkages. Trace amounts of water also affect the reactions. These results are consistent with previous reports[12–18].

(3) If both *ortho*- and *para*-linked initially-formed intermediates are available at the initial curing stage, the *para–para* methylene linkages will be formed at relatively low temperatures because the initial *para*-linked intermediates are less stable. The *ortho–para* and then the *ortho–ortho* linkages are formed with increasing temperature.

(4) Various imine and amide products are also formed during the decomposition and in the other reactions. The imine structures could mainly originate from the decomposition and/or dehydrogenation of the initially formed intermediates while the amides could be generated by oxidation. Some can thermally decompose

or undergo further reactions to produce methylene linkages, and others can even remain in the crosslinked network up to 205°C. The *ortho*-linked imines and amides are also more stable than the *para*-linked ones.

In this study of model systems[2,4–7], various reaction pathways have been postulated based on the structural changes observed by $^{13}$C n.m.r. spectroscopy. Benzyl quinone methide is likely to play a key role in the thermal decomposition and further reactions of the initially formed intermediates to produce methylene linkages and various other products. Oxidation by air is predominant in reactions at higher temperatures if curing takes place under an air atmosphere. Liberated $CH_2=NH$, a trace amount of formaldehyde and water also play certain roles in various reactions. The study on model systems provides possible reaction pathways for the curing of novolacs, and it is believed that the curing mechanisms of the resins and the reactions in model systems are similar. This understanding of the chemistry of the curing of novolac resins is important when considering possible modifications of the structures and extending the applications of conventional resins.

In the study of curing novolac resins with HMTA, we found that the curing reactivity and the chemical structures of finally-cured resins can be controlled by the HMTA level and chemical structures of the initial resins used[3]. This result is understandable according to the reaction pathways obtained from the study on model systems reported here. When the HMTA level is high, the reactive sites of the resins may be exhausted after the formation of those initially-formed intermediates, and the methylene linkages mainly originate from the thermal decomposition of those intermediates. This should occur at relatively high temperatures. In contrast, if the HMTA level is low, the methylene linkages are predominantly derived from the reactions of the first-formed intermediates and the vacant sites of the resins. This causes the crosslinked network to be formed at a relatively low temperature. The result also indicates that the crosslinking density of the cured resins is not simply determined by the amount of HMTA used in the curing. When curing novolac resins at a relatively low temperature (e.g. 150–180°C), a network linked by methylene bridges is produced at low HMTA levels, whereas a high level of HMTA results in a network mainly linked by nitrogen-containing structures such as benzoxazines, benzylamines, amides, imides, imines, and at least two methylenes are consumed for each linkage.

The stability of the *ortho*- and *para*-linked intermediates also emphasizes the importance of the novolac structure in determining the reaction pathway and reactivity. If the resins contain more *para*-vacant reactive sites, curing reactions will occur at a relatively low temperature to form a network linked by methylene linkages. On the other hand, if the ratio of *ortho*-reactive sites is high, stable *ortho*-linked intermediates will be produced during the curing, and their decomposition and further reactions will occur at relatively high temperatures. If a high level of HMTA is used for a resin containing a high ratio of *ortho*-reactive sites, substituted benzoxazines will be the major first-formed intermediates and they will remain in the system until very high temperatures due to their high stability. The amount of nitrogen-containing structures in the finally cured resins may be high. The amount of volatile products released at high temperatures will also be high due to thermal decomposition and further reactions of the intermediates.

However, since these model studies were carried out on small molecular non-crosslinked systems, the situation is slightly different to that encountered in the curing of novolac resins where a highly crosslinked polymer network results. This could be the reason why a large amount of nitrogen-containing structures such as imines and amides still remain in the finally cured resins, while only a very minor amount remains in our model systems. In addition, imide structures were obtained in the curing of novolac resins due to further oxidation of amides[3] but they were not observed in the model systems. The reactivity of the model systems is also somewhat different from the curing of the resins due to differences such as pH, molecular weight, stereo-structure and molecular mobility. Therefore, reactions in model systems may occur at a different temperature to that formed in the resin systems. The amount of each side-product is also different in the two systems at a given temperature, and generally it is higher in the resins after curing to high temperatures. Further studies currently being carried out on the reactions of model compounds of novolac oligomers[8] will extend the curing chemistry from phenols to novolac resins, and the results are to be published soon.

## ACKNOWLEDGEMENTS

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