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The chemistry of novolac resins: Part 8. Reactions of *para*-hydroxybenzylamines with model phenols

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The reactions of 2,4-xylenol and 2,6-xylenol, with bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines derived from the reaction of 2,6-xylenol with hexamethylenetetramine (HMTA) were studied as models for the curing of novolac resins. The structural changes during the process were examined by ^{13}C and ^{15}N n.m.r. spectroscopy. The results indicate that reactions between bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines and 2,4-xylenol (containing an *ortho* reactive sites) produce *para–para*, *ortho–para*, and *ortho–ortho* methylene linkages between phenolic rings via a number of reaction pathways. Heating bis- and tris(4-hydroxy-3,5-dimethylbenzyl)-amines with 2,6-xylenol only produces *para–para* methylene linkages, but the reactions occur at relatively low temperatures compared to those of the thermal decomposition of the bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines. Numerous side-products were observed during the process, but most of these can be further reacted or oxidised to form methylene linkages, and only minor amounts remain after heating to 205°C. Reaction mechanisms and possible reaction pathways are postulated based on structural changes. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: novolac resins; hexamethylenetetramine; xylenols)

INTRODUCTION

In this series study on the curing chemistry of novolac resins[1–6], we have reported on the use of xylenols as models for novolac resins[2] and on the self reaction of the *para*-hydroxybenzylamine intermediates derived from 2,6-xylenol and HMTA[6]. This paper will examine the reactions of *para*-hydroxybenzylamine intermediates with vacant reactive sites in novolac resins, which could compete with the self-decomposition, using 2,4- or 2,6-xylenols as models for the phenolic structures present in novolac resins.

EXPERIMENTAL

Samples

The reaction between 2,6-xylenol and HMTA produced a mixture of 55% bis(4-hydroxy-3,5-dimethylbenzyl)amine, 35% tris(4-hydroxy-3,5-dimethylbenzyl)amine and 10% of triazine-type products[6]. Since all of these structures are present in novolac/HMTA curing processes[3,7,8], we carried out the further reaction with the xylenols using this mixture.

2,4-Xylenol and 2,6-xylenol were obtained from Eastman Kodak company Inc. and Aldrich Chemical Company Inc. respectively. The *para*-hydroxybenzylamine compounds were mixed with 2,4-xylenol or 2,6-xylenol in a weight ratio of 1:1 and then heated in a Eurotherm 902 oven under the cycle used in our studies on novolac resins and model systems[3–6]. The samples were taken after heating 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 and ^{15}N n.m.r. spectra were recorded immediately after dissolution of the samples in a solvent using a JEOL JNM-GX400 (^{13}C spectra (100 MHz), $CDCl_3$ 99.8% as solvent) and JNM-FX100 NMR (^{15}N spectra (10.1 MHz), acetone-d_6 99.9% as solvent) spectrometers. ^{13}C DEPT spectra were observed using the normal DEPT pulse sequence with $\theta = 135°$. The $\tau = 1/(2J_{CH})$ was 3.7 ms. 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. Some ^{13}C n.m.r. chemical shifts of bis- and tris(4-hydroxy-3,5-dimethylbenzyl) amine vary slightly from that report[6] in which acetone-d_6 was used as a solvent.

RESULTS AND DISCUSSION

The reaction of the *para*-hydroxybenzylamine intermediates with a free *ortho*- or *para*-phenolic position can be modeled using bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines and 2,4- or 2,6-xylenol. The ^{13}C and ^{15}N spectra of these compounds have been assigned previously[5,6]. In the ^{15}N spectrum, the two major peaks at 46.6 and 53.9 ppm correspond to the bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines, respectively, consistent with the $-CH_2-$ carbon resonances at 52.3 and 56.9 ppm in the two compounds. A minor ^{13}C resonance at 40.4 ppm corresponds to the *para–para* methylene linkage of 4,4′-methylene-2,2′,6,6′-tetramethyldiphenol (hereafter called the *para–para* dimer), derived from the decompositions[6]. The *ortho*- and *para*-phenolic methyl carbons of

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2,4-xylenol appear at 15.7 and 20.3 ppm, while the *ortho*-unsubstituted phenolic carbon appears at 115.1 ppm. For 2,6-xylenol, the two *ortho*-methyl carbons appear at 15.7 ppm while the *para*-unsubstituted phenolic carbon appears at 120.4 ppm. Less attention has been paid to the complicated aromatic carbon resonances of the systems.

para-Hydroxybenzylamine/2,4-xylenol reactions

The ^{13}C n.m.r. spectra of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines and 2,4-xylenol after heating are shown in *Figures 1 and 2*. The circles indicate CH carbon resonances in the 100–200 ppm range, and CH or CH_3 carbons in the 10–80 ppm range, which appear as negative peaks in the ^{13}C DEPT spectra relative to the CH_2 carbons.

Evidence for the reaction between bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines and 2,4-xylenol is the formation 2,4′-methylene-4,2′,6,6′-tetramethyldiphenol (the *ortho–para* dimer) at 36.5 ppm after heating to 90°C. Since all *ortho*-phenolic positions in bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines were blocked by methyl groups, the *ortho–para* dimer can only be derived from reaction with 2,4-xylenol, for instance in *Scheme 1*, via reactions between bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines and hydrogen-bonded 2,4-xylenol. The carboanion generated from the amines then attaches a 2,4-xylenol molecule and produces the *ortho–para* dimer. Meanwhile, the resonance intensity at 40.4 ppm further increased after heating, indicating the formation of the *para–para* dimer from bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amine via a number of pathways[6]. Compared to the self-decomposition of the system, the intensities of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amine decreased faster with the presence of 2,4-xylenol, suggesting an increase of the reactivity, especially

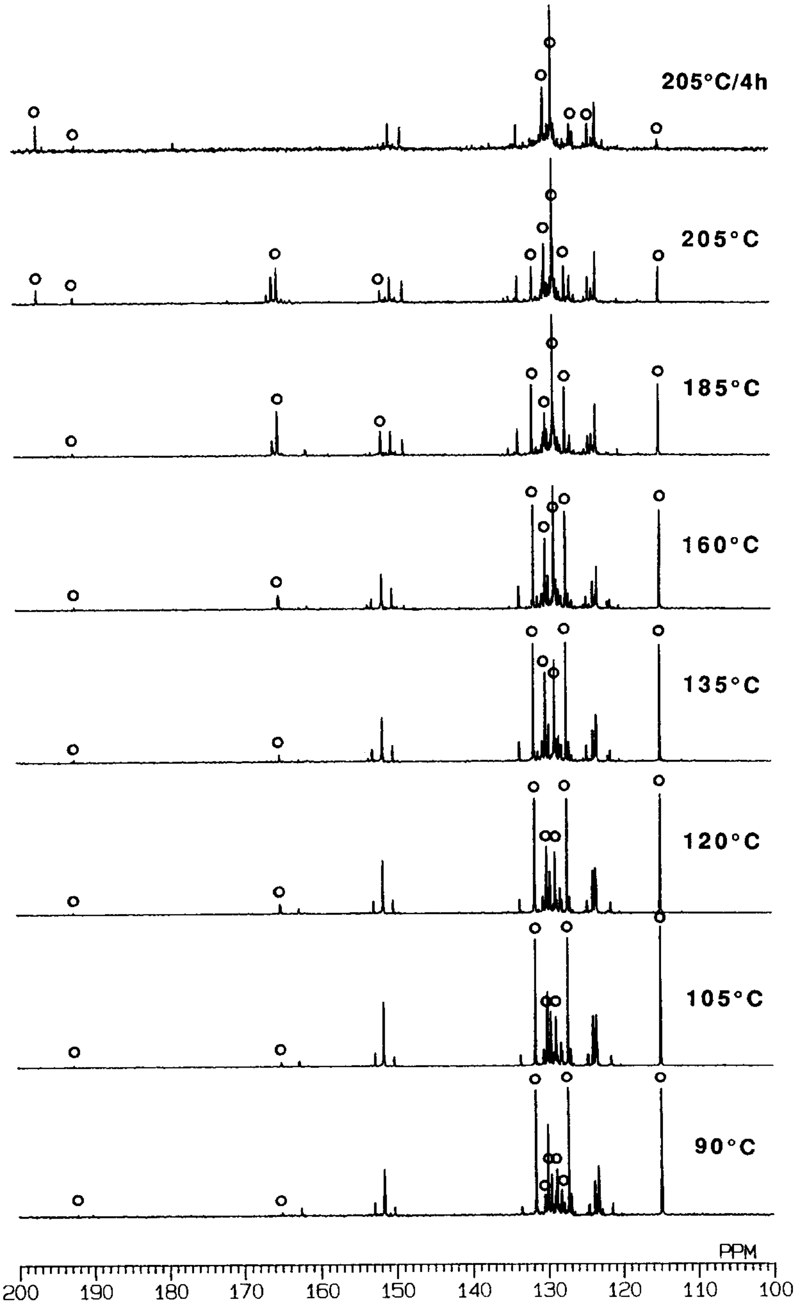


Figure 1 ^{13}C n.m.r. spectra (100–200 ppm) of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines/2,4-xylenol after heating to various temperatures. The resonances with circles indicate CH carbons, which appeared as negative peaks in the ^{13}C DEPT spectra relative to the CH_2 carbons

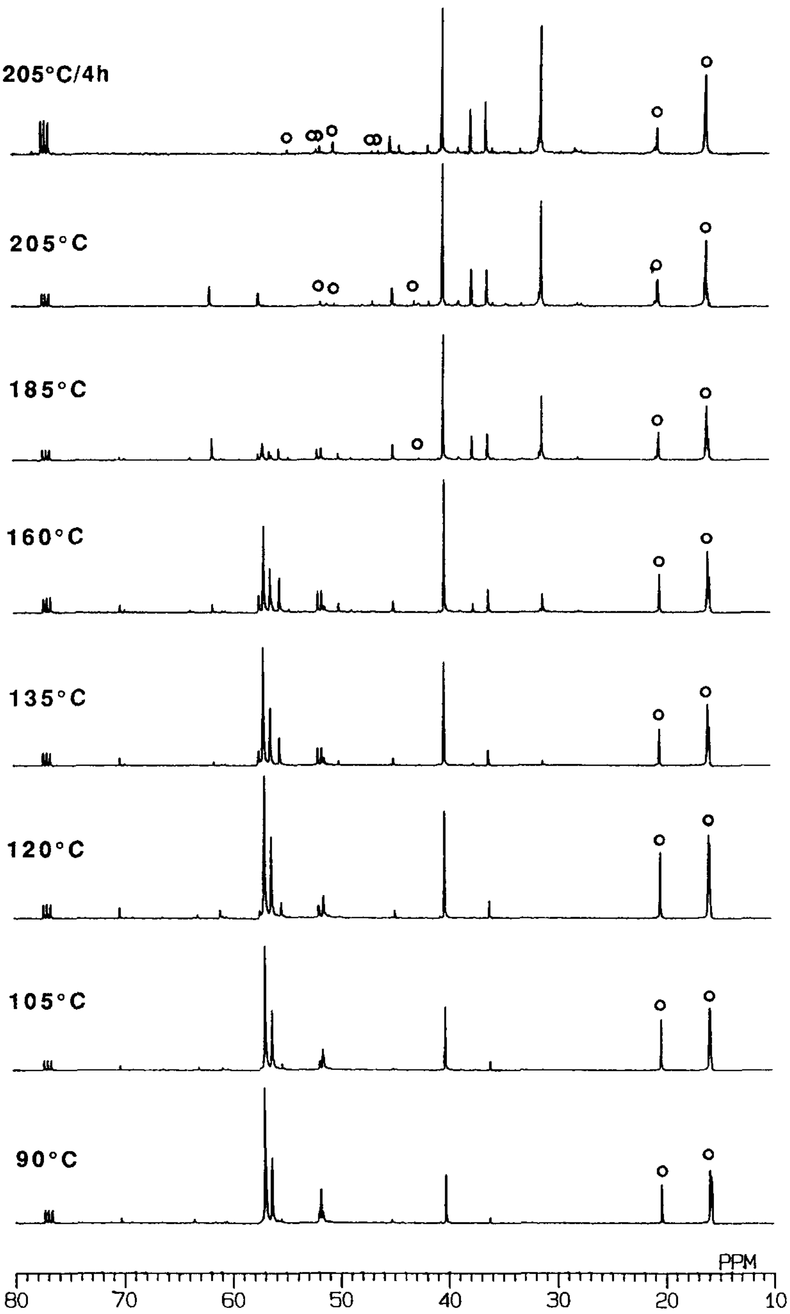
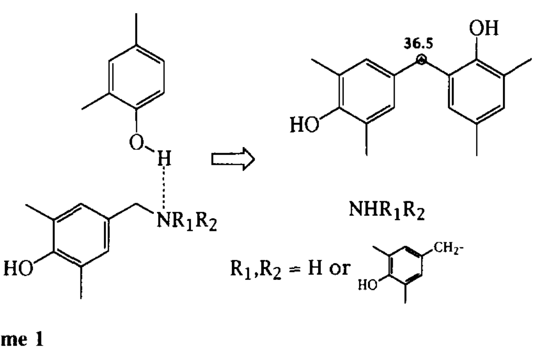


Figure 2 ^{13}C n.m.r. spectra (10–80 ppm) of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amine/2,4-xylenol after heating to various temperatures. The resonances with circles indicate CH or CH_3 carbon resonances which appeared as negative peaks in the ^{13}C DEPT spectra relative to the CH_2 carbons

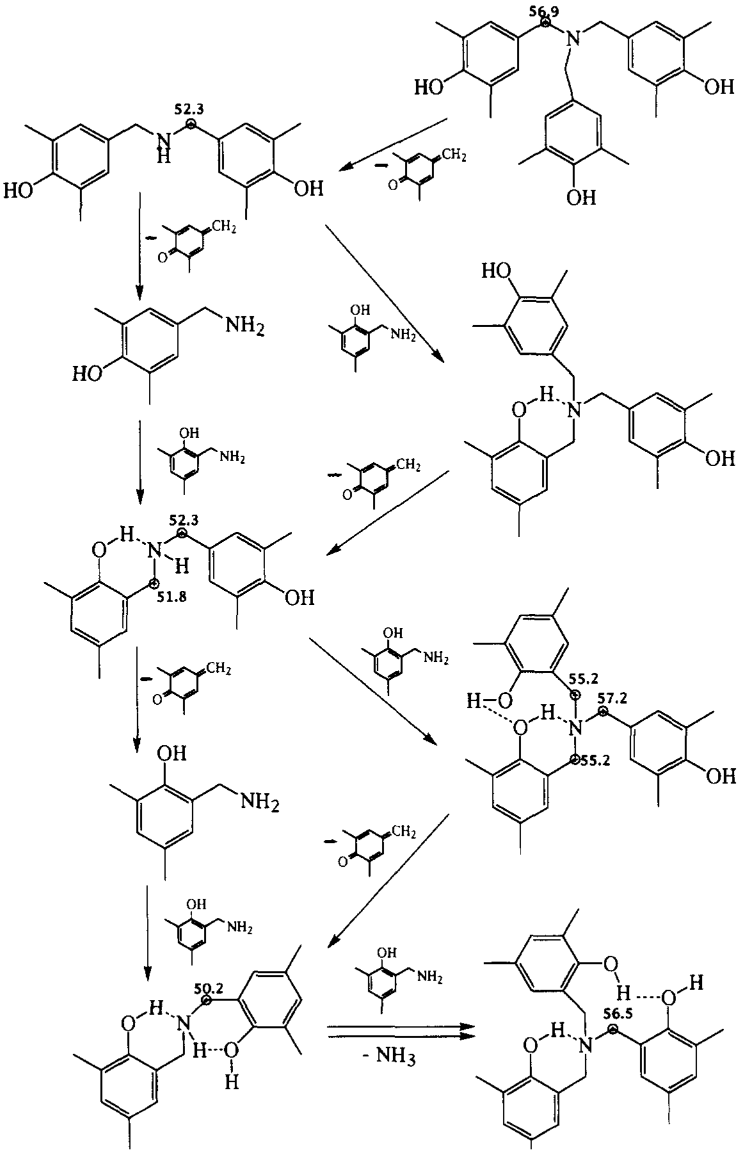
for bis(4-hydroxy-3,5-dimethylbenzyl)amine. Other products, such as 4-hydroxy-3,5-dimethylbenzyl alcohol ($-\underline{C}H_2OH$, 63.6 ppm)[6,9], di-methylene ether linkage ($-\underline{C}H_2-O-\underline{C}H_2-$, 70.3 ppm)[3,6,9], 4-hydroxy-3,5-dimethylbenzaldehyde ($-\underline{C}HO$, 192.3 ppm), 2-hydroxy-3,5-dimethylbenzaldehyde ($-\underline{C}HO$, 197.1 ppm)[9], and 4-hydroxy-3,5-dimethylbenzylamine ($-\underline{C}H_2NH_2$, 45.3 ppm)[3,6], were also observed due to side-reactions as suggested previously[4–6]. The resonance at 37.8 ppm due to the *para–para* ethylene linkage between phenolic rings[3,6] was observed above 135°C, and its intensity was relatively stronger compared to the self-decomposition of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines[6].



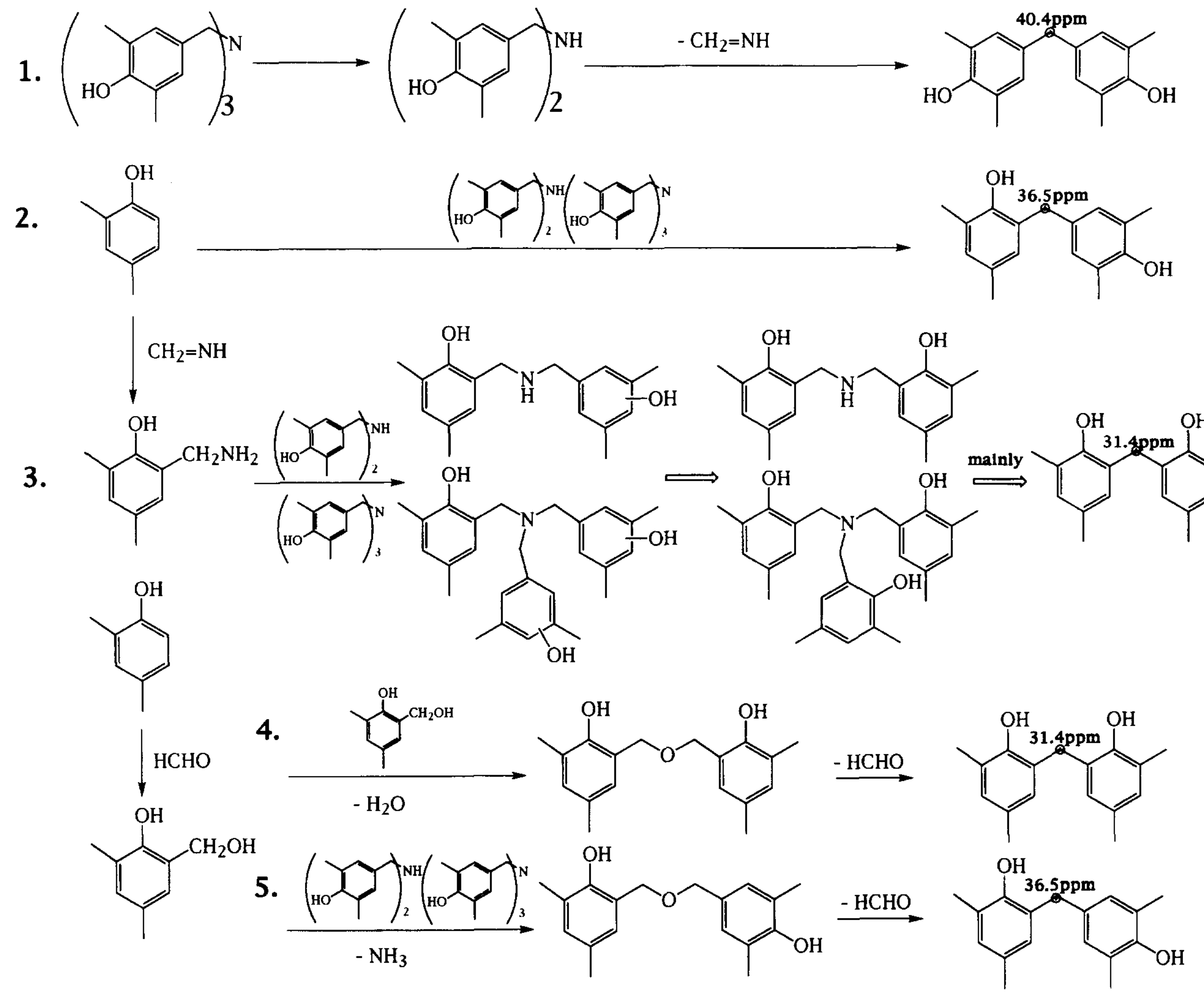
Scheme 1

Further evidence of the reactions between bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines with 2,4-xylenol is the formation of mixed bis- and tris(hydroxybenzyl)amines, and bis- and tris(2-hydroxy-3,5-dimethylbenzyl)amines. Note that after heating the sample to 90°C, resonances were observed at 51.8, 55.9 and 56.5 ppm, together with those at 52.3 and 56.9 ppm which are characteristic of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines[2]. Increasing temperature caused a decrease of the intensities of tris(4-hydroxy-3,5-dimethylbenzyl)amines, while those of bis(4-hydroxy-3,5-dimethylbenzyl)amines disappeared at 105°C. Meanwhile the resonances at 50.2, 51.5, 51.9 and 55.9 ppm appeared due to the formation of mixed bis- and tris(hydroxybenzyl)amines and bis- and tris(2-hydroxy-3,5-dimethylbenzyl)amines[2] as depicted in *Scheme 2*. The driving force of these reactions is the formation of a stable six-member ring structure through intramolecular hydrogen bonding in *ortho*-linked hydroxybenzylamines, which is not possible for bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines. Bis- and tris(2-hydroxy-3,5-dimethylbenzyl)amines are more stable, and can remain in the system at relatively high temperatures. The 2-hydroxy-3,5-dimethylbenzylamine in *Scheme 2* could be generated from the reaction between the 2,4-xylenol and $HN{=}CH_2$ unit, which is derived from the decomposition of bis(4-hydroxy-3,5-dimethylbenzyl)amine[6]. The *para*-benzoquinone methide eliminated from the system can undergo further reactions to produce dimers and other side-products [6]. At elevated temperatures, these mixed bis- and tris(hydroxybenzyl)amines, and bis- and tris(2-hydroxy-3,5-dimethylbenzyl) amines may decompose to produce *ortho–para* dimer ($-\underline{C}H_2-$ at 36.5 ppm) and 2,2′-methylene-4,4′,6,6′-tetramethyldiphenol (*ortho–ortho* dimer, $-\underline{C}H_2-$ at 31.4 ppm) via similar pathways as suggested in Ref. [6]. As predicted, the *ortho–ortho* dimer was generated at a higher temperature (above 135°C) compared to the other two dimers. The intensities of amines decreased significantly above 185°C and disappeared after heating to 205°C, whereas the *ortho–ortho* dimer increased in intensity to a greater extent concurrently.

The reaction pathways for the formation of *para–para*, *ortho–para* and *ortho–ortho* dimers are summarised in *3 3*. The ratio of the three dimers at 205°C was 0.44/0.14/0.38, respectively, and the remaining 4% was *para–para* $-CH_2-CH_2-$linked structure, as obtained by ^{13}C n.m.r. spectra. The *para–para* dimer was predominantly formed via the first pathway at lower temperatures, while the initial *ortho–para* dimer was suspected to be formed via the second pathway, and possibly via the third and fifth pathways as well at later stages. Since the amount of *ortho–para* dimer was small, it is likely that the mixed bis- and tris(hydroxybenzyl)amines preferred to undergo further reactions to form bis- and tris(2-hydroxy-3,5-dimethylbenzyl)amines rather than to give *ortho–para* dimers via



Scheme 2



Scheme 3

decomposition. Therefore, a certain amount of bis- and tris(2-hydroxy-3,5-dimethylbenzyl)amines was observed at higher temperatures and, thereafter, *ortho–ortho* dimers were formed via the third pathway. These results provide direct evidence for the reaction of vacant *ortho*-phenolic reactive sites with *para*-hydroxybenzylamine intermediates.

^{15}N n.m.r. spectra of the bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines and 2,4-xylenol mixed system after heating are shown in *Figure 3*. As the temperature increased above 90°C, the resonance of the bis(4-hydroxy-3,5-dimethylbenzyl)amine decreased significantly which is consistent with the ^{13}C n.m.r. spectra (*Figures 1 and 2*). The minor resonance around 40 ppm is consistent with the existence of 2-/4-hydroxy-3,5-dimethylbenzylammonium ions[3,8]. The ^{15}N resonances at 47.4–47.6, 50.2–50.4, 51.9–52.2 and 53.9–54.2 ppm are consistent with the existence of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines, mixed bis- and tris(hydroxybenzyl)amines and bis- and tris(2-hydroxy-3,5-dimethylbenzyl)amines, and the variation of these chemical shifts are due to the change in molecular environment as the temperature increased[3,8,11]. When the temperature reached 205°C, all of the amines (^{15}N: 47–55 ppm) and hydroxybenzylammonium ions (^{15}N: 40 ppm) disappeared. Compared to the self-decomposition of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines[6], the imine resonances (^{15}N: 280–300 ppm) were more pronounced in the mixed system while the amides (^{15}N: 90–150 ppm) only appeared at relatively higher temperatures (above 185°C). We note that this temperature corresponds to that at which colour changes have been observed in other novolac systems. Three imine structures detected by ^{15}N spectra are assigned to imines (**1**), (**2**) and (**3**) in *Scheme 4*, respectively, as taken from references of previous reports[3–6,8,9]. The ^{15}N resonances at 125–141 ppm are attributed to a number of amides[3–6,8,9], however, it is difficult to assign these amide structures in this complicated system because their signals are weak and the chemical shifts are similar. After heating to 205°C for 4 h, most resonances in a range of 160–170 ppm in ^{13}C spectra (*Figure 2*) disappeared, indicating that most amides and imines were thermally decomposed to dimers (*Scheme 4*). The two remaining amides at 97.8 and 95.9 ppm in ^{15}N spectra (*Figure 3*) may be (**5**) and (**6**) in *4 4*. The number of scans for all ^{13}C spectra was only 1000–2000, while for ^{15}N spectra, 100–200 scans were acquired for measuring the spectra of samples heated to 90°C, but 24 700 scans for the sample heated to 205°C for 4 h. Thus, the signals of amides can be noticed in the ^{15}N n.m.r. spectra at high temperatures, but not in ^{13}C n.m.r. spectra.

At 205°C, a resonance at 178.8 ppm in ^{13}C n.m.r. spectra (*Figure 2*) was detected corresponding to a carboxyl carbon of a salicylic acid, which may originate from further oxidation of a hydroxybenzaldehyde. Several minor

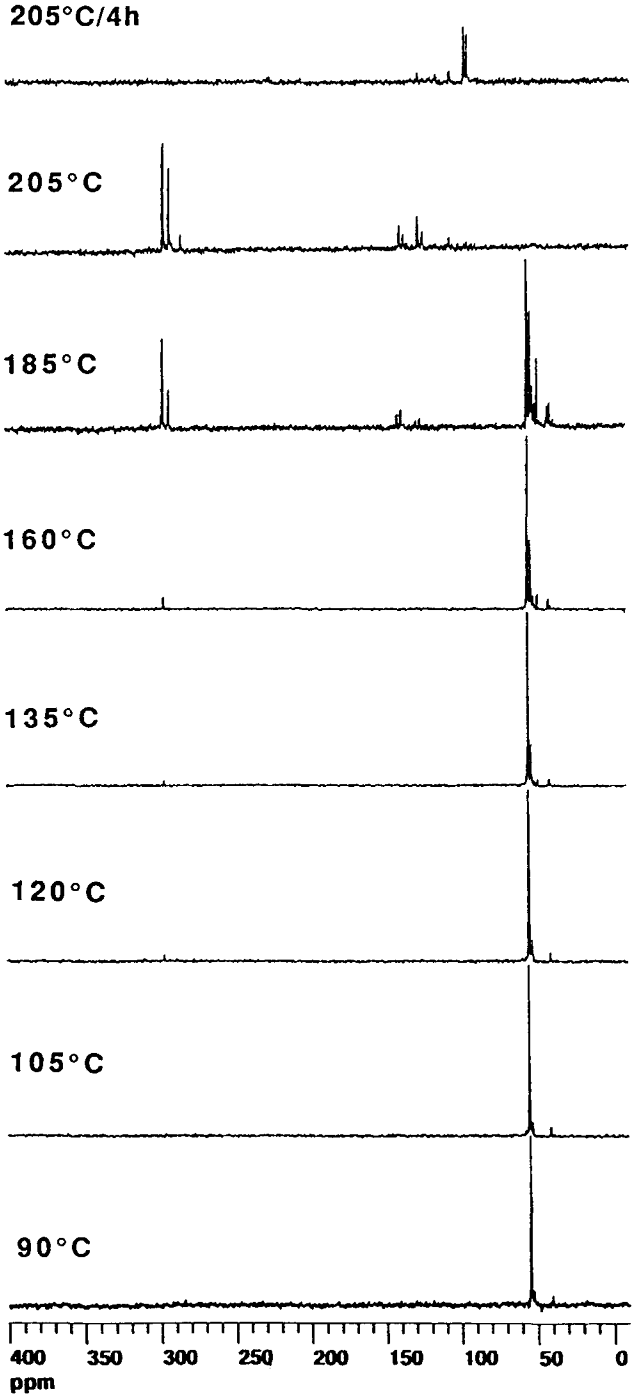
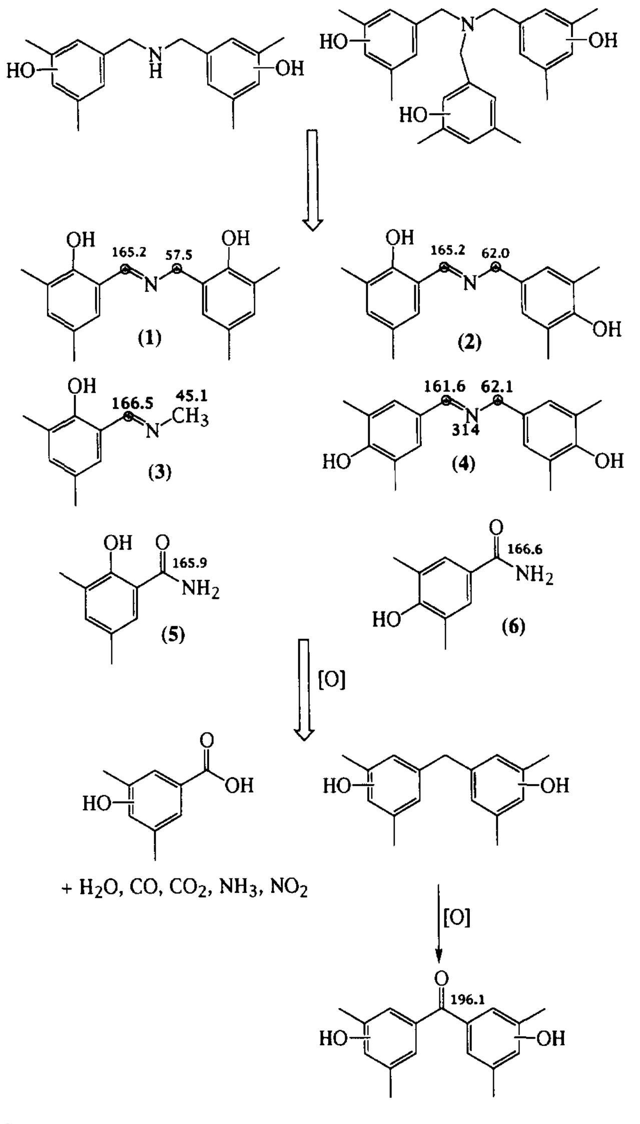


Figure 3 ^{15}N n.m.r. spectra of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines/2,4-xylenol after heating to various temperatures

resonances around the 50–55-ppm range which were observed at 205°C, are consistent with some side-reactions at methylene linkages as suggested previously[6,10].

para-Hydroxybenzylamine/2,6-xylenol reactions

The ^{13}C n.m.r. spectra of the system of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines with 2,6-xylenol after heating are shown in *Figures 4 and 5*. Only *para*-phenolic positions are available to take part in reactions in this system, thus the *para–para* dimer was the final product obtained, and the chemistry would be expected to be similar to the self-decomposition of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines[6]. However, some differences were observed, and most reactions occurred at relatively low temperatures when 2,6-xylenol was present. After heating the system to 90°C, the signals at 52.3 and 56.9 ppm, which are due to bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines respectively, significantly decreased, while a strong resonance at 40.4 ppm appeared corresponding to the formation of the *para–para* dimer. The signal at 52.3 ppm disappeared when the temperature reached 120°C, but it remained until 135°C in the self-decomposition[6]. Triazine structures disappeared above 90°C, while diamine structures remained until 120°C at 71 and 56–57 ppm[6]. The enhancement of the reactivity could be due to the decrease of pH when 2,6-xylenol was present.



Scheme 4

The side-product 4-hydroxy-3,5-dimethylbenzylamine was observed at 45.3 ppm at 90°C, while the resonances at 161.7 and 64.2 ppm (a $-N{=}CH-$ and a $Ar{-}CH_2{-}N\leqslant$ carbon) are due to imine (**4**) in *Scheme 4*[6]. ^{13}C DEPT spectra indicate that the 161.6 ppm peak corresponds to a methine carbon while the resonances at 45.3 and 64.6 ppm are methylene carbon. The 4-hydroxy-3,5-dimethylbenzyl alcohol (62.1 ppm here) was observed at 120–180°C, while 4-hydroxy-3,5-dimethylbenzaldehyde was detected after heating to 105°C, and remained in the system until 205°C/4 h. Above 160°C, ethylene linkages between phenolic rings (37.8 ppm) appeared simultaneously with

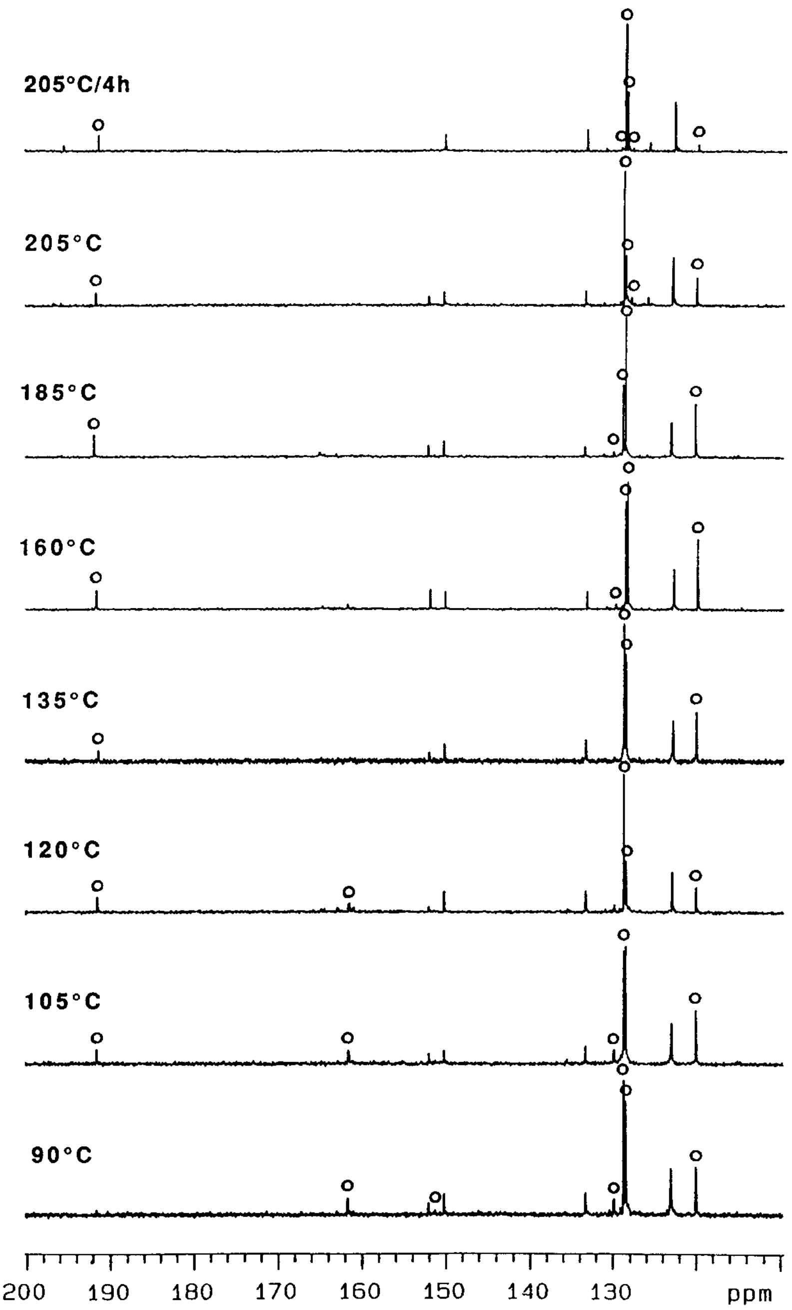


Figure 4 ^{13}C n.m.r. spectra (110–200 ppm) of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines/2,6-xylenol after heating to various temperatures. The resonances with circles indicate CH carbons which appeared as negative peaks in the ^{13}C DEPT spectra relative to the CH_2 carbons

trimethyl phenol (*para*-$\underline{C}H_3$ at 20.3 ppm). The resonance at 196.1 ppm (observed after heating to 185°C but disappeared in the ^{13}C DEPT spectrum) may correspond to the Ar–$\underline{C}$O–Ar′ carbonyl carbon which originated from oxidation at methylene linkages (*Scheme 4*). This is similar to the thermal decomposition of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines at higher temperatures[6], where reactions between the *para–para* dimer, methanol and hydroxybenzyl alcohol also occurred to produce methyl phenol ether structures (O$\underline{C}H_3$ at 54.9 ppm) and cross-linking at methylene linkages (> $\underline{C}$H– 51.9 ppm and $\underline{C}H_2$ 41.8 ppm), respectively. The major product after heating to 205°C/4 h is the *para–para* dimer.

During the process, the intensity of 2,6-xylenol decreased as the temperature increased, and became minor after heating to 205°C/4 h. The weight loss of the system after heating to 205°C/4 h was 46%, indicating that 20% of 2,6-xylenol has converted to the *para–para* dimer, possibly via reaction pathways as shown for 2,4-xylenol in *Scheme 3-2* and *Scheme 3-3*.

CONCLUSION

The ^{13}C and ^{15}N n.m.r. study provides direct evidence for the formation of methylene linkages between phenolic rings from reactions of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines with vacant *ortho-* and *para*-phenolic reactive sites. In the presence of 2,4-xylenol, the *para*-hydroxybenzylamines still undergo thermal decomposition to produce the *para–para* methylene linkages, but also react with 2,4-xylenol (containing an *ortho*-reactive site) to result in the *ortho–para* and *ortho–ortho* methylene linkages via a number of pathways, such as hydrogen-bonding mechanism, mixed bis- and tris(hydroxybenzyl)amines,

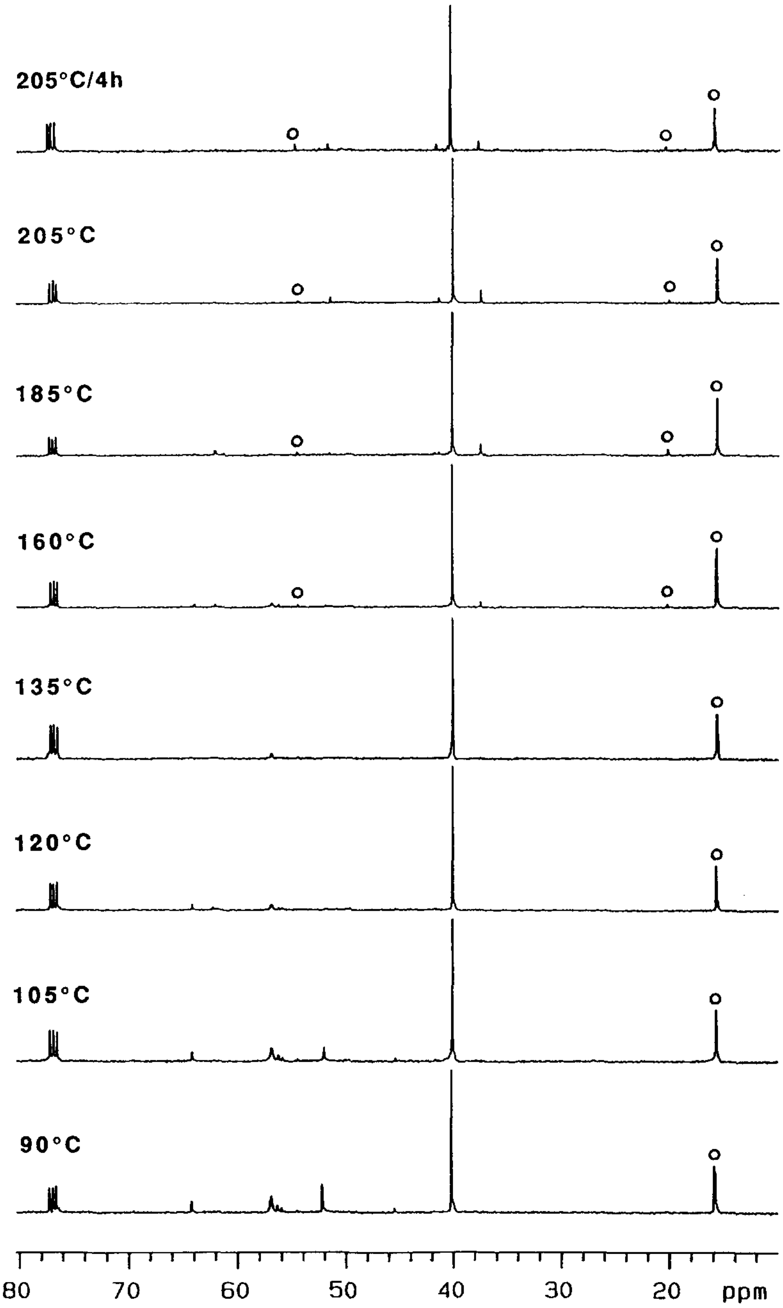


Figure 5 ^{13}C n.m.r. spectra (10–80 ppm) of bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amines/2,6-xylenol after heating to various temperatures. The resonances with circles indicate CH or CH_3 carbons, which appeared as negative peaks in the ^{13}C DEPT spectra relative to the CH_2 carbons

and possibly ether intermediates as well. With the presence of 2,6-xylenol (containing a *para*-reactive site), only the *para–para* dimer was produced but reactions occurred at relatively lower temperatures. Minor amounts of side-products were observed during the reaction, and some of them can even remain to 205°C/4 h. The results provide further mechanistic information which can be applied to the curing of novolac resins with HMTA. Combining these results with those reported in the previous papers[4–6], it can be concluded that the reaction can be varied by changing the chemical structures of the initial resins and the amount of HMTA when curing novolac resins with HMTA. A highly *ortho*-linked resin (containing a high ratio of *para*-reactive sites) and a relatively low amount of HMTA will result in a crosslinked network at relatively low temperatures with lower amounts of side-products. A general discussion of the reaction mechanisms of the first-formed intermediates will be discussed in a following paper on *ortho*-hydroxybenzylamines, which will be submitted soon.

ACKNOWLEDGEMENTS

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REFERENCES

1. Looney, M.G. and Solomon, D.H., *Aust. J Chem.*, 1995, **48**, 323.
2. Dargaville, T.R., de Bruyn, P.J., Lim, A.S.C., Looney, M.G., Potter,

A.C., Solomon, D.H. and Zhang, X., *J. Polym. Sci. Polym. Chem.*, 1997, **35**, 1389.

3. Zhang, X., Looney, M. G., Solomon, D. H. and Whittaker, A. K., *Polymer*, 1997, **38**, 5835.
4. Zhang, X., Potter, A. C., Solomon, D. H., Polymer in press.
5. Zhang, X., Solomon, D. H., Polymer in press.
6. Zhang, X., Potter, A. C., Solomon, D. H., Polymer in press.
7. Kopf, P.W. and Wagner, E.R., *J. Polym. Sci. Polym. Chem.*, 1973, **11**, 939.
8. Values taken from: *The Sadtler Standard Carbon-13 NMR Spectra*, Sadtler Research Laboratories, Philadelphia, 1977.
9. Levy, G. C. and Lichter, R. L., *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*, John Wiley & Sons, New York, 1979.
10. Hatfield, G.R. and Maciel, G.E., *Macromolecules*, 1987, **20**, 608.
11. Maciel, G.E., Chuang, I.-S. and Gollob, L., *Macromolecules*, 1984, **17**, 1081.