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Model studies of the curing of resole phenol-formaldehyde resins Part 1. The behaviour of ortho quinone methide in a curing resin

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Abstract

Model compounds have been used to investigate the curing behaviour of resole phenol formaldehyde resins. These models have shown that an *ortho* quinone methide intermediate is very site specific, preferring to react at a free *ortho* site of phenols. This study also shows that phenoxy type bridges can be formed by ether exchange between a phenolic OH and an ether bridge. These results help explain some of the structures observed in cured resins.

Keywords: Phenol-formaldehyde; Curing; Quinone methide

1. Introduction

Phenol-formaldehyde polymers are increasingly being used as precursors for carbon, replacing ceramic and pitch based materials in refractory applications. This has renewed interest in their chemistry. The initial reaction of formaldehyde with phenol has been reviewed [1–3], and there has been work published recently [4–8]. In contrast, there is relatively little information available [9,10] on the processes occurring during the subsequent curing of the resin.

A resole resin is formed from the reaction of phenol with greater than one equivalent of formaldehyde, usually under basic conditions. Heating the resin (curing) causes cross-linking, generating a hard, intractable material. There has been some characterisation of cured phenol/formaldehyde resins by solid state ^{13}C NMR [11,12]. Quinone methides have been proposed as key intermediates in the curing (condensation) of phenol formaldehyde polymers [2,3]. The quinone methide mechanism is not thought to be significant at temperatures below 150°C [3].

In this study, model compounds **1**, **2**, and **3**, which contain the functional groups found in resole resins, have been used to provide insight into the curing process. The compounds used have only one active site, so reaction is limited in extent and the products generated are relatively straightforward to separate and identify. As with all model systems, there is the possibility of a different reaction mechanism from the system being modeled. However, the species isolated from the reaction studied are analogous to those seen in real cured resole systems [2,3,11].

2. Experimental

2.1. Materials

2,4-Dimethylphenol (**1**), phenol (**11**), 2-methylphenol (**13**), 2,6-dimethylphenol (**2**) and 2,3-dimethyl-butane-2,3-diol (pinacol) were purchased from Aldrich. **1** was distilled in a Kugelrohr apparatus and **2**, **11**, **13**, and pinacol were sublimed (10^{-4} bar) before use. 2-Hydroxymethyl-4,6-dimethylphenol (**3**) was synthesised using a variation of a known method [13].

2.2. Characterisation and analysis

Analysis was by ^{1}H NMR, using a 300 MHz Varian. Deuterated chloroform ($CDCl_3$, Cambridge Chemicals) was used as the solvent. Product yields were obtained by peak integration and reference to the internal standard. Melting points are uncorrected. ^{1}H and ^{13}C NMR for characterisation were made on a 400 MHz Varian Unity spectrometer using Pulse Field Gradient and Broad Band probes respectively. Mass spectra were obtained from a V.G. Micromass 7070F spectrometer at 70 eV, and elemental analyses were carried out on a Carlo Erba 1108 CHNO-S analyser.

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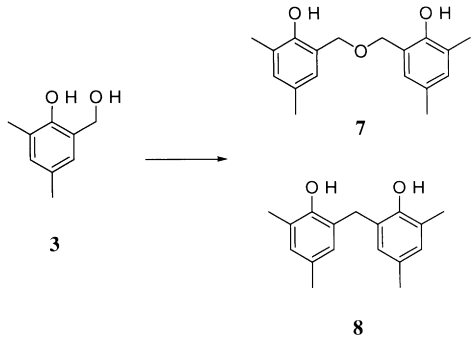

Fig. 1. Products from the self reaction of **3**.

2.3. Reactions of model compounds and products

For each model reaction, the appropriate amounts of **1**, **2** and **3** were mixed in a mortar and pestle and placed in glass ampoules, approximately 100 mg of material per ampoule. Pinacol was used as an internal standard [14] in the kinetic runs, with 0.1 mole equivalent of the limiting reagent used in the mixture. The ampoules were flushed with nitrogen, sealed and immersed in an oil bath. On removal from the oil bath, each sample was stored at −30°C until analysed. Two samples were prepared without pinacol for each reaction, providing a check that the standard was not interfering with the reaction.

Reaction was carried out in a melt, rather than solution. It was decided that resole curing conditions [3] were best modelled using a melt reaction.

2.4. Synthesis

2.4.1. 2-Hydroxymethyl-4,6-dimethylphenol (3)

In a modification of a known [13] procedure, 2,4-dimethylphenol (12.35 g), 37% aqueous formaldehyde solution (10.2 g), water (25 ml) and NaOH (4.75 g) were mixed at room temperature and stirred for three days. The mixture

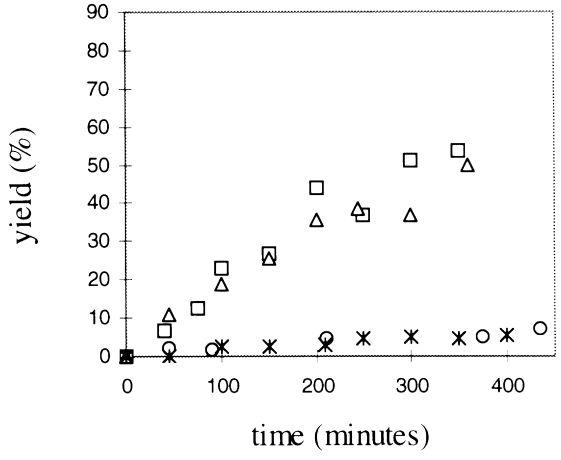

Fig. 2. Generation of methylene compound **8**. Yield is based on limiting component. Self reaction of **3** (○); 1:1 with **2** (∗); 1:1 with **1** (△); 2:1 with **1** (□).

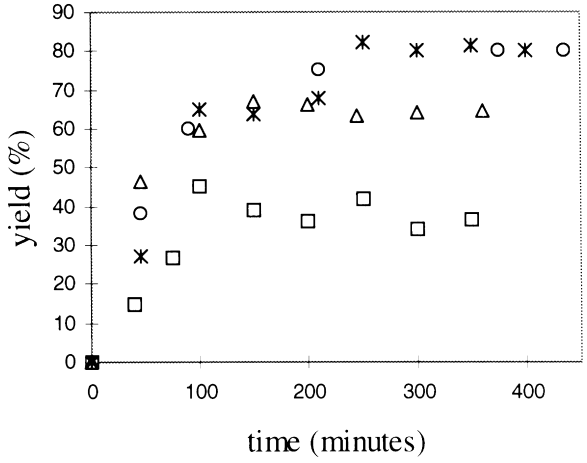

Fig. 3. Generation of ether compound **7**. Yield is based on limiting component. Self reaction of **3** (○); 1:1 with **2** (∗); 1:1 with **1** (△); 2:1 with **1** (□).

was then neutralised over ice with conc. hydrochloric acid and stirred at room temperature for a further 2 days. Extraction (chloroform 3 × 50 mL), followed by sublimation gave 2-hydroxymethyl-4,6-dimethylphenol (**3**) (8.5 g, 55%) m.p 57–58°C (Ref. [13], 57–58°C) ^{1}H NMR ($CDCl_3$): $\delta = 2.22$ (s, 6H) 4.80 (s, 2H) 6.69 (s, 1H) 6.91 (s, 1H) ^{13}C NMR ($CDCl_3$): $\delta = 15.53$, 20.31, 64.8, 123.76, 125.08, 125.82, 128.69, 131.35, 151.91 IR (KBr disc) υ_{max} (cm^{-1}) 3243, 1486, 1386, 1228, 1214, 1032, 1000, 972, 850 MS: m/z 152 (M^+ 58%), 134 (100), 106 (32), 91 (54) elemental analysis (%) calc. for $C_9H_{12}O_2$ C: 71.05, H: 7.89 found C: 71.24, H: 7.88

2.4.2. Bis (2-hydroxy-3,5-dimethylbenzyl) ether (7)

2-Hydroxymethyl-4,6-dimethylphenol (**3**) (0.979 g) was heated in a stirred round bottom flask for 5 h at 120°C under dry nitrogen. The crude product, separated by column chromatography (silica Merck, 250–400 mesh), eluted with 1:4 ethyl acetate:hexane, gave ether **7** (0.687 g, 71%) m.p. 98.5–99.5°C. (Ref. [15] 100°C) ^{1}H NMR ($CDCl_3$): $\delta =$ 2.22 (s, 12H), 4.67 (s, 4H), 6.70 (s, 2H), 6.93 (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 15.61$, 20.34, 70.72, 120.87, 124.86, 127.25, 128.89, 131.88, 151.72 IR (KBr disc) υ_{max} (cm^{-1}) 3500–3200 (w), 3100–2800 (w), 1472, 1229, 1187, 1150 MS: m/z 286 (M^+, 2%), 152 (43), 135 (82), 134 (100), 106 (15), 91 (77) elemental analysis (%) calc. for $C_{18}H_{22}O_3$ C: 75.52, H: 7.69 found C: 75.50, H: 7.69

2.4.3. Bis (2-hydroxy-3,5-dimethylbenzyl) methylene (8)

2,4-Dimethylphenol (**1**) (0.83 g) and 2-hydroxymethyl-4,6-dimethylphenol (**3**) (0.72 g) were heated in a stirred round bottom flask at 120°C under dry nitrogen for 5 h. Column chromatography (silica, Merck, 250–400 mesh), eluted with chloroform, gave methylene compound **8** (0.18 g, 30%) m.p. 148.5–149.5°C. (Ref. [16], 145–147°C) ^{1}H NMR ($CDCl_3$): $\delta = 2.14$ (s, 6H), 2.17 (s, 6H), 3.83 (s, 2H), 6.75 (s, 2H), 6.89 (s, 2H) ^{13}C ($CDCl_3$): $\delta =$ 16.68, 20.61, 31.53, 125.11, 128.14, 129.46, 129.74, 130.92,

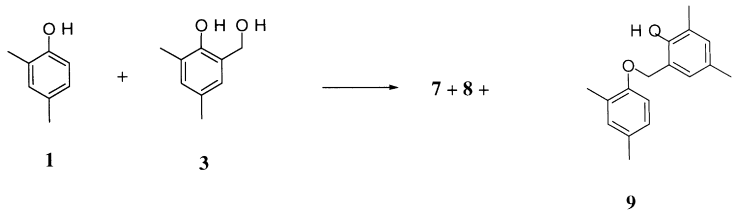

Fig. 4. Products from the reaction of **3** with 2,4-dimethylphenol (**1**).

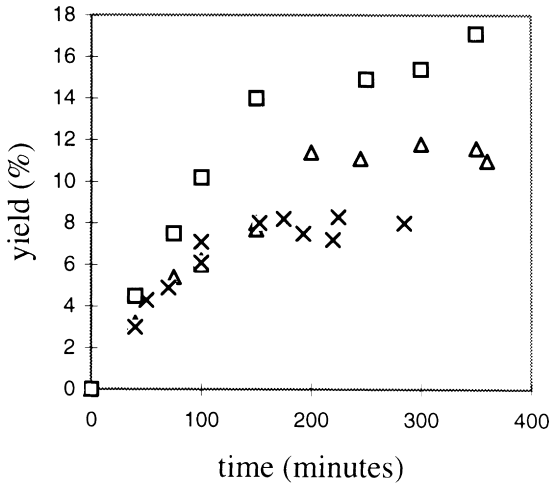

Fig. 5. Generation of phenoxy compound **9**. Yield is based on limiting component. 1:1 with **1** (△); 2:1 with **1** (□); 1:1:1 with **1** and **2** (×).

150.44 IR (KBr disc) υ_{max} (cm^{-1}) 3320, 3000, 2910, 2850, 1490, 1200, 850, 780 MS m/z 256 (M^+, 69%), 135 (94), 122 (100).

2.4.4. 2-Methyl-(2′,4′-dimethylphenoxy)-4,6-dimethylphenol (9)

2,4-Dimethylphenol (**1**) (0.83 g) and 2-hydroxymethyl-4,6-dimethylphenol (**3**) (0.72 g) were heated at 120°C under dry nitrogen in a stirred round bottom flask for 5 h. Column chromatography (silica, Merck, 250–400 mesh), eluted with chloroform, gave phenoxy compound **9** (0.06 g, 5%) as an oil. ^{1}H NMR ($CDCl_3$) 2.24 (s 6H) 2.25 (s, 3H) 2.27 (s, 3H) 5.12 (s, 2H), 6.82/6.84/6.87 (m, 2H), 6.93/6.95/6.98 (m, 3H) ^{13}C NMR ($CDCl_3$): $\delta = 24.35$, 24.89, 29.06, 29.12, 78.72, 120.61, 129.78, 133.96, 135.09, 135.37, 135.84, 137.58, 139.61, 140.36, 140.51, 160.37, 162.45 IR (KBr disc) υ_{max} (cm^{-1}) 3429 (w), 2900 (w), 1614, 1479, 1250, 1200, 1114, 1021, 800 MS: m/z 256 (M^+, 17%), 135 (100), 122 (85), 107 (36), 91 (58).

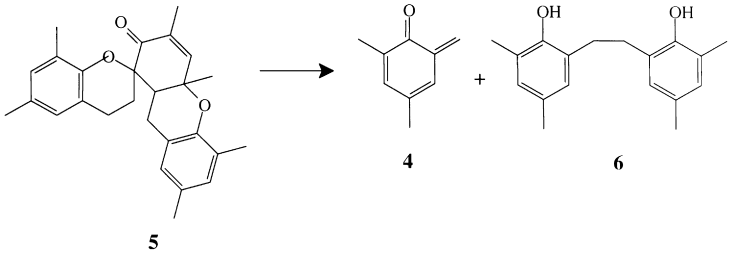

Fig. 6. The partial retro-Diels-Alder reaction of the trimer **5** at 150°C.

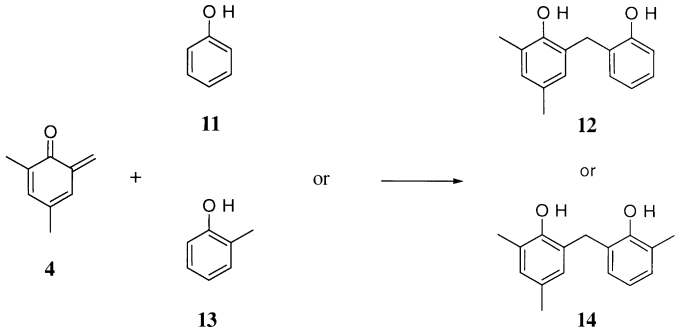

Fig. 7. The exclusive reaction of **4** at the free *ortho* site of phenol (**11**) and 2-methylphenol (**13**).

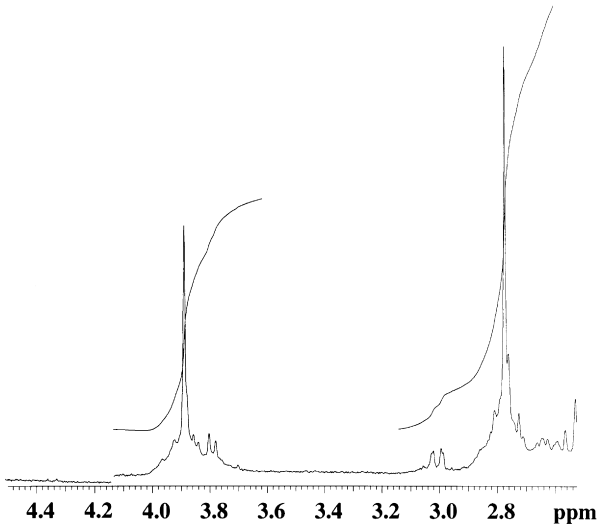

Fig. 8. ^{1}H NMR of crude reaction product obtained by reaction of **11** with **5** (3:1 molar ratio) for 9 h at 150°C. The peak at 3.88 ppm is assigned to the CH_2 of methylene compound **12**, and the peak at 2.78 ppm is assigned to the CH_2–CH_2 of ethylene compound (**6**). Residual trimer is visible in the baseline below 3 ppm.

*2.4.5. 2-Methyl-(2′,6′-dimethylphenoxy) 4,6-dimethylphenol (**10**)*

2,6-Dimethylphenol (**2**) (0.54 g) and 2-hydroxymethyl-4,6-dimethylphenol (**3**) (0.34 g) were heated at 120°C under dry nitrogen in a stirred round bottom flask for 8 h. Column chromatography (silica, Merck, 250–400 mesh), eluted with chloroform, gave **10** (0.005 g, 0.8%) as an oil. ^{1}H NMR ($CDCl_3$): $\delta = 2.26$ (s, 3H) 2.28 (s, 3H) 2.35 (s, 6H) 4.95 (s, 2H) 6.74 (s, 1H) 6.85/7.00/7.02 (m, 2H), 7.06/7.08 (d, 2H) ^{13}C NMR ($CDCl_3$): $\delta = 15.74$, 16.52, 20.38, 73.92, 121.43, 124.67, 125.39, 125.90, 128.83, 129.11, 130.75, 131.52, 151.76, 155.05 IR (KBr disc) υ_{max} (cm^{-1}) 3450 (w), 2920 (w), 1600, 1500, 1200, 1143, 1021, 857 MS: m/z 256 (M^+, 10%), 135 (100), 122 (28), 107 (15), 91 (14).

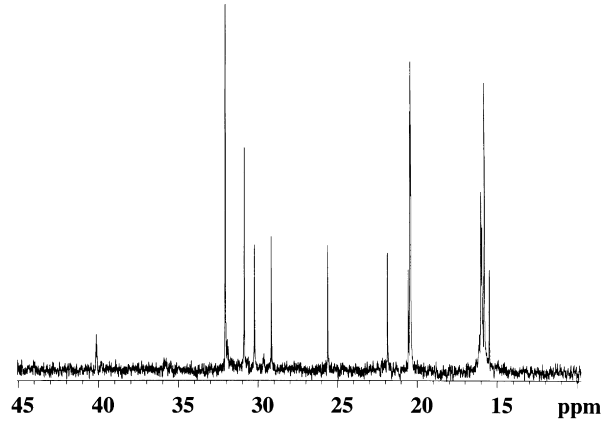

Fig. 9. ^{13}C NMR of the crude reaction product between **5** and **11** after 9 h. The peaks are assigned to the ethylene CH_2 (32 ppm), the *o–o* methylene bridge (30.9 ppm) and trimer **5** (30.2, 29.2 and 25.1 ppm).

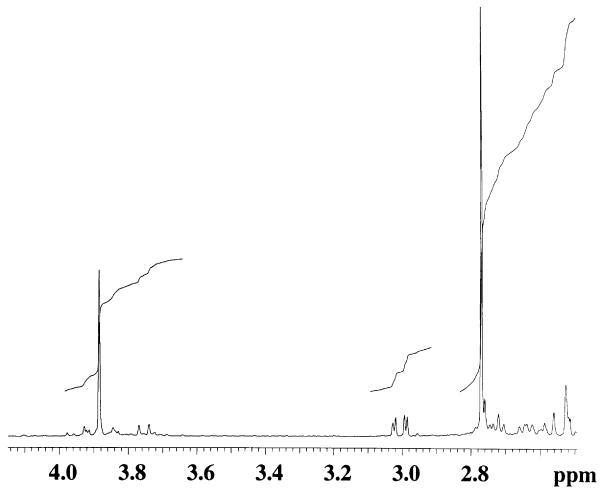

Fig. 10. ^{1}H NMR of crude reaction product obtained by reaction of 2-methylphenol (**13**) with trimer **5** for 9 h at 150°C (3:1 molar ratio). The methylene (3.88 ppm) and ethylene (2.76 ppm) bridges integrate 2:1, showing that the molar ratio of the two products is 1:1.

3. Results and discussion

*3.1. Reactions of 2-hydroxymethyl-4,6-dimethylphenol (**3**)*

The self reaction of 2-hydroxymethyl-4,6-dimethylphenol (**3**) at 120°C produced bis(2-hydroxy-3,5-dimethylbenzyl) ether (**7**) and bis(2-hydroxy-3,5-dimethyl-benzyl) methylene (**8**) as major products (Fig. 1), with the ether being produced much faster than the methylene compound (Figs. 2 and 3).

Compare the self reaction of **3** with the reaction of **3** with one and two molar equivalents of 2,4-dimethylphenol (**1**); three products were obtained (Fig. 4); the ether compound (**7**), the methylene compound (**8**) and a phenoxy compound (**9**) (Figs. 2, 3 and 5). The initial rates[1] of ether formation in the case of a 1:1 mixture of **1** and **3** and the self-reaction of **1** (Fig. 3, △ and ○ respectively) are approximately the same; the curves overlap at less than 200 min. As more **1** is added the effect of dilution becomes apparent (Fig. 3, □), and the rate of ether formation falls.

The methylene compound **8** forms much faster in the presence of 2,4-dimethylphenol (**1**) than with self reaction (Fig. 2 △, □ vs ○). However, the relative rate of methylene formation does not change significantly between one and two equivalents of **1**; the time taken to convert a given fraction of **3**, and hence reach a given yield, is independent of the amount of **1** present and the curves overlap (Fig. 2, □ and △).

The behaviour of 2-hydroxymethyl-4,6-dimethylphenol (**3**) in the presence of 2,6-dimethylphenol (**2**) was virtually indistinguishable from the self reaction of 2-hydroxymethyl-4,6-dimethylphenol; thus the rates of formation of

[1] It is important to note that since these reactions were carried out in a melt, the reaction composition changes considerably over the course of the reaction. For this reason no rates of reaction are presented.

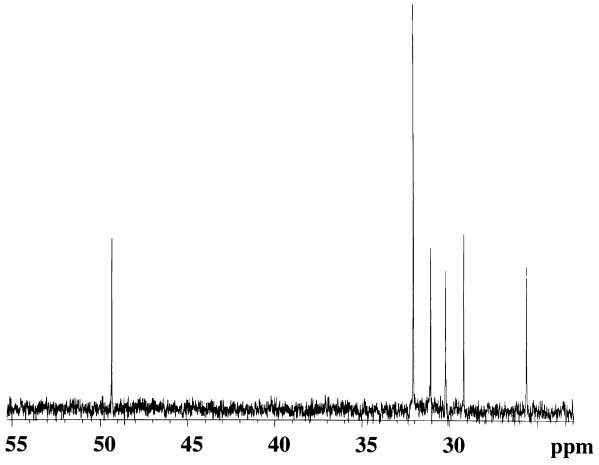

Fig. 11. ^{13}C NMR of the crude reaction product between **5** and 2-methylphenol (**13**) after 9 h at 150°C. The peaks are assigned to trimer **5** (49.4 ppm), the ethylene CH_2 (32 ppm), the *o–o* methylene bridge (31.1 ppm) and **5** (30.2, 29.2 and 25.6 ppm).

ether and methylene compounds are similar (Figs. 2 and 3, ∗ and ○); the graphs of the two reactions overlap. No significant quantities of *ortho-para* linked methylene compound was generated over the timescale studied. A small quantity of phenoxy **10** was isolated.

3 was then heated with **1** and **2** in a 1:1:1 molar ratio, and similar trends were observed. The data set has been omitted from the figures for clarity. Methylene formation in the 1:1:1 mixture initially (<150 min) followed the curve of 1:1 and 1:2, but then dropped away. Ether formation fell midway between 1:1 and 1:2 in the 1:1:1 mixture. The limiting ether yield tended towards an asymptote in the following order: self-reaction of **3** (80%) > 1:1 of **1** and **3** (60%) > 1:1:1 of **1**, **2** and **3** (50%) > 1:2 of **1** and **3** (35%).

The observed behaviour by which both the ether and methylene compounds were formed strongly suggests that in both cases the reaction mechanism includes a first order rate limiting step. In a first order reaction, the time taken for a given fraction of starting material to react is independent of the starting material concentration. The rate of formation of **8** when **1** and **3** were reacted together was unaffected by doubling the ratio of **1** to **3**. When the concentration of **3** was halved by addition of **2**, the rate of methylene formation and ether formation was unchanged from the self-reaction case. The results strongly suggest that the active species is *ortho* quinone methide, formed by the intramolecular loss of water from **3**. It is the proximity of the hydroxymethyl group to the phenolic OH which allows water loss to occur intramolecularly, and this step would be first order in **3**. Quinone methide formation has been previously suggested as unimportant below 150°C [3]. These results suggest that it may be present at a lower temperature than this.

2 was found to have minimal reactivity towards **3** in the melt reaction, suggesting that the *ortho* quinone methide did not react with the available *para* position. This was unexpected since *para* preference is observed in phenolic resins

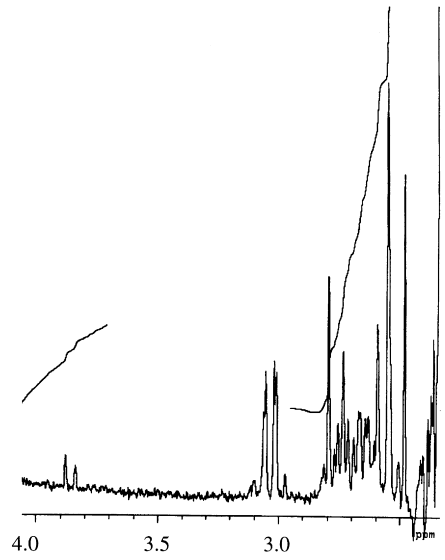

Fig. 12. ^{1}H NMR of the crude reaction product between 2,6-dimethylphenol (**2**) and **5** after 10 h at 150°C. The multiplets below 3.1 ppm are due to **5**. The small peaks above 3.8 ppm are products.

[3]. Therefore, this behaviour was further investigated with the quinone methide trimer (**5)** (Section 3.2).

3.2. Reaction of ortho quinone methide

The results from the above xylenol models suggested that there was a considerable difference between the reactivity of *ortho* quinone methide towards a free *ortho* and a free *para* aromatic site. An alternative means of generating *ortho* quinone methide, by thermolysis of **5**, was developed, which avoided the need for reactive hydroxymethyl groups in the system. Isolation of **5** has been described elsewhere [17].

The trimer **5** was separately heated in glass ampoules at 150°C by itself, and with phenol (**11**), 2-methylphenol (**13**), 2,4-dimethylphenol (**1**) and 2,6-dimethylphenol (**2**) in a 3:1 molar ratio (phenolic:trimer). Under the self-reaction

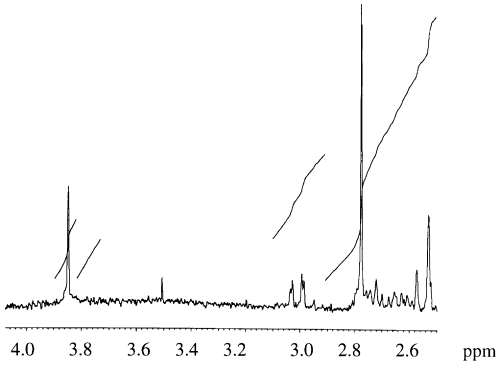

Fig. 13. ^{1}H NMR of the crude reaction product of 2,4-dimethylphenol (**1**) and trimer (**5**) after 9 h at 150°C. Integration of the product (3.85 ppm) and **5** shows that reaction is much more advanced than with 2,6-dimethylphenol (**2**) (Fig. 12) under the same conditions.

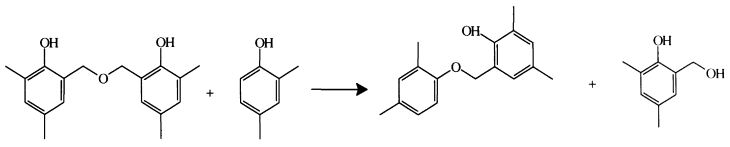

Fig. 14. Ether exchange between **7** and **1** generates **3** and the phenoxy **9**. Here **3** will either self-react, regenerating **7**, or react with **1** to give the methylene **8**.

conditions a partial retro-Diels-Alder reaction occurred, giving one equivalent each of the *ortho* quinone methide (**4)** and the bis (2-hydroxy-3,5-dimethylphenyl) ethane (**6**) (Fig. 6).

The generation of **4** was deduced from the formation of methylene bridged phenol derivative **12** (Fig. 7). The isolation and direct observation of **4** at cryogenic temperatures has also been described elsewhere [17].

With phenol or 2-methylphenol (**13**), the *ortho* quinone methide (**4)** was found to react entirely at free *ortho* sites. The exclusive *ortho* attack was demonstrated by the distinctive ^{13}C signal of an *ortho-ortho* methylene bridge at 30 ppm (Figs. 9 and 11) with no signal observed at 35 ppm, where an *ortho-para* methylene bridge would appear [16,18,19]. The ^{1}H NMR of the crude reaction mixtures (Figs. 8 and 10) show the 1:1 molar ratio of methylene bridge to ethylene bridge. With 2,4-dimethylphenol (**1**), the reaction was found to proceed much faster than with 2,6-dimethylphenol (**2**); the ^{1}H NMR (Figs. 12 and 13) shows a much greater loss of **5**, and corresponding formation of products, in the presence of **1** compared with **2**.

From these results we would predict that a high *ortho* bridged resin would be formed when conditions favour the production of *ortho* quinone methide. This would require a resin which contains predominately *ortho* hydroxymethyl substituents, and condensation at high temperature, preferably in solvents which encourage dehydration of the *ortho* hydroxymethyl functionality. The conditions which have been demonstrated to generate a high *ortho* phenol formaldehyde resin are high condensation temperatures in solvents which generate an azeotrope with water [3]. The catalysts used have been shown to promote *ortho* addition of formaldehyde; subsequent involvement of the catalyst in the condensation reaction has not been demonstrated [20].

3.3. Ether exchange reactions

The phenoxy linked compounds **9** and **10** were isolated from both the reaction of **3** with **1** and **3** with **2**. Such phenoxy compounds were not observed in the reaction of *ortho* quinone methide (**4**) with any of the phenol and methylphenols. When the ether **7** was heated in the presence of D_2O, it decomposed slowly to **3**. When **7** was mixed with **1** the phenoxy compound **9** was rapidly generated, along with **3** and **8**. From this it was concluded that the phenolic OH undergoes an ether exchange (Fig. 14), and it is the subsequent reaction of **3** with **1** which generates **8**.

That the phenol was not acting as an acid catalyst for ether hydrolysis was shown by heating the ether with conc. HCl, which did not noticeably degrade the ether.

A solid state ^{13}C signal obtained from a cured resin by Maciel et al. [11] was assigned to the phenoxy crosslink, and three possible mechanisms by which the phenoxy bridge could be generated were proposed. No experimental evidence was given. The results of this study show that ether exchange is certainly one mechanism by which a phenoxy bridge can be generated in a cured resole resin. The mechanism requires the presence of ether links and unsubstituted phenols. Since similar compounds were not observed in the self-reaction of **3**, it is concluded that hydroxymethyl phenols preferentially react to form ether and methylene bridges rather than phenoxy links. In a resole, it would be expected that the amount of phenoxy generated as a function of the formaldehyde:phenol ratio would pass through a maximum, where the free methylol required to form ether links is balanced by unsubstituted phenol required for ether exchange.

4. Conclusions

The *ortho* quinone methide (**4**), which it is proposed is formed by the dehydration of 2-hydroxymethyl-4,6-dimethylphenol (**3**), showed a strong preference for reaction at free *ortho* sites rather than free *para* sites. A trimer **5** of *ortho* quinone methide (**4**) was successfully used to support this conclusion, and also showed that *ortho-ortho* ethylene bridges can be obtained via a partial retro-Diels-Alder reaction of the trimer **5**. When **3** was reacted with 2,4-dimethylphenol (**1**) and 2,6-dimethylphenol (**2**) the observed behaviour on changing the concentration of **1** and **2** strongly suggests that *ortho* quinone methide is the active species. Its generation at 120°C shows that *ortho* quinone methide can be produced at significantly lower temperatures than has previously been suggested [3], and this has important consequences for resin curing. Phenoxy bridges were shown to be formed by ether exchange between phenolic OH and a bridging ether.

Acknowledgements

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References

[1] Drumm MF, LeBlanc JR. Chapter 5. In: Solomon DH, editor. Step-growth polymerizations, 3. New York: Marcel Dekker, 1972.
[2] Solomon DH. The chemistry of organic film formers. New York: Krieger, 1977.
[3] Knop A, Pilato LA. Phenolic resins. Berlin: Springer, 1985.
[4] Grenier-Loustalot MF, Larroque S, Grenier P, Leca JP, Bedel D. Polymer 1994;35(14):3046.
[5] Grenier-Loustalot MF, Larroque S, Grande D, Grenier P, Bedel D. Polymer 1996;37(8):1363.
[6] Grenier-Loustalot MF, Larroque S, Grenier P, Bedel D. Polymer 1996;37(6):939.
[7] Grenier-Loustalot MF, Larroque S, Grenier P, Bedel D. Polymer 1996;37(6):955.
[8] Grenier-Loustalot MF, Larroque S, Grenier P. Polymer 1996; 37(4):639.
[9] Zhang X, Solomon DH. Chem Mater 1999;11(2):384.
[10] Solomon DH, Zhang X. Chem Mater 1998;10(7):1833.
[11] Maciel GE, Chuang IS, Gollob L. Macromolecules 1984;17:1081.
[12] Fyfe CA, McKinnon MS, Rudin A, Tchir WJ. Macromolecules 1983;16:1216.
[13] Tramontini M. Synthesis 1973;5:703.
[14] Sprung MM, Gladstone MT. J Am Chem Soc 1949;71:2907.
[15] Hultzsch K. Ber Dtsch Chem Ges 1941;74:902.
[16] Pethrick RA, Thomson B. Br Polym J 1986;18(3):171.
[17] Qiao GG, Lenghaus K, Solomon DH, Reisinger A, Bytheway I, Wentrup C. J Org Chem 1998;63(26):9806.
[18] Werstler DD. Polymer 1986;27:750.
[19] Fitzgerald EA, Tadros SP, Almeida RF, Sienko GA, Honda K, Sarubbi T. J Appl Poly Sci 1992;45:363.
[20] Pizzi A, Stephanou A. J Appl Poly Sci 1993;49:2157.