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The chemistry of novolac resins: Part 7. Reactions of *para*-hydroxybenzylamine intermediates

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As part of our systematic study on the curing reaction of novolac resins with hexamethylenetetramine (HMTA), the reactions between 2,6-xylenol (a model phenol) and HMTA, and the thermal decomposition of their first-formed products bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines have been studied by ^{13}C and ^{15}N n.m.r. spectroscopy. The thermal decomposition of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines results in the formation of *para–para* methylene linkages between phenolic rings. Other products are formed during the process, and only minor amounts of these remain after heating to 205°C/4 h; however, these minor products provide important information on the reaction pathways. The possible reaction mechanisms/pathways for the formation of cross-linked networks from *para*-hydroxybenzylamine intermediates are postulated on the basis of these structural changes. © 1998 Elsevier Science Ltd. All rights reserved.

(**Keywords: novolac resins; curing reaction;** *para*-hydroxybenzylamine intermediates)

INTRODUCTION

In the curing of novolac resins with hexamethylenetetramine (HMTA), various substituted benzoxazines and benzylamines are the dominant first-formed intermediates[1–6]. In previous papers in this series, which is concerned with novolac–HMTA reactions, we have reported on the further reactions of the first-formed products derived from HMTA and 2,4-xylenol, i.e. the benzoxazine[7,8]. This system represents the pathway for reaction of HMTA when the phenol has a vacant *ortho* phenolic position. Phenols with only a free *para* position, of which 2,6-xylenol is a simple model, cannot form benzoxazine, but react with HMTA to form di- and tribenzylamines[5]. In this paper we report on the further reactions of the *para* intermediates, bis- and tris(4-hydroxy-3,5-dimethylbenzyl)-amines, derived from reaction between 2,6-xylenol and HMTA. The HMTA used in this work was labelled with both ^{13}C and ^{15}N, and therefore gave strongly enhanced resonances for the nuclei derived from HMTA and thus provided significant information on the reaction mechanisms and pathways. The reactions of the *para*-hydroxybenzylamines with phenols are reported in the following paper.

EXPERIMENTAL

Samples

2,6-xylenol (2,6-dimethylphenol) and HMTA (10% ^{13}C and 99% ^{15}N labelled) were mixed in the molar ratio 3:1 and stirred at 110°C for 3 h. The products were dissolved in CH_2Cl_2 and washed with water at room temperature to remove unchanged HMTA. The solvent was removed *in vacuo* at room temperature, and the solid residue was finally dried *in vacuo* for 2 days. The mixture was separated by medium-pressure liquid chromatography (m.p.l.c.) using a column prepared with Merck Silica (No. 9175) and 99:1 CH_2Cl_2–CH_3OH as solvent, to give a product which, as shown by ^{1}H and ^{13}C n.m.r. spectra, comprised 55% bis (4-hydroxy-3,5-dimethylbenzyl)amine, 35% tris(4-hydroxy-3,5-dimethylbenzyl) amine, 10% N1,N3,N5-tris(4-hydroxy-3,5-dimethylbenzyl)hexahydrotriazine, and a minor amount of 4,4′-methylene-2,2′,6,6′-tetramethyldiphenol. Since all of these structures are present amongst the initial curing intermediates with novolac resins[4,6], we did not study their reaction behaviour separately, but carried out the thermal decomposition on the mixture, to parallel more closely the reactions of the novolac–HMTA system[6].

The mixture was heated in a Eurotherm 902 oven under the same conditions as used for the curing of novolac—HMTA and the model benzoxazine intermediates[6–8]. To study the structural changes during the process, samples were taken after heating to 90°C for 6 h, at 105, 120, 135, 160, 185 and 205°C, and finally after holding at 205°C for 4 h.

N.m.r. experiments

Solution ^{13}C and ^{15}N n.m.r. spectra were recorded immediately after dissolution of the samples in acetone-d_6 (99.9%) solvent on JEOL JNM-GX400 (^{13}C spectra) and JNM-FX100 (^{15}N spectra) n.m.r. spectrometers at resonant frequencies of 100 MHz for carbon-13 and 10.1 MHz for nitrogen-15. ^{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 the 90° pulse for ^{1}H and ^{13}C was 24.6 and 10 μs respectively. Tetramethylsilane (TMS) was used as an internal chemical shift reference for ^{13}C spectra, while HMTA at 44.0 ppm (relative to liquid NH_3 at 25°C) in aqueous solution was taken as an external reference for ^{15}N spectra.

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RESULTS AND DISCUSSION

The ^{13}C and ^{15}N n.m.r. spectra of the products obtained from the reaction between 2,6-xylenol and labelled HMTA are shown in *Figure 1* together with the assignment of the main ^{13}C and ^{15}N resonances. The ^{13}C peak at 52.3 ppm is due to the $-CH_2-$ between phenolic rings and the nitrogen in bis(4-hydroxy-3,5-dimethylbenzyl)amine, while for tris(4-hydroxy-3,5-dimethylbenzyl)amine the $-CH_2-$ appears at 56.9 ppm. The nitrogen resonances at 46.6 and 53.6 ppm are assigned to bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amine respectively[5,6]. The ^{15}N resonance at 50.5 ppm is assigned to a triazine structure (*Figure 1*) with its $-CH_2-$ resonances at 73–75 ppm and 55–57.5 ppm in the ^{13}C spectrum[5]. The ^{13}C resonance at 40.8 ppm corresponds to the *para–para* methylene linkage of 4,4′-methylene-2,2′,6,6′-tetramethyldiphenol (hereafter called the *para–para* dimer). The *ortho*-methyl substituent carbons of these compounds appear at 16.7 ppm.

The ^{13}C n.m.r. spectra of the mixture of the bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amine mixture after heating are shown in *Figures 2 and 3*. The intensity of the *ortho*-methyl carbon on the phenolic rings (at 16.7 ppm) did not change during the process, and was therefore taken as an internal reference. Note that the intensities of the resonances at 52.3 and 56.9 ppm which correspond to the bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines decreased with increasing temperature and then disappeared when the temperature reached 135°C. Simultaneously, the resonances due to the *para–para* dimer at 152.1, 134.1, 129.5, 124.8 and 40.8 ppm increased as the temperature increased, and became dominant above 135°C. After heating the samples to 205°C for 4 h, the *para–para* dimer was the main product, and the amount of side-products was minor. This result provides direct evidence that the decomposition of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines produces *para–para* methylene linkages between phenolic rings.

During the heating process, many minor resonances were also observed over a wide chemical shift range. The changes in these minor resonances during heating provide information about the structures of side-products and the reaction pathways. By referring to previous reports, some of these resonances can be assigned, and the structures of side-products with their characteristic ^{13}C chemical shifts are summarized in *Scheme 1*.

The 20.3 and 37.8 ppm peaks are due to the *para*-methyl substituent of the phenolic ring[9] and the *para–para* $-CH_2-CH_2-$ linkage between phenolic rings (**5**)[6] respectively. These two resonances increase in intensity as the heating temperature is increased. The resonance at 63.9 ppm became apparent after heating to 105°C and remained until 205°C. It can be assigned to the $-CH_2OH$ carbon of 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**)[9]. The peak at 191.6 ppm is assigned to the carbonyl carbon of 4-hydroxy-

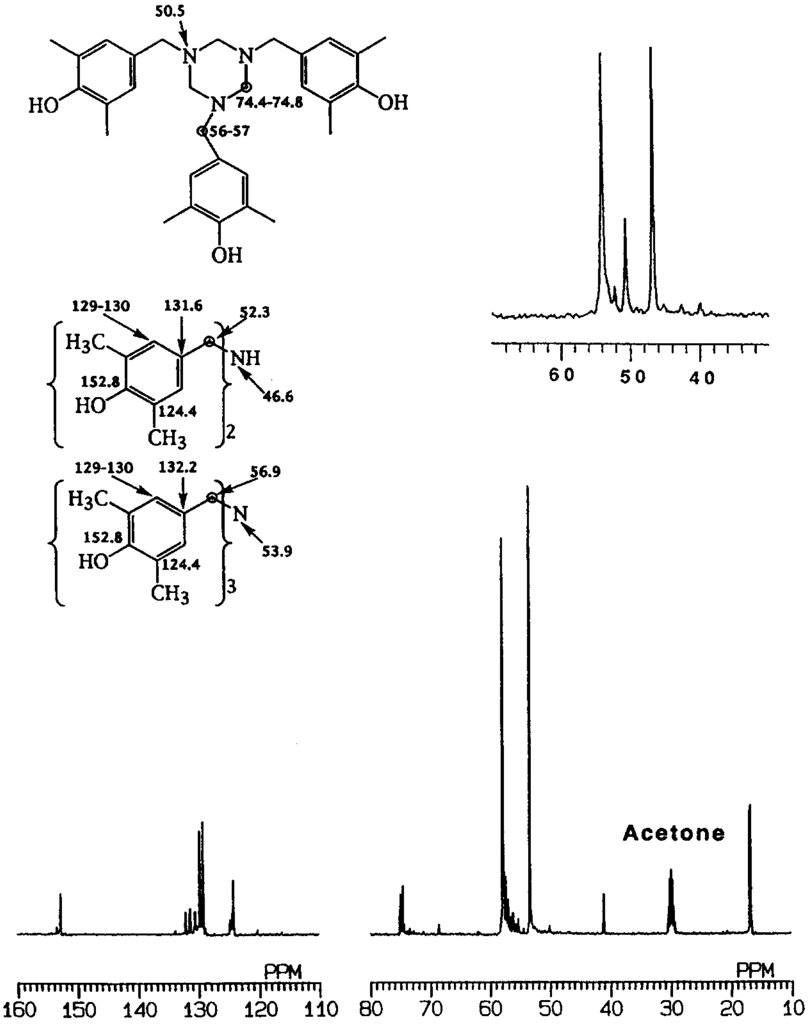


Figure 1 ^{13}C and ^{15}N (upper right) solution n.m.r. spectra of the mixture of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines obtained from the reaction between 2,6-xylenol and HMTA

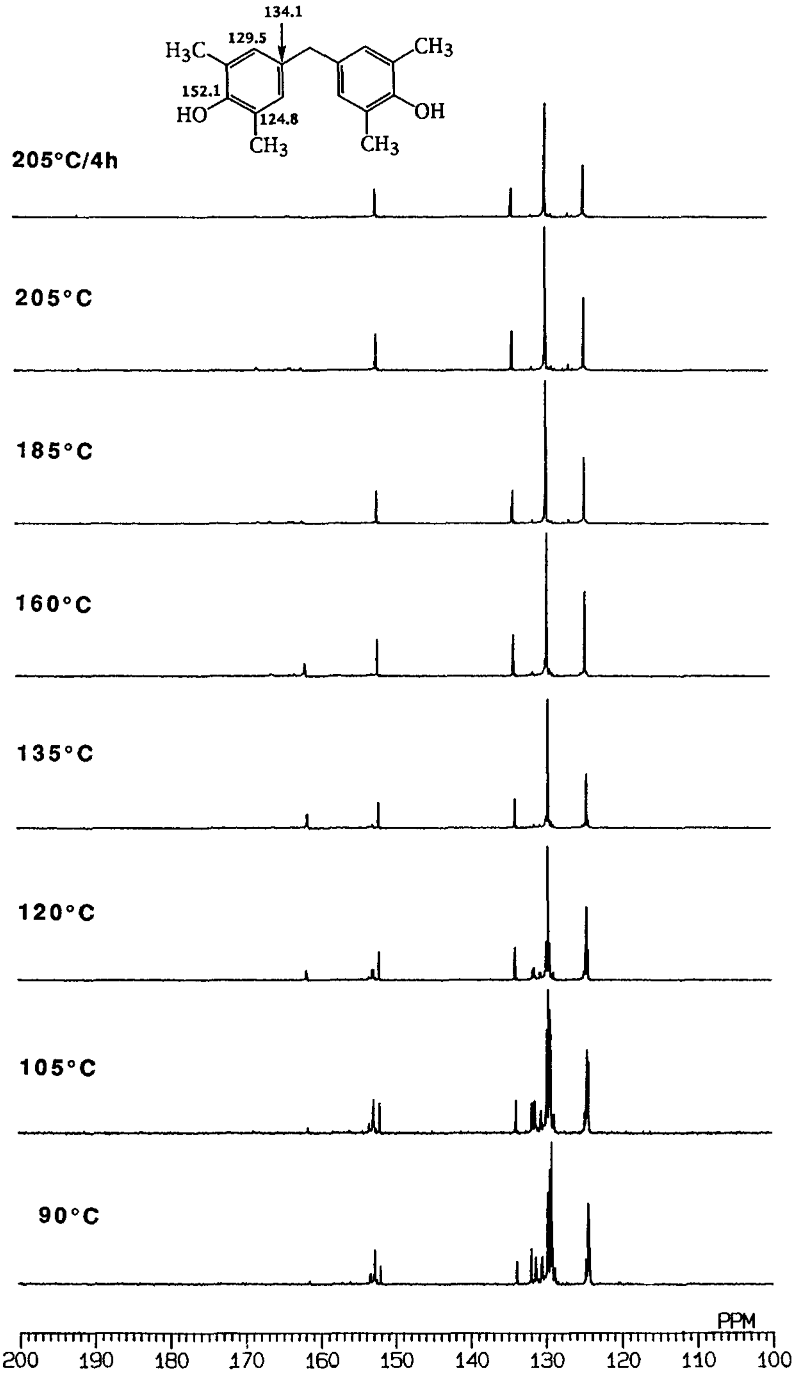


Figure 2 ^{13}C n.m.r. spectra (10–80 ppm range) of the mixture of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines after heating

3,5-dimethylbenzaldehyde (**7**)[9], and was observed during the curing process, although the intensity was weak. A broad peak at 46.4 ppm due to 4-hydroxy-3,5-dimethylbenzylamine (**8**)[6], was observed at 90–120°C, and then disappeared at higher temperatures. Several other minor resonances at 71–76 and 55–57 ppm may be due to the methylene carbons of triazines and diamines[4,6], which disappeared above 135°C because of decomposition. On the other hand, the $-OCH_2-$ carbons characteristic of various ether structures also appeared in the 71–76 ppm chemical shift range. The 72.6 ppm peak corresponds to bis(4-hydroxy-3,5-dimethylbenzyl)ether (**9**)[9], and disappeared above 185°C. The 73.5 ppm resonance is consistent with the methylene carbon in a hydroxybenzyl phenyl ether (**10**)[10]. This structure is relatively stable and remains even up to 205°C.

The ^{13}C resonances in the range 160–170 ppm and some other resonances in the range 40–65 ppm are due to various imine and amide structures. The existence of these nitrogen-containing structures is significant in the ^{15}N spectra shown in *Figure 4*. It is difficult to assign all of the ^{15}N resonances, because not only is the mixture complex but the same structure could also have a different chemical shift in a different matrix[4,11]. Briefly, ^{15}N resonances appearing in the range 24–65 ppm are due to various amine structures and the resonances around 38–42 ppm are consistent with tris-, bis- and mono(4-hydroxy-3,5-dimethylbenzyl)ammonium ions[4,5]. The ^{15}N resonances at 95–135, 200 and 288–314 ppm correspond to various amide and imine structures[11]. As the heating temperature increased, the ^{15}N resonance intensities of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines (at 46.6 and 53.9 ppm) decreased,

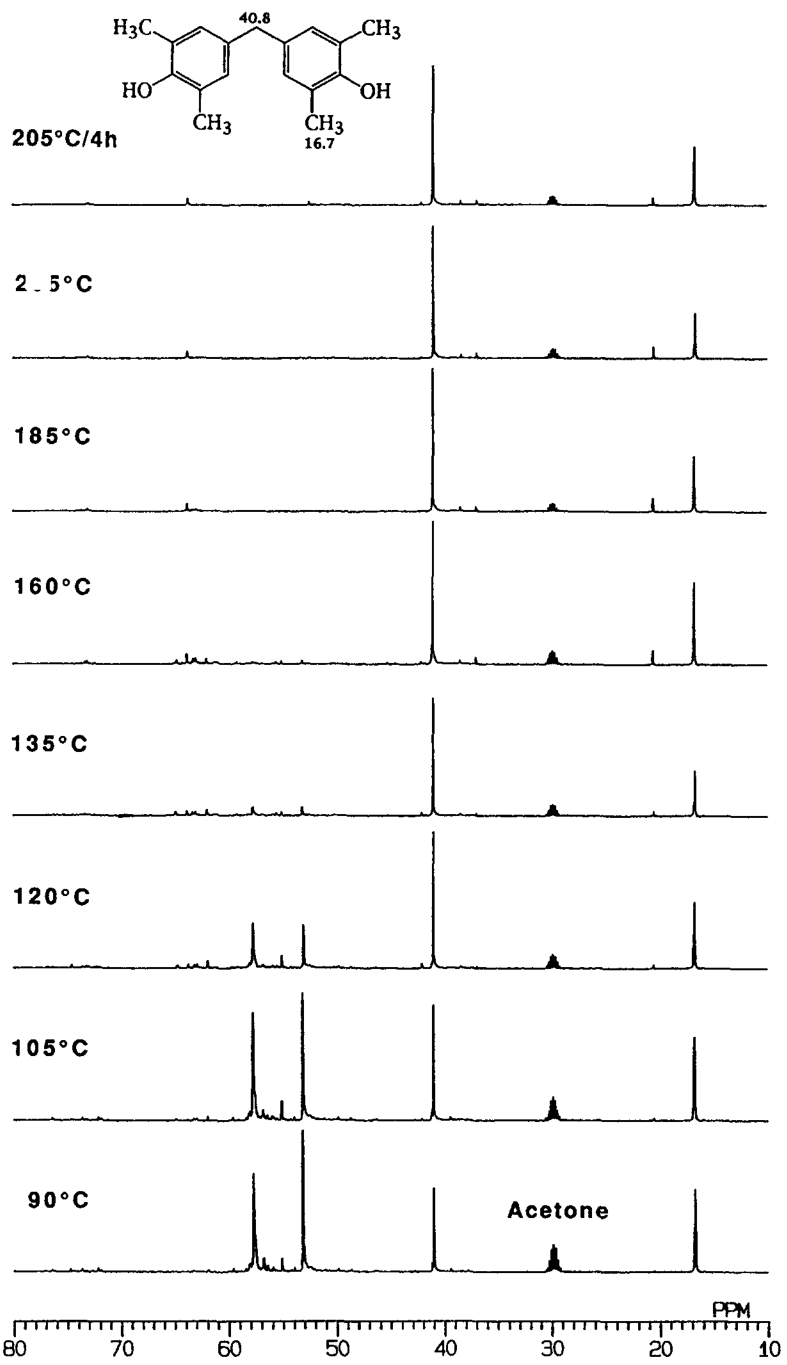
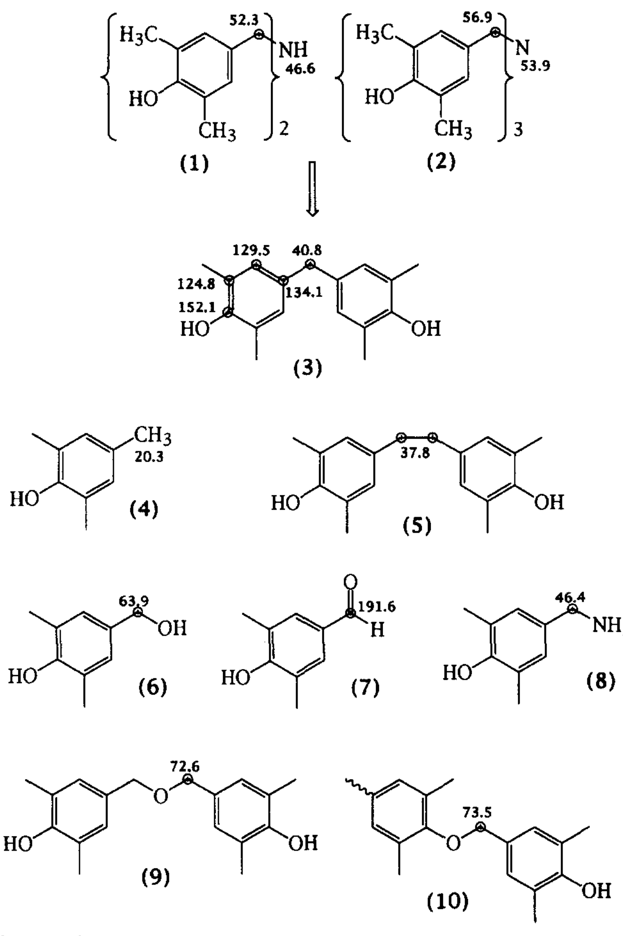


Figure 3 ^{13}C n.m.r. spectra (100–200 ppm range) of the mixture of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines after heating

and resonances due to amine, amide and imine structures appeared above 105°C, corresponding to the formation of nitrogen-containing structures and a change in the pH of the system. The ^{15}N resonances of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines disappeared when the heating temperature was above 135°C, which is consistent with the ^{13}C spectra. Above 185°C, most of the amine resonances also disappeared, and the major nitrogen-containing structures were amides at higher temperatures.

Several possible imine and amide structures formed in the process are shown in *Scheme 2*. In the ^{15}N n.m.r. spectra, the first imine peak was observed at 314 ppm after heating to 105–135°C, and disappeared above 160°C. The resonances at 161.6 and 62.1 ppm in the ^{13}C spectra (CH and CH_2 respectively, as detected by DEPT spectra) showed similar behaviour. We assign these resonances to imine (**11**). The $=N-CH_3$ methyl carbon of imine (**13**) should occur around 45–48 ppm[9]. Correspondingly a CH_3 resonance (detected by DEPT spectra) at 47.5 ppm in ^{13}C spectra was observed for the samples heated to 160–185°C and then disappeared on heating to 205°C. The CH carbon resonance at 162.2 ppm showed similar behaviour, as did the ^{15}N resonance at 288 ppm. Hence those resonances are assigned to imine (**13**). The imine peak at 200 ppm observed at 205°C is assigned to the nitrogen of N-(4-hydroxy-3,5-dimethylbenzylidene)amine (**14**)[5]. No $-N=CH_2$ carbon peak was observed, indicating that imine (**12**) might not exist, or was converted to (**13**) or reacted as soon as it formed.

The situation with amide structures is relatively complicated. For the samples heated to 120°C, the ^{15}N spectrum indicates that mainly one amide (at 125 ppm) and one imine (at 314 ppm) structure exist with a similar intensity. But in the range 160–170 ppm of the ^{13}C spectrum, only the



Scheme 1

161.6 ppm peak was observed. The ^{13}C DEPT spectrum indicates that the peak is due to CH carbons (or mainly so), since it is negative relative to positive CH_2 carbons and the relative intensity does not change significantly in the DEPT spectrum. For the four amide structures (**15**)–(**18**), only structure (**16**) has a methine carbon located in this chemical shift range (CHO carbon). Therefore we deduce that (**16**) is the first amide to appear at lower temperatures (161.6 ppm for $\underline{C}HO$, while the Ar–$\underline{C}H_2$–NH– carbon is at 42.2 ppm)[12]. The carbon resonances at 168 and 166 ppm (quaternary carbons), 45.8 ppm (–CH_2–) and 33.8 ppm (CH_3) are consistent with the other amide structures in *Scheme 2*, but detailed assignment requires further clarification.

In summary, heating a mixture of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines to 205°C for 4 h results in formation of *para–para* dimer (**3**) as the dominant product. Other minor side-products are 2,4,6-trimethylphenol (**4**), 1,2-bis(4-hydroxy-3,5-dimethylphenyl)ethane (**5**), 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**), 4-hydroxy-3,5-dimethylbenzaldehyde (**7**) and some amide structures. Several ether, amine and imine structures also appeared during the heating, but they disappeared at high temperatures due to further decomposition and oxidation processes.

Both ^{13}C and ^{15}N n.m.r. spectra provide information about the structural changes of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines during heating, and enable us to postulate the reaction mechanisms/pathways.

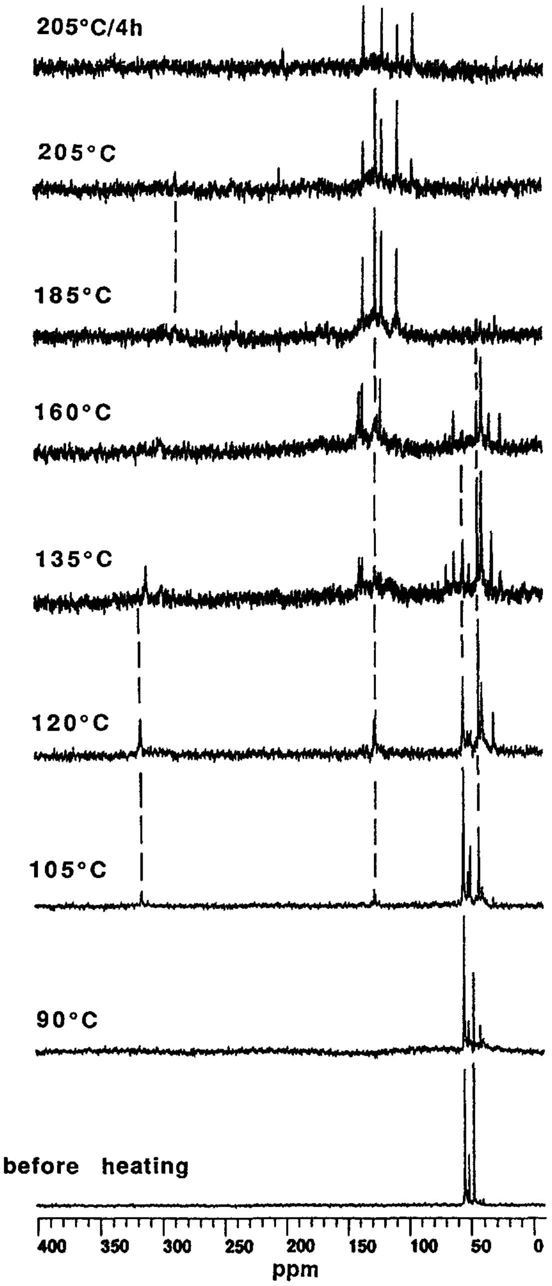


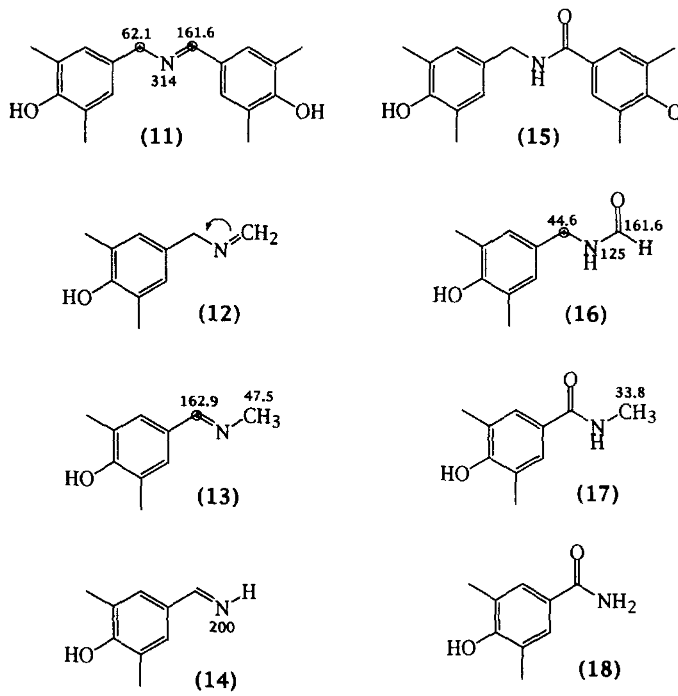
Figure 4 ^{15}N n.m.r. spectra of the mixture of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines after heating

The *para–para* dimer (**3**) obtained at lower temperatures may be derived from bis- or tris(4-hydroxy-3,5-dimethylbenzyl)amines directly via the decomposition pathway shown in *Scheme 3-1*. The bis(4-hydroxy-3,5-dimethylbenzyl)amine is more likely to follow this pathway by losing a $CH_2 = NH$ unit. The $CH_2 = NH$ can be hydrated or oxidized as soon as it forms (*Scheme 3-2*) and then be liberated from the system or take part in further reactions. However, it is unlikely that the dimer (**3**) forms via loss of N-(4-hydroxy-3,5-dimethylbenzylidene)methylamine (**12**) from tris(4-hydroxy-3,5-dimethylbenzyl)amine. If this were the case, the imine (**12**) and/or (**13**) would have appeared first at lower temperature. We observed imine (**13**) only above 160°C when most of the tris(4-hydroxy-3,5-dimethylbenzyl)amine had already decomposed. The tris(4-hydroxy-3,5-dimethylbenzyl)amine may form the *para–para* dimer (**3**) via transformation to bis(4-hydroxy-3,5-dimethylbenzyl)amine through loss of a benzoquinone methide (*Scheme 3-1*).

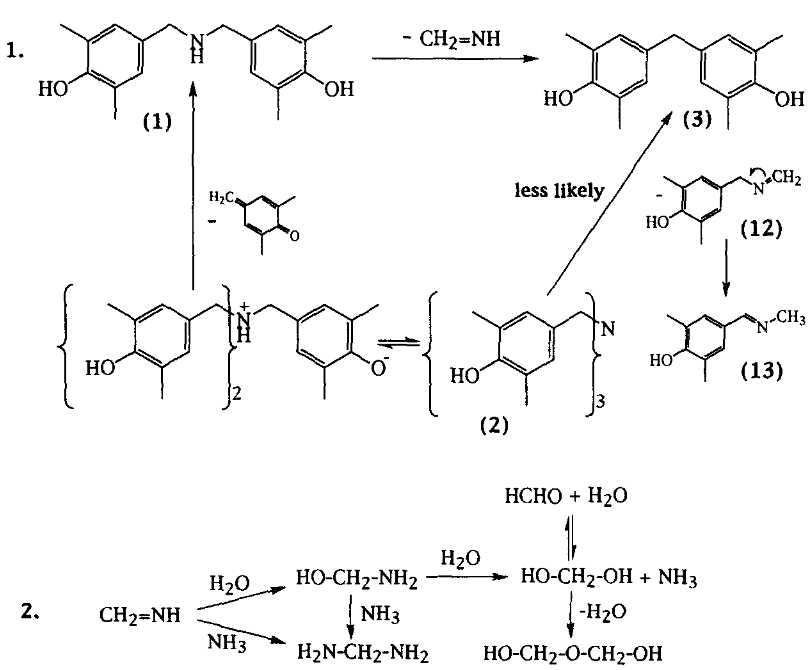
The formation of benzoquinone methide is critical for the formation of various intermediates and the *para–para* dimer. All of the tris-, bis- and mono(4-hydroxy-3,5-dimethylbenzyl)amines can liberate benzoquinone methide units. Some possible reaction pathways are summarized in

4. Protonation of hydroxybenzylamines is likely to occur first, with the protons originating from the phenolic hydroxyl groups. This is consistent with a previous report that 92% of hydrogen in NH_3 liberated from the curing of substituted phenols with HMTA comes from phenolic hydroxyl groups[13]. Hydration of the benzoquinone methide leads to 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**), and further condensation results in an ether structure (**9**). The 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**) could also react with bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines to form the ether structure (**9**). In addition, 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**) can also be dehydrogenated/ oxidized to form 4-hydroxy-3,5-dimethylbenzaldehyde (**7**). The ether structure (**9**) can form the dimer (**3**) through loss of formaldehyde, or the 4-hydroxy-3,5-dimethylbenzaldehyde (**7**) through loss of 2,4,6-trimethylphenol (**4**). Hydrogen abstraction by the benzoquinone methide can result in 2,4,6-trimethylphenol (**4**). Of the above compounds, the 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**) can remain in the system even after heating to 205°C (see the 63.9 ppm ^{13}C peak), since its boiling point is high.

Coupling of two benzoquinone methide units followed by hydrogen abstraction from other phenolic hydroxyl groups or by disproportion (which requires a high concentration), as shown in *Scheme 5-1*, could produce 1,2-bis(4-hydroxy-3,5-dimethylphenol)ethane (**5**)[14,15]. The structure (**5**) may also



Scheme 2

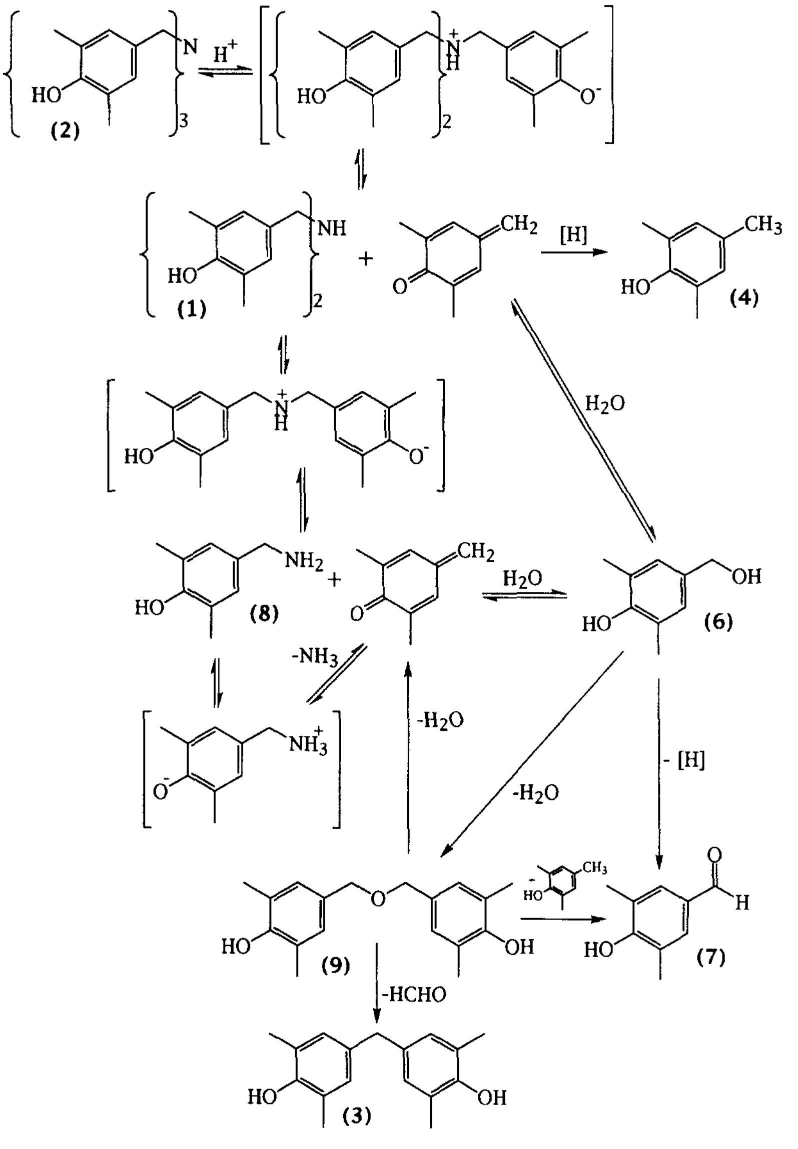


Scheme 3

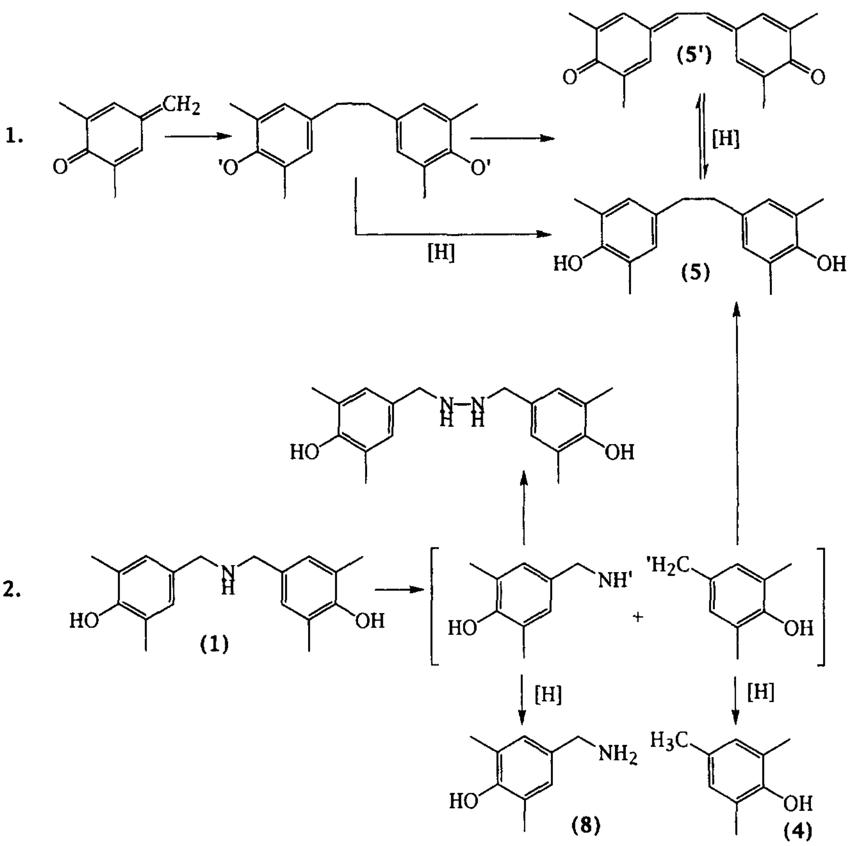
originate from free-radical reactions[16,17] as shown in *5 5-2*, which involves homolysis of the C–N bond. The $\text{Ar–CH}_2\text{–NH}^\cdot$ or the $\text{Ar–CH}_2^\cdot$ radicals generated in *Scheme -2* can be terminated to form $\text{Ar–CH}_2\text{–NH}_2$ (**8**) or Ar–CH_3 (**4**) after gaining a hydrogen radical. The (**5′**) structure may also be present, since a resonance at 152.0 ppm was observed as a negative peak relative to positive $-\text{CH}_2-$ resonances in the ^{13}C DEPT spectra (thus the = CH–CH = carbons) above 135°C. However, due to the low concentration of the benzoquinone methide or such free radicals, only a minor amount of ethylene linkage structures (**5**) was obtained.

Possible reactions to form various imine structures are summarized in *Scheme 6*. Since imine (**11**) was obtained first at lower temperatures, it probably originated from the bis(4-hydroxy-3,5-dimethylbenzyl)amine via dehydrogenation. The tris(4-hydroxy-3,5-dimethylbenzyl)amine could also form imine (**11**) by loss of 2,4,6-trimethylphenol (**4**); note that the *para*-CH_3 peak at 20.3 ppm of 2,4,6-trimethylphenol was observed above 90°C. The reaction between 4-hydroxy-3,5-dimethylbenzylamine (**8**) and 4-hydroxy-3,5-dimethylbenzaldehyde (**7**) could result in imine (**11**). Amine (**8**) can also react with formaldehyde to produce imine (**12**) and then imine (**13**) through rearrangement. Imine (**14**) is unlikely to be formed from a reaction between the 4-hydroxy-3,5-dimethylbenzaldehyde (**7**) and ammonia, because the 4-hydroxy-3,5-dimethylbenzaldehyde and ammonia appear in the system even after heating to 90°C, but the imine (**14**) was obtained after heating to 205°C. It probably originated from the dehydrogenation of 4-hydroxy-3,5-dimethylbenzylamine (**8**). Some other imine structures were reported, as shown in *Scheme 7*[18]. The ^{15}N resonances at 61 and 66 ppm may correspond to the amino nitrogen in structures (**19**)–(**22**). The triazine intermediate (**19**) is not stable at higher temperatures; thus it breaks down as soon as it forms and accordingly no corresponding signals are observed at higher temperatures.

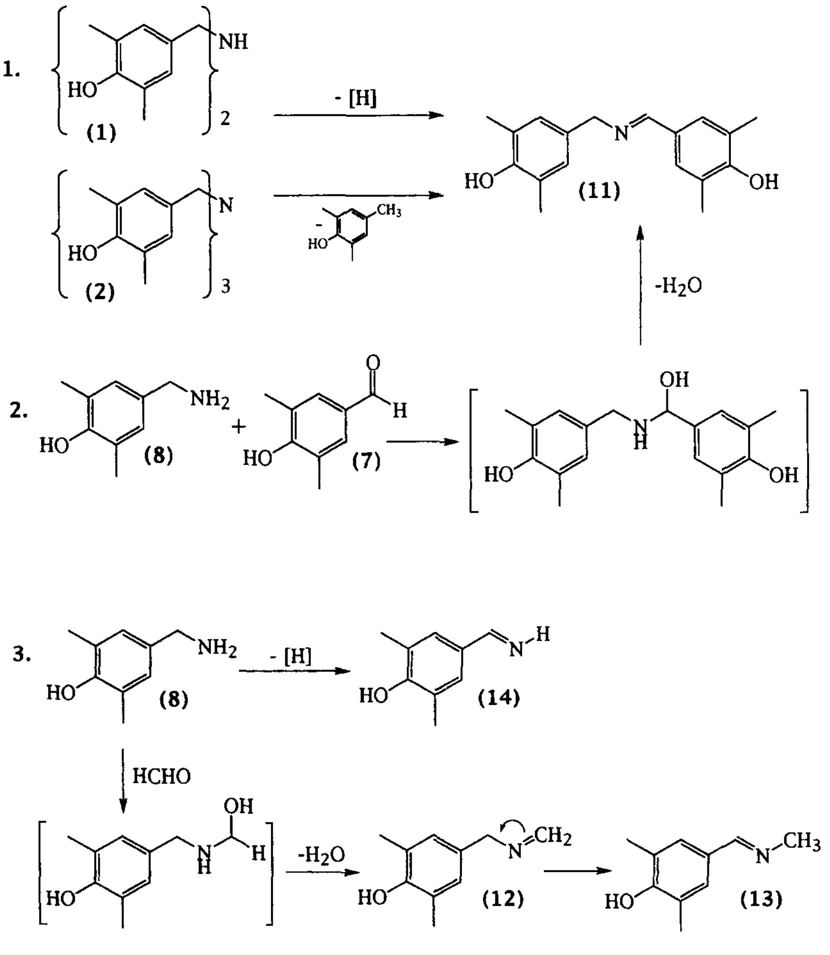
It is likely that most of the amides originate from oxidation. The initial amide (**16**) (at 120°C) could be formed by reaction of 4-hydroxy-3,5-dimethylbenzylamine (**8**) with formic acid (HCOOH) which originated from formaldehyde. Increasing temperature could result in the oxidation of imines (**11**)–(**14**) to form amides (**15**)–(**18**) respectively. Some amides might be formed also via the oxidation of the tris-, bis- and mono(4-hydroxy-3,5-dimethylbenzyl)amines. Elemental analysis indicated an increase in the oxygen content of novolac resins after curing[6], suggesting that most oxidation is due to oxygen from the air.



Scheme 4

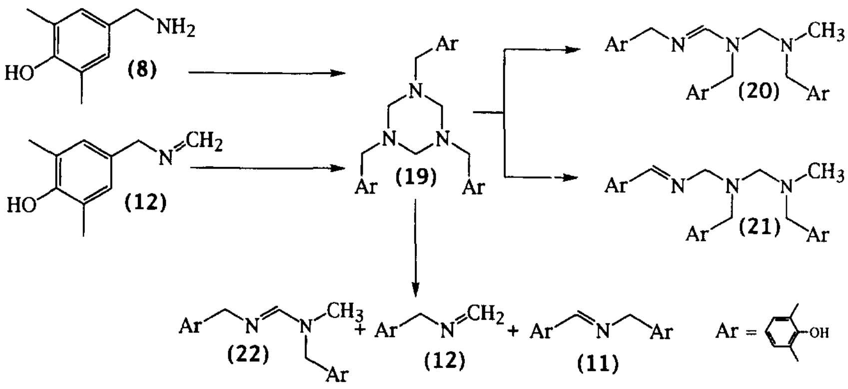


Scheme 5

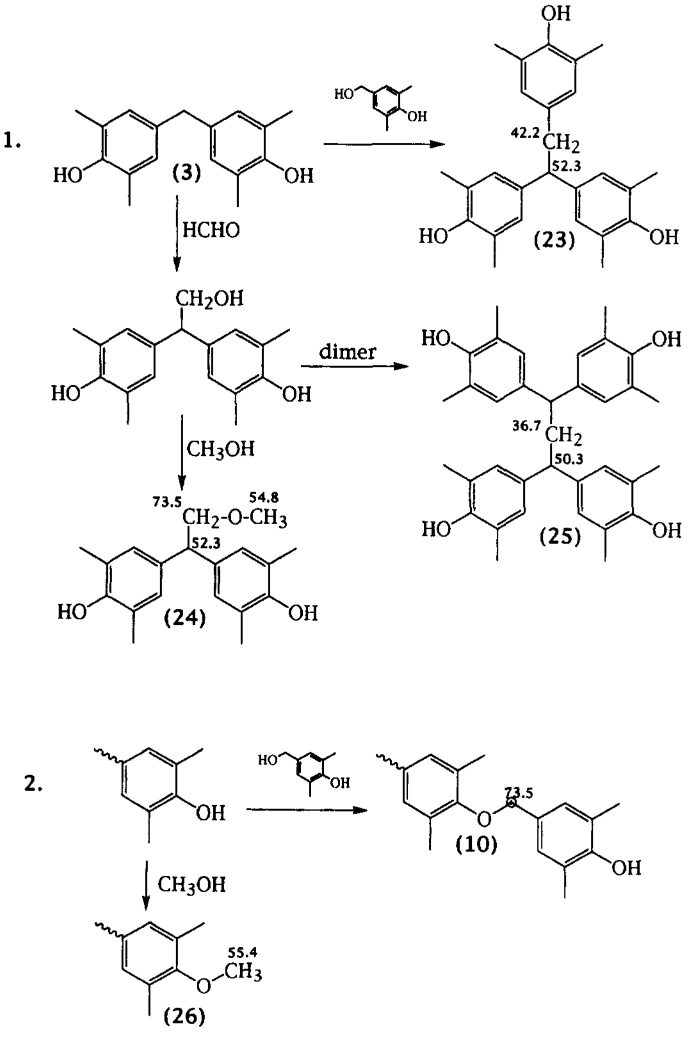


Scheme 6

Formaldehyde is a very important reagent in the curing of phenolic resins, and has been studied in numerous curing reactions[10,19–25]. In our system, formaldehyde could be formed via the reactions as shown in *Schemes 3* and *4*. Since all reactive sites (*ortho* and *para* vacant phenolic positions) are blocked in the phenol, reactions between formaldehyde and phenolic reactive sites should not occur. However, reactions between formaldehyde and the methylene linkage[10] of the dimer shown in *Scheme 8-1* could occur, especially at higher temperatures. In addition, 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**) may also react with the methylene linkage at higher temperatures (*Scheme 8-1*). In the ^{13}C DEPT spectra of samples heated to 185–205°C, two negative peaks were observed at 50.3 and 52.3 ppm relative to positive CH_2 peaks, which could be due to the CH carbon in (**23**)–(**25**)[10], while the 42.2 and 36.7 ppm peaks (positive peaks in ^{13}C DEPT spectra) may be due to the CH_2 carbons in structures (**23**) and (**25**). The reaction between the hydroxyl group of the phenolic rings and 4-hydroxy-3,5-dimethylbenzyl alcohol (**6**) and CH_3OH



Scheme 7



Scheme 8

could result in the ether structure (**10**) and (**26**) (*Scheme 8-2*). The minor ^{13}C resonances at 54.8 and 55.4 ppm appearing as negative peaks relative to the CH_2 resonances correspond to the OCH_3 carbons in structures (**24**) and (**26**) respectively[12]. Note that water is also involved in some reactions in *Schemes 4* and *6*. Previous reports indicated that a trace amount of water is necessary for the curing reaction of novolac resins[26–29]. The water can originate from the atmosphere or be liberated from other reactions. In addition, although the number of possible reaction steps is large, only a catalytic amount of water is required to perform these transformations. Assuming that the change from bis- and tris(4-hydroxy-3,5-dimethylbenzyl) amines to the *para–para* dimer is due to liberation of nitrogen and CH_2 and no other structures formed, the weight loss will be 10.1%. The measured value of 11.8% after heating the sample to 205°C for 4 h is consistent with that *para–para* dimer being the dominant product after thermal decomposition.

CONCLUSIONS

The ^{13}C and ^{15}N n.m.r. studies provide direct evidence of the formation of the methylene linkage between phenolic rings from the decomposition of *para*-hydroxybenzylamine intermediates. Reaction mechanisms are postulated based on the structural changes observed. The bis(4-hydroxy-3,5-dimethylbenzyl)amine could form a methylene linkage via direct decomposition, while the tris(4-hydroxy-3,5-dimethylbenzyl)amine could break down via the bis(4-hydroxy-3,5-dimethylbenzyl)amine around 90–120°C. Side-reactions result in the formation of various products (including nitrogen-containing products) during the process, but most of these are converted to the methylene linkage after heating to high temperatures. The benzoquinone methide intermediate is likely to be a critical intermediate for the formation of various products. Liberated formaldehyde and trace amounts of water also play certain roles in side-reactions.

The results provide valuable information on the reaction pathways for curing novolac resins with HMTA, which are important for understanding the curing chemistry. The *para*-hydroxybenzylamine intermediates are less stable as compared to benzoxazines[7], and can be thermally decomposed to methylene linkages at relatively low temperatures. This is consistent with the result obtained in curing novolac resins[6], where *para*-linked methylene linkages (*para–para* and *para–ortho*) were obtained at relatively low temperatures derived from the break-up of *para*-linked intermediates. On the other hand, less side-products are obtained from the decomposition of *para*-hydroxybenzylamines, compared with those from benzoxazine. The distinct reaction courses taken by the *ortho*- and *para*-linked intermediates further emphasize the importance of novolac structure in determining the curing reactivity and the chemical structures of the finally cured resins. In general, if a highly *ortho*-linked novolac resin (containing a high ratio of *para*-reactive sites) is cured by HMTA, the curing reactions occur at relatively low temperatures and most of the intermediates decompose to form methylene linkages at relatively low temperatures. In addition, the amount of side-products is also relatively low. In contrast, if a conventional novolac resin (containing a high ratio of *ortho*-reactive sites) is used, the curing reactions occur at relatively high temperatures and consequently the methylene linkages are produced at higher temperatures. The amount of side-products, e.g. the nitrogen-containing structures, is also relatively higher. The difference in the chemical structure of the cross-linked resins will certainly influence the properties and the application of the resins.

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