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Kinetics of phenolic resol resin formation by HPLC. 2. Barium hydroxide

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The evolution of phenolic resol resin catalysed by barium hydroxide under controlled temperature, formaldehyde to phenol ratio and water dilutability was quantitatively followed by liquid chromatography. Disappearance of phenol and formaldehyde and formation of addition products were quantitatively followed during synthesis. Higher molecular species formed by condensation reactions were diaryl compounds bonded by methylene bridges via *para,para* and *ortho,para* positions. No *ortho,ortho* bonds were detected by [13]C n.m.r. spectroscopy. Gas chromatography was used to follow the evolution of the final resin stored at three temperatures. Temperatures below zero are advisable for storing purposes of these phenolic resol resins. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Phenolic resins are obtained by step-growth polymerisation of difunctional aldehydes with phenols (functionality greater than 2). Substituted phenols of lower functionality are used to incorporate specific properties in the resin (coatings, adhesives). Temperature and pH conditions under which chemical reactions are carried out, as well as formaldehyde to phenol ratio (F/P), influence the final properties of the crosslinked resin. At pH above 5 the rate of phenol/formaldehyde consumption depends on the hydroxyl ion concentration which contributes to the formation of phenolate ions (*Figure 1*)[1]. These phenolates form an intermediate state in which the cation of the catalyst is involved. In the series of alkali and alkaline earth-metals the chelating strengths or stabilising constants can be correlated with the e^2/r value of the ion, where e is the charge of the cation and r the radius of the cation[2]. Depending on the charge and size of the cation, addition of hydroxymethyl groups is oriented to either of the free positions in the phenolic ring. It has been recognised that the *ortho* substitution is enhanced when metal hydroxides of the first and second groups among the series K < Na < Li < Ba < Sr < Ca < Mg are used as catalysts[3]. Hydroxides of these cations were classified into two families as a function of their addition orienting behavior: KOH, NaOH, and LiOH as monovalent ones, and Ba(OH)$_2$ and Mg(OH)$_2$ as divalent hydroxides[4].

Following the investigations on the influence of the different types of basic catalysts reported in a previous paper[5], barium hydroxide was chosen as representative of the hydroxides of divalent metal ions. The influence of this catalyst in the mechanisms, kinetics and properties of resols in comparison with sodium hydroxide has been studied by several teams[4,6,7]. In order to complete the knowledge

about barium hydroxide as catalyst for phenolic resins, and to state the kinetic comparisons on the prepolymers formed by catalysis with other type of basic catalysts, the evolution of products formed from the addition of formaldehyde onto phenol and later condensation reactions has been analysed. This study will be completed in another report by the study of a resol catalysed under the same conditions by zinc acetate (CH$_3$COO)$_2$Zn).

In this paper, we study the kinetics of a resol synthesised following the same procedure of resols reported elsewhere[5] but catalysed by barium hydroxide (Ba(OH)$_2$). The evolution during condensation of the first formed products has been followed by high-performance liquid chromatography (HPLC). The final prepolymers have been analysed by gas chromatography (GC) and carbon nuclear magnetic resonance spectroscopy ([13]C n.m.r.).

EXPERIMENTAL

Synthesis of resol

Phenol (> 99%), formaldehyde (37% aqueous solution) and alkaline catalyst were commercial products used without further purification.

Prepolymer was synthesised in the Bakelite-Ibérica factory by mixing phenol and formaldehyde in a molar ratio of $F/P = 1.8$. The pH was then fixed to 8.0 with barium hydroxide, Ba(OH)$_2$. The mixture was heated to 80°C (heating rate, 2.5–3.5°C/min) and stirred during reaction. Samples were taken during condensation reaction. Zero time was defined as time taken for the mixture to reach the condensation temperature. The reaction was stopped when the resin showed a 1/1 g/g dilutability in water by putting the reactor in a cold water bath. Intermediate samples taken during synthesis were kept at −4°C, whereas final samples were kept at −20°C, 4°C and room temperature (17–23°C) in order to study by GC the

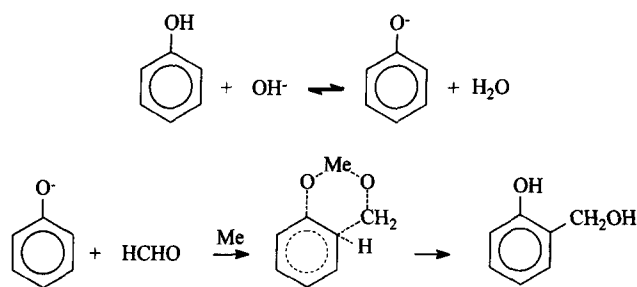* To whom correspondence should be addressed

Figure 1 Reaction mechanism for formation of phenolate ions and addition of formaldehyde onto phenol at the *ortho* position via chelate transition state. Me, metal ion
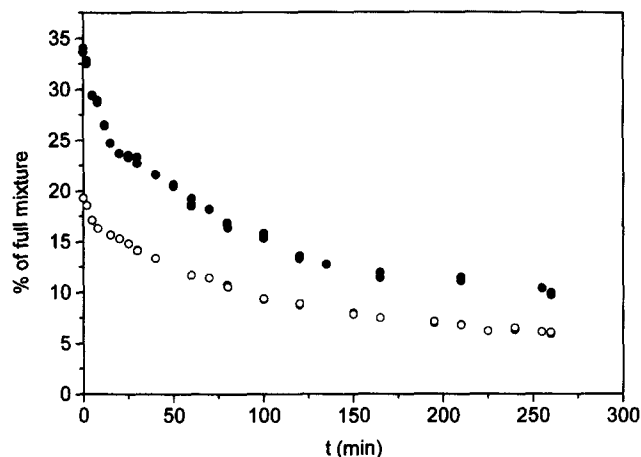

Figure 2 Disappearance of free formaldehyde (O) and phenol (●) during synthesis

evolution of free phenol as a parameter of stability for these resins.

High-performance liquid chromatography (HPLC)

Analyses were conducted with a Waters 510 chromatograph equipped with a Waters 486 u.v. detector, set at 280 nm. The column was a Spherisorb ODS-2 (5 μm). In order to decrease the viscosity of the solvents, the column was thermostated to 35°C. A mobile phase of methanol/water was used with an elution gradient of 20–80% of methanol in 180 min, and 80–100% in 5 min.

Gas chromatography (GC)

Samples were analysed in a HP5890 Series II chromatograph connected to a HP3396A Integrator equipped with a flame ionisation detector (FID) using helium as carrier gas. An HP-20M (Carbowax 20M) high-performance capillary column of 0.2 μm film thickness, 50 m length and 0.2 mm internal diameter was used. *p*-Cresol (250 mg) was added to the sample solutions in methanol as internal standard.

Carbon nuclear magnetic resonance spectroscopy (^{13}C n.m.r.)

High-resolution ^{13}C n.m.r. spectra in liquids were recorded with a Varian VXR-300 spectrophotometer. The following conditions were used: sweep width, 16 501.7 Hz; pulse width, 14.8 μs (90°); pulse delay, 1.0 s; acquisition time, 0.908; and data points, 29 952.

Final prepolymers were redissolved in deuterated dimethylsulfoxide (DMSO-d_6). and deuterated acetone (acetone-d_6). ^{13}C chemical shifts were measured with respect to tetramethylsilane (TMS) as internal standard

(δ(DMSO-d_6) = 39.5 ppm, δ(acetone-d_6) = 29.8 and 205.7 ppm).

RESULTS AND DISCUSSION

In a previous paper[5] the influence of two types of catalyst (sodium hydroxide and triethylamine) on the addition and condensation reactions of resols was studied. Depending on the catalyst used, different rates for addition reactions were observed. Prepolymer synthesised by amine showed higher addition in the free *ortho* positions of the phenolic ring with respect to that for the resol catalysed by sodium hydroxide. The mechanism of formaldehyde addition onto phenol was controlled by the catalyst. The presence of hydroxyl ions gave the resin a red colour, whereas the addition of an amine made the resin yellow, the characteristic colour of the phenolic resins synthesised under an acidic medium (novolacs) cured with hexamethylenetetramine[3]. However, the final resin seemed to be qualitatively formed by the same condensation products as no different compounds were detected.

In order to continue with the analysis of the influence of a wide group of alkaline catalysts in the formation and kinetics of phenolic resins, a resin was synthesised under the same controlled conditions of pH, temperature and formaldehyde to phenol ratio, as those used for the resins catalysed by sodium hydroxide and triethylamine, previously reported[5].

The mixture of formaldehyde and phenol was adjusted to pH 8 by the addition of catalyst, and was condensed until a 1/1 dilutability in water was achieved. The water dilutability, which is affected by the content of alkali and solvents, depends mainly upon the extent of resin condensation and represents a good criterion for molecular weight[3].

The mixture needed 263 min to reach the prefixed final point, the moment at which reaction was stopped by putting the reactor in a cold bath. As in the case of the resol catalysed by sodium hydroxide, the mixture took a reddish colour due to the formation of phenolate ions through the extraction of the phenolic proton by the hydroxyl anion of the catalyst. Both resins also showed a similar time of condensation, longer than the amine-catalysed resol, as a result of the better solubility of the formed anions[3].

The evolution of free formaldehyde during synthesis was followed by chemical assay[8], while the disappearance of phenol and formation of addition and condensation products were quantitatively followed by liquid chromatography (HPLC). The disappearance of the reactive species (formaldehyde and phenol) is shown in *Figure 2*. The high values at zero time suggests that very little addition products have been formed during the process of warming up to the cooking temperature (80°C). In fact, the concentrations of phenol and formaldehyde decreased by 5 and 3%, respectively, giving rise to the formation of 3% of 2-HMP. However, once this temperature has been reached, both curves show a disappearance process which can be divided into three steps: during the first 20 min of reaction, the rate of consumption of both species was very fast; after this period and until 120 min of reaction, formaldehyde and phenol kept on disappearing, but at a lower rate, becoming much slower for the last 145 min. At the first 20 min of reaction, addition of formaldehyde onto phenol is favoured due to the high concentration of free phenol and the low presence of species that can give rise to condensation reactions. After the substituted phenols have been formed, the rate of phenol consumption decreases due to two factors.
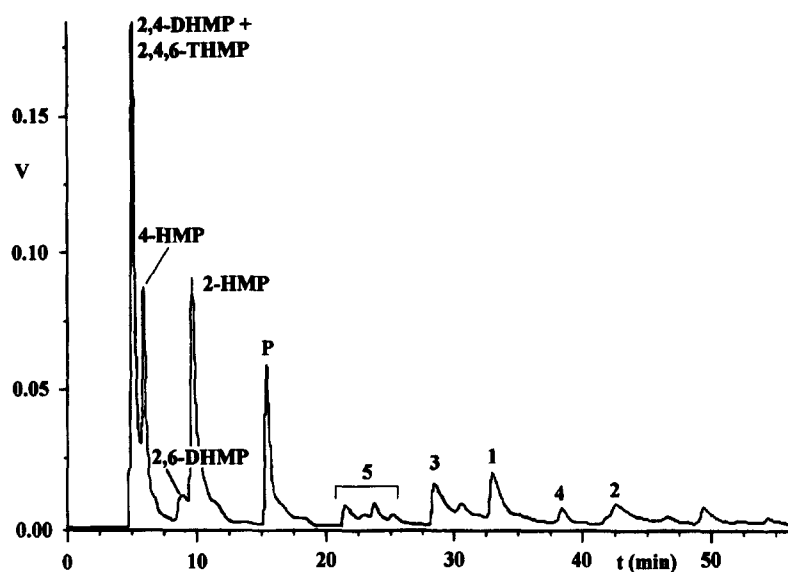
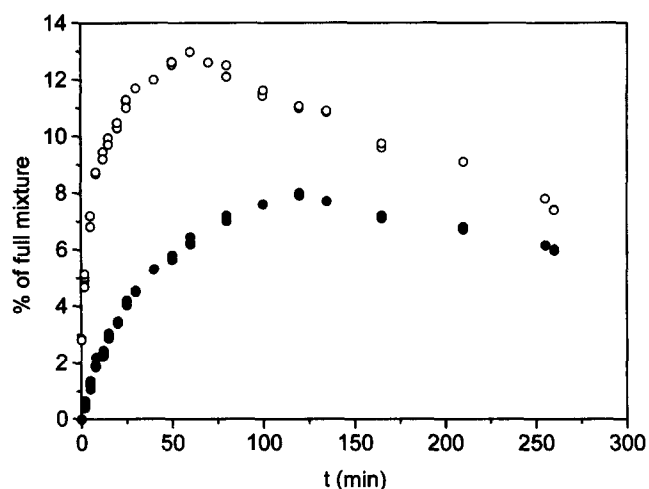**Figure 3** HPLC chromatogram of resol at the prefixed final point

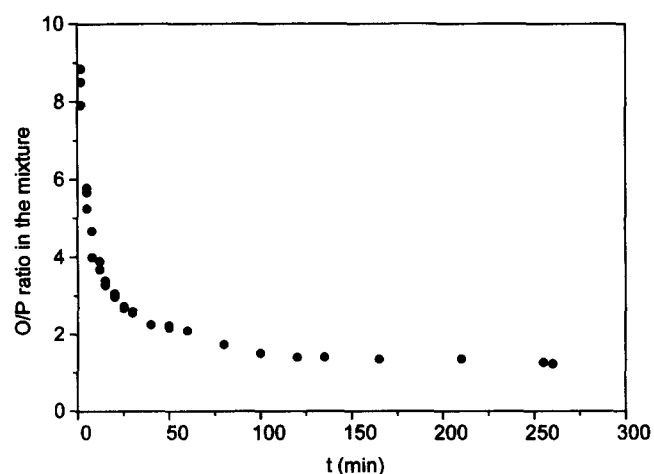**Figure 4** Evolution of 2-hydroxymethylphenol (O) and 4-hydroxymethylphenol (●) during synthesis

Figure 5 *Ortho/para* ratio during synthesis

Firstly, formaldehyde continues adding onto mono- and disubstituted phenols, and condensation reactions are held among the formed phenols and also with free phenol; on the other hand, free formaldehyde adds to free phenolic positions as long as these exist, but it does not disappear completely because of the formation of more free formaldehyde from the condensation of methylol groups[3].

Figure 3 shows a HPLC chromatogram of the resol at the prefixed final point. One phenolic ring addition products elute before phenol, which is followed by diaryl species, and finally higher molecular weight chains, not fruitfully separated.

The evolution of formed monosubstituted hydroxymethylphenols, 2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP) was quantitatively followed by HPLC, and is depicted in Figure 4. The former is the only product formed before the condensation temperature (80°C) was reached. The fast formation of 2-HMP during the first 20 min of reaction coincides with the most rapid decrease in concentration of formaldehyde and phenol discussed above. In 60 min of cooking, the concentration of 2-HMP had reached its maximum value (12.3%) and started to decrease as a result of addition onto the free *para* position left in its ring and the first condensation reactions. The concentration curve of 4-HMP shows slower rates of formation and disappearance (the maximum concentration (7.8%) was reached after 120 min of synthesis), but at the prefixed final point the concentrations of both monosubstituted compounds become very similar. Figure 5 shows the 2-HMP/4-HMP weight ratio (*O/P*) during synthesis. Although during the first 60 min of reaction a value *O/P* > 2 was observed, beyond this point, where the concentration of 2-HMP was maximum, it became lower than 2, a value which corresponds to equal reactivity of active positions in the ring. The decrease in concentration showed by 2-HMP, after it had reached its maximum value, makes the concentration of 4-HMP relatively higher with respect to that of the former. Due to steric hindrance and interactions between phenolic and benzylic hydroxyl groups, the *para* position in the phenolic ring is more reactive than the *ortho* positions. In the case of the resol catalysed by barium hydroxide, methylolation of the *para* position becomes relevant only after an

important amount of addition onto the *ortho* position has occurred. Besides, as shown in *Figure 4*, the concentration of 2-HMP remains higher with respect to that of 4-HMP, which is the opposite to resol catalysed by sodium hydroxide.

The evolution of disubstituted and trisubstituted phenols, 2,4-dihydroxymethylphenol (2,4-DHMP), 2,6-dihydroxymethylphenol (2,6-DHMP), and 2,4,6-trihydroxymethylphenol (2,4,6-THMP), is presented in *Figure 6*. 2,4-DHMP and 2,4,6-THMP did not separate under the chromatographic conditions used. The upper curve represents the evolution of both species together. The formation of these disubstituted and trisubstituted phenols takes longer because they are products formed from the first formed addition products, 2-HMP and 4-HMP. After one hydroxymethyl group has been added onto one free position in phenol, a second one can bond the free position left. In the case of the resol studied here, although the formation of 2-HMP was favoured at the beginning of reaction, the addition of a second hydroxymethyl group to the free *ortho* position left did not start until 12 min of reaction. However, this 2,6-DHMP formation reached the maximum value only
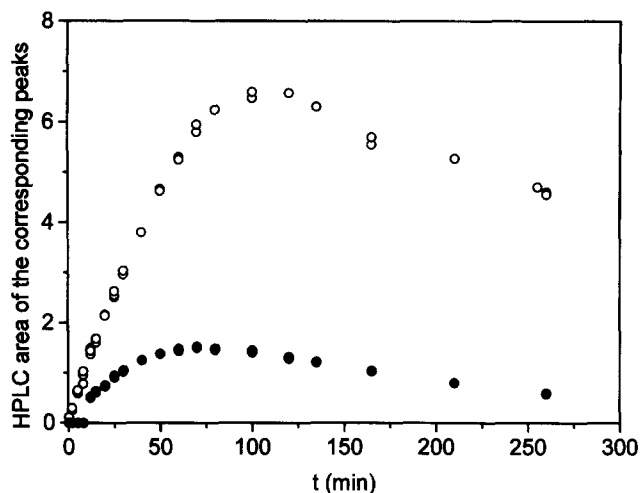
after 70 min of reaction, slightly later than for 2-HMP. Both species are formed at the same time and disappear together. On the other hand, the curve that represents the evolution of 2,4-DHMP and 2,4,6-THMP reaches its maximum after 100 min of reaction because of two factors. Firstly, the formation of the trisubstituted 2,4,6-THMP occurs as a result of the third addition reaction of formaldehyde onto a phenolic ring, which implies that the evolution curve keeps on growing longer than the rest. Secondly, due to the *ortho* directing characteristics of the catalyst used, the addition of formaldehyde onto *para* positions is not as favoured as that onto the *ortho* sites, and it occurs later than the former. Similar to the evolution of 4-HMP, which formed more slowly than 2-HMP, until 120 min, the addition onto the *para* site of the *ortho*-substituted phenols (2-HMP and 2,6-DHMP) was less favoured as long as there were *ortho* free sites left.

The formation of the major condensation products was analysed by HPLC following the identification procedure reported in our previous paper[5]. At the same time that addition products were being produced, condensation reactions started to appear. Initially, *para,para*-diphenylmethanes (*p,p*-DPM) were observed followed by almost simultaneous formation of *ortho,para*-diphenylmethanes (*o,p*-DPM). As in the case of the prepolymers studied before[5], the species formed in higher concentrations were: 2,6,6'-trihydroxymethyl-*p,p'*-dihydroxyDPM (1), 2,6-dihydroxymethyl-*p,p'*-dihydroxyDPM (2), 2,2',6,6'-tetrahydroxymethyl-*p,p'*-dihydroxyDPM (3), 2,6'-dihydroxymethyl-*p,p'*-dihydroxyDPM (4) and *ortho,para*-DPMs (5), which showed lower retention times than the *para,para*-DPMs. Again[5], as was corroborated by liquid ^{13}C n.m.r. studies carried out in deuterated dimethylsulphoxide (*Figure 7*) and deuterated acetone (*Figure 8*), no *ortho*, *ortho*-diphenylmethanes are formed. Once again, free *para* positions are preferred by the hydroxymethyl groups, either in *ortho* or *para*, to form methylene bridges.

De Breet *et al.*[9] confirmed that the structure of formaldehyde in formalin solution is not that of free formaldehyde, but rather of oligomers of oxymethylene and hemiformals. Thus, addition of these oxymethylene species onto phenolic rings can give rise to hemiformal species of the type, ϕ-CH$_2$O(CH$_2$O)$_x$CH$_2$OH, where ϕ represents the phenolic ring. Based on the predicted and observed chemical shifts reported by Werstler[10], the peaks

Figure 6 Evolution of 2,6-dihydroxymethylphenol (O) and 2,4-dihydroxymethylphenol + 2,4,6-trihydroxymethylphenol (●) during synthesis
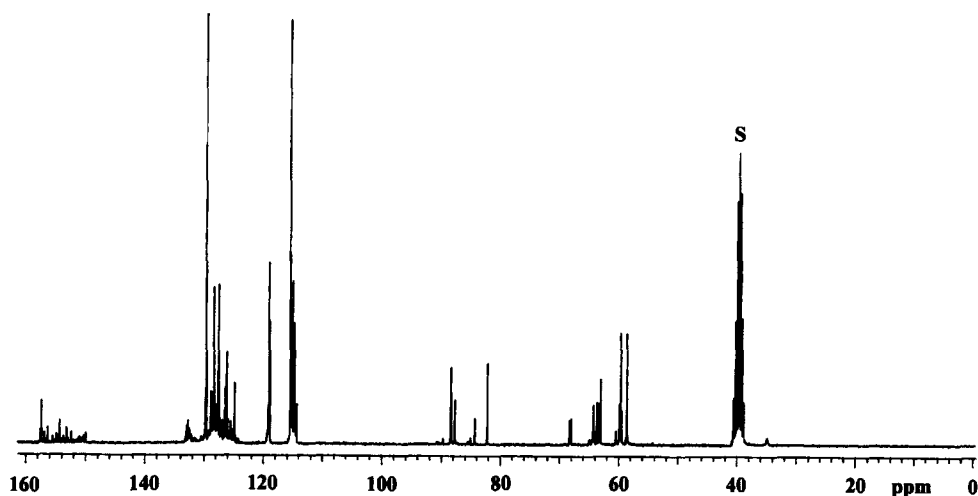

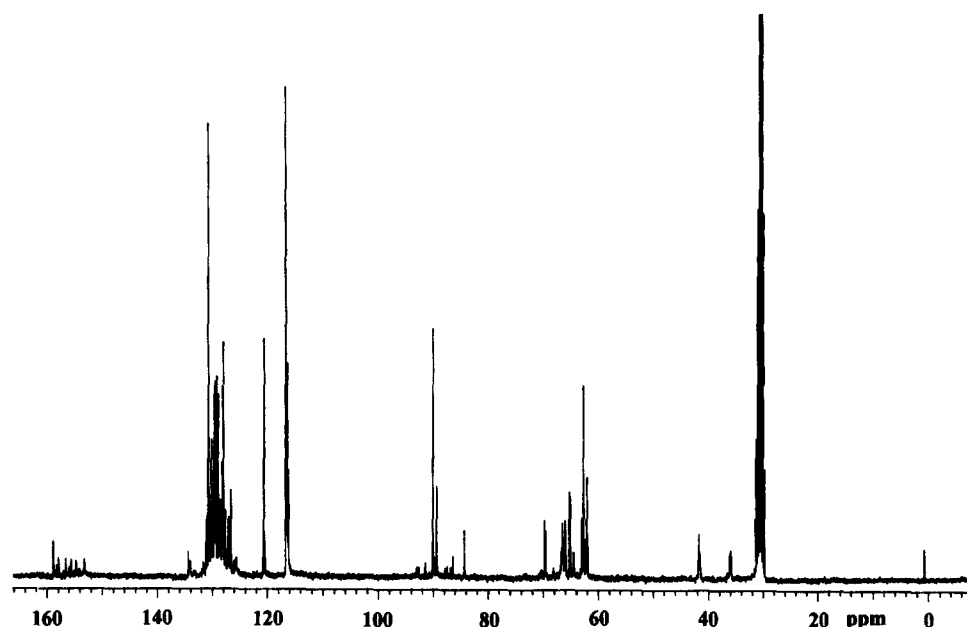**Figure 7** ^{13}C n.m.r. spectrum in deuterated dimethylsulphoxide (S)

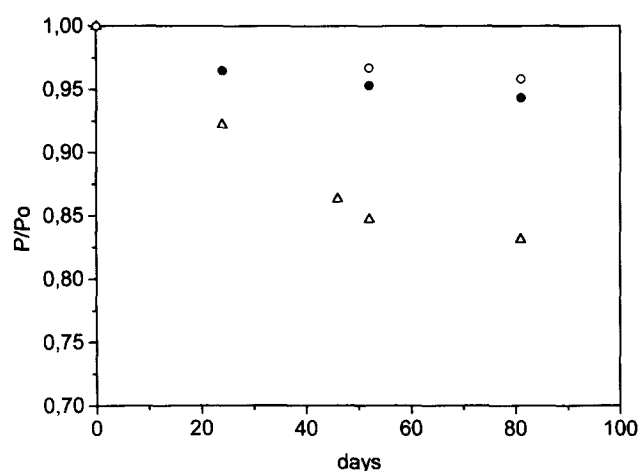**Figure 8** ^{13}C n.m.r. spectrum in deuterated acetone (S)

Figure 9   Evolution of free phenol by GC during storage at different temperatures: —20°C (○), 4°C (●), and room temperature (△)

of the 80–90-ppm region of liquid ^{13}C n.m.r. studies (shown in *Figures 8 and 9*) can be assigned to oxymethylene and hemiformal species, which have been already detected in other resols[10,11]. The hemiformal molecules are potential sources of free formaldehyde, because in the presence of a high amount of water the oxymethylene units bonded to the ring will cleave and react with other phenolic rings[10,12]. Therefore, hydroxymethyl groups for addition during further chemical processes, such as curing, will be available in solution.

The reactivity of phenolic resols during storage is a well-known problem. Prepolymers increase in viscosity, change in colour, and consume free formaldehyde and phenol. Due to all these transformations, storage of resols becomes a problematic task which needs further study. The evolution of free phenol by gas chromatography was carried out in samples stored at room temperature, in a fridge (4°C) and in a freezer (—20°C). *Figure 9* shows the free phenol concentration (*P*) with respect to that measured at the time of resol synthesis (*P₀*). As expected, the prepolymer stored

in the laboratory at room temperature shows the highest decrease in phenol concentration, followed by the sample stored in the fridge and afterwards, by the sample kept in the freezer. The consumption of the former is much more important (16% after 81 days) than the other two, which showed changes of the same range, 4–6%. Therefore, consumption of free phenol remains active but depends on the storage temperature. A low temperature around 0°C is advisable for resol storage conditions.

CONCLUSIONS

High-performance liquid chromatography was successfully used in the study of prepolymer formation kinetics of phenolic resol resin catalysed by barium hydroxide. The evolution of reactive species (phenol and formaldehyde), addition of formaldehyde onto phenol and further condensation reaction products were analysed in comparison to two resols catalysed by sodium hydroxide and triethylamine previously reported[5]. The presence of hydroxyl groups in the catalyst gave the prepolymer similar characteristics (reddish colour, time of condensation to reach the final prefixed point, condensation products) to that for the resol catalysed by NaOH. However, the catalysis with barium hydroxide favoured larger addition of formaldehyde onto *ortho* phenolic sites with respect to that for sodium hydroxide, but lower than for triethylamine. Therefore, the *ortho* directing properties of the catalysts studied increase in the order triethylamine > barium hydroxide > sodium hydroxide.

Condensation reaction products, followed by liquid chromatography and ^{13}C n.m.r. spectroscopy studies of the final prepolymer, demonstrated that the diphenylmethanes formed were bonded by methylene bridges. Most of them bonded *para,para* positions as well as some *ortho,para*, whereas no *ortho,ortho* bridges were detected. The hydroxymethyl group bonded to the *para* position was less affected by steric or chemical effects between the phenolic and benzylic hydroxyls with respect to the *ortho* substituted

groups, giving rise to a higher condensation of the *para* hydroxymethyl group.

The resin evolution during storage at three different temperatures was followed by gas chromatography. With regard to the evolution of the prepolymer increase with temperature, the sample stored at room temperature showed a larger transformation, whereas the evolution of the resins stored at 4 and −20°C was much lower. Temperatures below zero are advisable for storing phenolic resol resins.

ACKNOWLEDGEMENTS

REFERENCES

1. DeJong, J. I. and De Jonge, J., *Rec. Trav. Chim.*, 1953, **72**, 497.
2. Peer, H.G., *Rec. Trav. Chim.*, 1959, **78**, 851.
3. Knop, A. and Pilato, L. A., *Phenolic Resins.* Springer-Verlag, Berlin, 1985.
4. Grenier-Loustalot, M.-F., Larroque, S., Grande, D., Grenier, P. and Bedel, D., *Polymer*, 1996, **37**, 1363.
5. Astarloa-Aierbe, G., Echeverría, J. M., Egiburu, J. L., Ormaetxea, M. and Mondragon, I., *Polymer*, 1998, **39**, 3147.
6. Solomon, S. and Rudin, A., *J. Appl. Polym. Sci.*, 1990, **41**, 205.
7. Solomon, S. and Rudin, A., *J. Appl. Polym. Sci.*, 1990, **40**, 2135.
8. ISO 9397 Standard, 1987.
9. De Breet, A. J. J., Denkleman, W., Huysmans, G. B. and de Wit, J., *Angew. Makromol. Chem.*, 1977, **62**, 7.
10. Werstler, D. D., *Polymer*, 1986, **27**, 750.
11. Fisher, T. H., Chao, P., Upton, C. G. and Day, A. J., *Magn. Reson. Chem.*, 1991, **29**, 966.
12. Méchin, B., Hanton, D., Le Goff, J. and Tanneur, J. P., *Eur. Polym. J.*, 1984, **20**, 333.