

Influence of the initial formaldehyde to phenol molar ratio (F/P) on the formation of a phenolic resol resin catalyzed with amine

G. Astarloa Aierbe^a, J.M. Echeverría^b, M.D. Martín^a, A.M. Etxeberria^c, I. Mondragon^{a,*}

^aEscuela Universitaria de Ingeniería Técnica Industrial, Departamento Ingeniería Química y Medio Ambiente, Universidad País Vasco/Euskal Herriko Unibertsitatea, Av. Felipe IV, 1B, 20011 Donostia, Spain

^bBakelite Ibérica, Ctra. a Navarra. Epele, 39, 20120 Hernani, Spain

^cDepartamento Ciencia y Tecnología de Polímeros Universidad País Vasco/Euskal Herriko Unibertsitatea, Donostia, Spain

Received 16 September 1999; received in revised form 9 December 1999; accepted 7 January 2000

Abstract

The influence of the initial formaldehyde/phenol molar ratio (F/P) on the formation kinetics of five resol type phenolic resin prepolymers has been studied. Initial formaldehyde/phenol mixtures were fixed to pH = 8.0 by adding triethylamine as alkaline catalyst. The evolution of reactants and first formed addition products were followed by liquid chromatography (HPLC). ¹³C NMR spectroscopy was applied to final prepolymers. The necessary amount of catalyst to adjust the initial pH decreased with F/P, influencing the rates of consumption and formation of the species. Final formaldehyde and phenol concentrations depend on the initial F/P ratio and on the added amount of triethylamine. The maximum concentrations of first formed addition products decreased with F/P whereas the maximum concentration reached by di- and trisubstituted phenols was independent of this ratio. Higher molecular weight compounds were formed by joining phenolic rings by methylene bridges at *para,para* and *ortho,para* positions. No *ortho,ortho* bonds were detected. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Resol formation; Triethylamine; Formaldehyde/phenol ratio (F/P)

1. Introduction

Phenolic resins are known as the oldest thermosetting polymers and still have many industrial applications in sectors such as automotion, computing, aeronautical, and building [1,2]. Final structural and mechanical properties of the phenolic resins depend on many factors involved in the synthesis of the prepolymer: temperature and time of condensation, pH, nature and amount of the catalyst, and initial formaldehyde to phenol molar ratio (F/P). Many authors [3–7] have studied the influence of these parameters using several analytical techniques.

The initial F/P molar ratio is one of the factors that influences most the formation of phenolic resol resins. In the past, many authors have reported the influence of the initial formaldehyde to phenol molar ratio (F/P) for resins catalyzed with alkaline catalysts, such as sodium hydroxide and barium hydroxide [5,7,11–13]. Few studies can be found in the literature focused on the influence of F/P in resols catalyzed with triethylamine [1,14]. In these studies

each author used different synthesis parameters, such as time and temperature of condensation, amount of catalyst.

Following the systematic study of the influence of synthesis parameters on the formation of phenolic resol resins [8–10], we analyzed the influence of the initial formaldehyde to phenol molar ratio (F/P) on the prepolymer formation.

In this paper, we study the kinetics of five resols with varying initial formaldehyde to phenol molar ratio (F/P) catalyzed with triethylamine. The evolution of the first formed products during condensation at 80°C has been followed by high performance liquid chromatography (HPLC). The final prepolymers have been analyzed by carbon nuclear magnetic spectroscopy (¹³C NMR).

2. Experimental

2.1. Synthesis of resols

Phenol (>99%) and triethylamine (99%) were commercial products used without further purification. Formaldehyde (37% aqueous solution) was prepared from a 50% commercial solution adding distilled water. The pH of the

* Corresponding author.

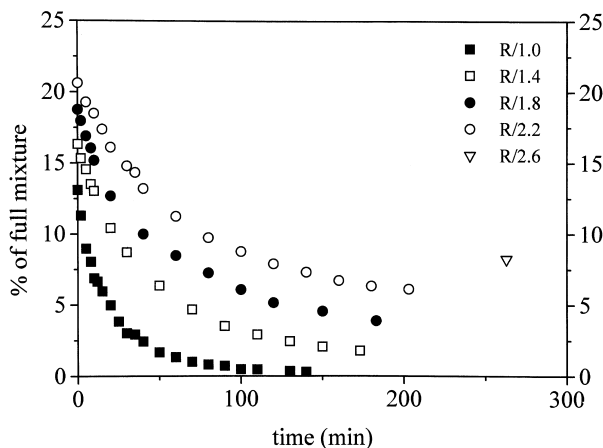


Fig. 1. Disappearance of free formaldehyde during synthesis of resols.

solution was then adjusted to 7.0 with sodium hydroxide (1 M).

Prepolymers were synthesized in Bakelite Ibérica factory by mixing phenol and formaldehyde aqueous solution in a three necked flask equipped with a thermometer, stirrer, and refrigeration column. The pH was then adjusted to 8.0 with triethylamine. The mixture (25–30°C) was heated to 80°C (heating rate: 2.5–3.5°C/min) and stirred during reaction. Samples were taken during synthesis. Zero time was defined as time to the mixture reached the condensation temperature (80°C). The reaction was stopped putting the reactor in a cold water bath, when the resin showed a 1/1 g/g dilutability in water. Samples were kept at 4°C.

Prepolymers are defined as R/1.0, R/1.4, R/1.8, R/2.2, and R/2.6, where 1.0, 1.4, 1.8, 2.2, and 2.6 represents the F/P molar ratio used in the synthesis.

2.2. High performance liquid chromatography

Analyses were conducted with a Waters 510 chromatograph equipped with a Waters 486 UV detector, set at 280 nm. The column was Spherisorb ODS-2 (5 μ m). In order to decrease the viscosity of the solvents, the column

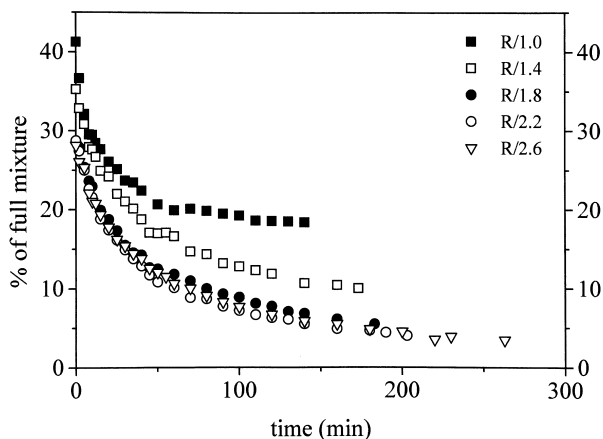


Fig. 2. Disappearance of free phenol during synthesis of resols.

was thermostated to 35°C. A mobile phase of methanol/water was used with an elution gradient of 20 to 80% of methanol in 180 min, and 80 to 100% in 5 min.

2.3. Carbon nuclear magnetic resonance spectroscopy (^{13}C NMR)

High resolution ^{13}C NMR spectra in liquids were recorded with a Varian VXR-300 spectrometer. The following conditions were used: sweep width = 16 501.7 Hz, pulse width = 14.8 μ s (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 { $\delta(\text{DMSO} - d_6) = 39.5$ ppm, $\delta(\text{acetone} - d_6) = 29.8$ and 205.7 ppm}.

3. Results and discussion

In this study the range of F/P ratio for resol fabrication was covered by analyzing five resols synthesized with five initial formaldehyde to phenol molar ratios (F/P = 1 – 2.6) and catalyzed with triethylamine. Every initial formaldehyde/phenol mixture was adjusted to pH = 8.0 with a different amount of catalyst, depending on the initial pH of the mixture. The added amount of catalyst decreased with F/P due to the influence of the pH of the formaldehyde solution (pH = 7.0) on the initial pH of the mixture. As a result of the varying added amount of catalyst the time needed to reach the final 1/1 g/g dilutability in water increased with F/P.

Fig. 1 shows the disappearance of free formaldehyde during synthesis measured by chemical assay [8] (for R/2.6 resol only the final value is shown). Final formaldehyde concentrations increase with the initial amount of formaldehyde used. R/2.6 shows the higher final concentration whereas free formaldehyde was completely consumed for R/1.0 after 140 min of reaction. These results are similar to those of Grenier-Loustalot et al. [12] for resols catalyzed with sodium hydroxide and with initial varying F/P ratios. On the contrary, the influence of the added amount of catalyst is observed in the rate of consumption and final value of free formaldehyde. The higher the amount of triethylamine needed (lower F/P) the shorter condensation time and the higher rate of formaldehyde disappearance was. The influence of the catalyst amount on the condensation evolution will be analyzed in a nextcoming work for a resol with a F/P ratio fixed.

The phenol consumption was followed by liquid chromatography (Fig. 2). The disappearance curves can be classified into three groups as a function of the followed evolution. For the first one, the R/1.0 resol shows a curve that can be divided in two different parts: the first 60 min, time at which the concentration of free formaldehyde in solution became almost zero (Fig. 1), represent the major

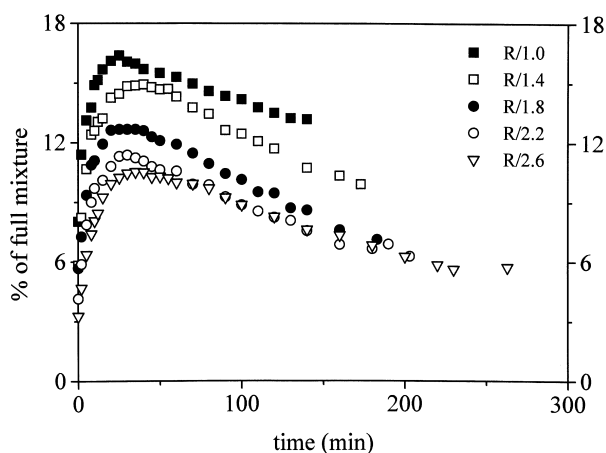


Fig. 3. Evolution of 2-hydroxymethylphenol (2-HMP) during synthesis of resols.

period of disappearance of free phenol, and hereafter a second time period in which no consumption of phenol is detected. The second group (R/1.8, R/2.2, and R/2.6 resols), showed similar and continuous phenol concentration decrease indicating that a limiting formaldehyde concentration exists under these F/P ratios. Finally, the R/1.4 resol shows an intermediate behavior. From these three consumption paths it can be concluded that an initial maximum formaldehyde to phenol ratio exists around 1.8, whereas $F/P = 1.0$ is below the minimum limiting value. Similar phenol evolution for resols with $F/P = 1.0$, and 1.3 and 1.5, the latter two approaching a residual concentration, were reported elsewhere [12].

As a result of the consumption of reactants, addition products were formed. The evolution of 2-hydroxymethylphenol (2-HMP) is shown in Fig. 3. Again, the influence of the initial formaldehyde concentration is observed in the maximum and final values. The maximum concentrations decrease with F/P ratio. The R/1.0 resol shows the higher maximum and final concentrations as well as the lowest

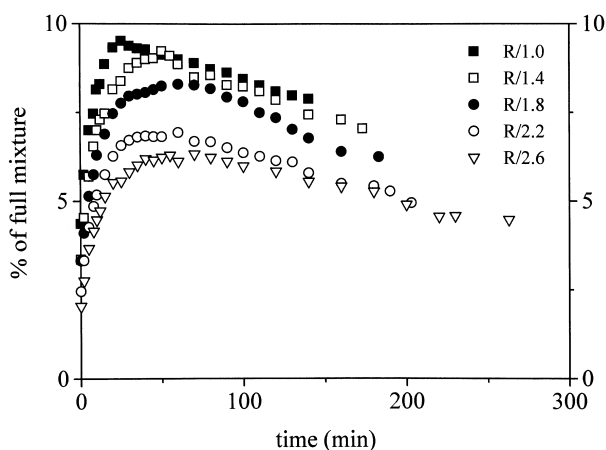


Fig. 4. Evolution of 4-hydroxymethylphenol (4-HMP) during synthesis of resols.

consumption from maximum to final concentration. The low amount of formaldehyde present in solution gave rise to low consumption of 2-HMP once the maximum was reached. In the case of resols with $F/P > 2.0$, the maximum concentrations were similar and the disappearance beyond this point was of the same magnitude as well. For the R/1.8 and R/1.4 resols, the 2-HMP evolution appears to be between the curves of resols with $F/P = 1.0$ and $F/P > 2.0$, the latter showing a higher maximum concentration of 2-HMP. Therefore, a limiting F/P value for the maximum formation of 2-HMP must exist in the vicinity of $F/P = 1.8$ – 2.0 .

Fig. 4 shows the evolution of 4-hydroxymethylphenol (4-HMP). The magnitude of reached maximum concentration is lower in comparison to that of 2-HMP because only one *para* site is present in each phenolic ring and also as a consequence of its reactivity. The regions for maximum and final concentrations showed similar aspects respect to the ones discussed for 2-HMP, except for R/1.8 whose 4-HMP evolution curve differs from those corresponding to resols with $F/P > 2.0$ more than in the case of 2-HMP. The concentration of formaldehyde present in solution for R/1.8 seems to be in the equilibrium for the first addition products (2-HMP and 4-HMP) formation and their slower consumption respect to those of R/2.2 and R/2.6.

As inferred from Figs. 3 and 4, the time needed to reach the maximum concentration of 2-HMP and 4-HMP increases with F/P from R/1.0 to R/1.4 and R/1.8 due to the lower amount of triethylamine used for the latter ratios. However, R/2.2 and R/2.6 (lower amount of catalyst) resols reached their respective maxima faster than R/1.4 and R/1.8 ones did because the excess of free formaldehyde present in solution was being added onto the free phenolic sites left, thus giving rise to further addition species.

First formed addition products are involved in second and third addition of formaldehyde onto free *ortho* and *para* phenolic sites giving rise to the formation of 2,4-dihydroxymethylphenol (2,4-DHMP), 2,6-dihydroxymethylphenol (2,6-DHMP), and 2,4,6-trihydroxymethylphenol (2,4,6-THMP). Fig. 5 shows the evolution of 2,6-DHMP. The maximum concentration decreases with F/P due to the higher presence of free formaldehyde searching for a reactive phenolic site. The higher reactivity of *para* sites respect to *ortho* positions makes the consumption of 2,6-DHMP be fast. As it can be observed in the scale of the HPLC area represented, the formation of 2,6-DHMP is less favoured than formation of 2,4-DHMP + 2,4,6-THMP (Fig. 6) due to steric and chemical restrictions between the involved hydroxyl groups. R/1.0 and R/1.4 resols reach the highest concentration maximum and final values followed by R/1.8 and R/2.2. As inferred from Fig. 5, increasing F/P ratio, the higher concentration of free formaldehyde present in solution makes easier the addition of a third formaldehyde molecule onto the remaining free *para* site, giving rise to the consumption of 2,6-DHMP. Competing with this third addition, condensation reactions to form two phenolic ring

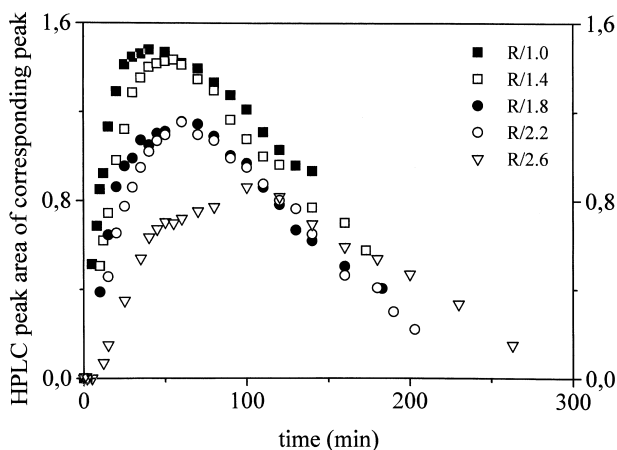


Fig. 5. Evolution of 2,6-dihydroxymethylphenol (2,6-DHMP) during synthesis of resols.

compounds are also present. R/2.6 resol shows the lower maximum concentration due to available free formaldehyde that is being added continuously even at high condensation times.

Fig. 6 shows the evolution of the HPLC area of the peak corresponding to 2,4-DHMP and 2,4,6-THMP. R/1.0 resol differs most from the other curves due to the low free formaldehyde concentration available for second and third addition reactions. Opposite to first formed 2-HMP and 4-HMP, the maximum and final values for this resol are lower as a result of the lack of formaldehyde and condensation reactions that follow the formation of addition species. The maximum concentration at around 50 min coincides with the formaldehyde concentration curve levelling off at 2% (Fig. 1), indicating there was not many free formaldehyde left for further formation of 2,4-DHMP and 2,4,6-THMP. The rest of resols show similar curves in relation to maximum and final values. Anyway, the reached maximum concentrations are all in a narrow range which means that there is a maximum limiting concentration for the

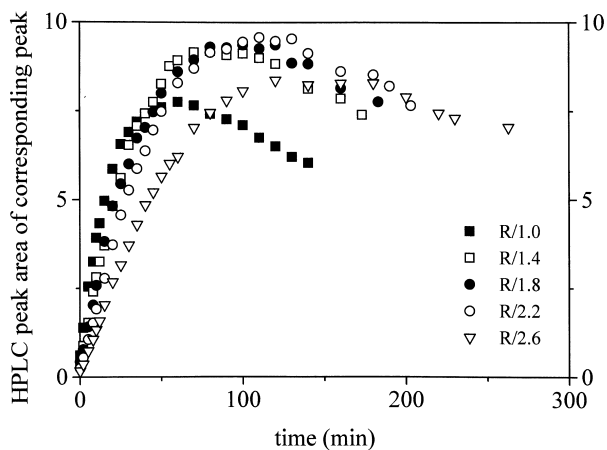


Fig. 6. Evolution of 2,4-dihydroxymethylphenol (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) during synthesis of resols.

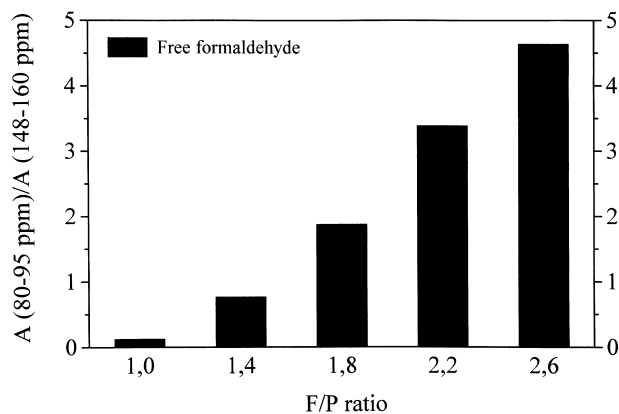


Fig. 7. Formaldehyde (80–95 ppm) in prepolymers analyzed in acetone- d_6 .

formation of these compounds before they start to condense giving rise to higher molecular weight species.

^{13}C NMR liquid spectroscopy of the prepolymers dissolved in $\text{dms}\text{-}d_6$ and acetone- d_6 were analyzed. Peak assignments were carried out on the basis of published data [11,13,15–19]. In order to make comparable the integration results, every peak area or group of peak areas were divided by the area corresponding to the *ipso* region area, i.e. the signals of the C atom bearing the oxygen of the hydroxyl group of phenolic rings (148–160 ppm).

Fig. 7 shows the peak areas of the 80–95 ppm region attributable to residual formaldehyde and its varying molecular weight polymers. The residual formaldehyde left in the prepolymer increases with F/P, corroborating the HPLC results for which residual free formaldehyde increases with F/P (Fig. 1). Holopainen et al. [13] found similar results for resols prepared with $\text{F/P} = 1.90 - 2.30$ and catalyzed with sodium hydroxide.

The free active *ortho* and *para* sites left on the phenolic rings can be also analyzed by ^{13}C NMR spectroscopy. The variation of phenolic *ortho* and *para* unreacted sites for the prepolymers in deuterated acetone can be observed in Fig. 8. As it was previously published in the literature [13,20],

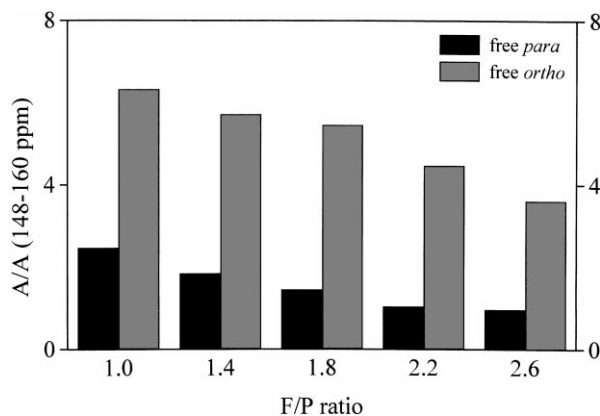


Fig. 8. Free *ortho* and *para* positions left unreacted in prepolymers analyzed in acetone- d_6 .

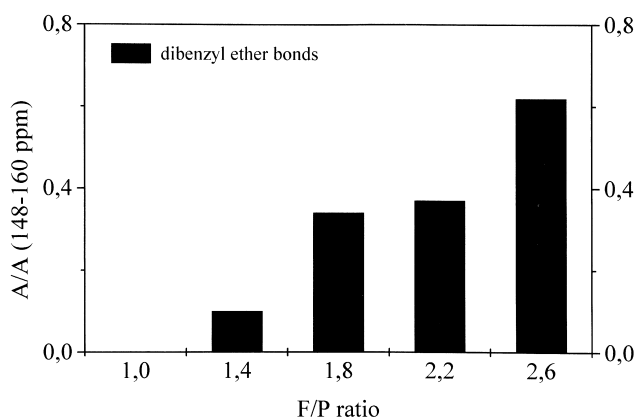


Fig. 9. Dibenzyl ether bonds in prepolymers analyzed in $\text{dms}\text{-d}_6$.

unreacted positions decrease with F/P as a consequence of the higher possibility of hydroxymethyl addition to occur and favoured conditions of these groups to condense giving rise to methylene and ether bonds.

Formation of phenolic rings connecting bonds depends on the initial F/P ratio. Fig. 9 shows the dibenzyl ether bridges formed on the prepolymers analyzed in $\text{dms}\text{-d}_6$. For R/1.0 there no ether bonds were detected, whereas beyond F/P = 1.4, their presence increases with F/P ratio, corroborating the results published elsewhere [5,14,15]. As discussed above, the less free active sites left on the phenolic rings were the higher amount of hydroxymethyl groups were available for condensation reactions. Fig. 10 shows the relative amount of *para,para* and *ortho,para* methylene bonds. No *ortho,ortho* bridges were detected. As in the case of ether bonds, methylene bridges increase with F/P ratio except for R/2.6.

4. Conclusions

The influence of the F/P molar ratio in the resol formation was analyzed by liquid chromatography and nuclear magnetic resonance spectroscopy. Five resols covering the

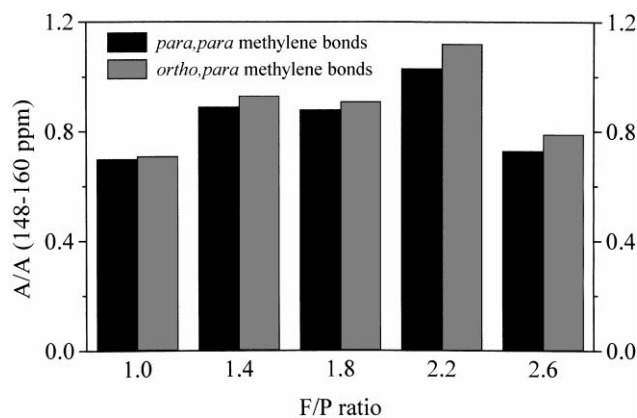


Fig. 10. *para,para* and *ortho,para* methylene bonds in prepolymers analyzed in acetone-d_6 .

F/P = 1.0–2.6 range and catalyzed with triethylamine were synthesized.

The necessary amount of catalyst to adjust the pH decreased with F/P ratio and influenced the rate of consumption of reactants as well as the formation of products and condensation times of prepolymers.

^{13}C NMR spectroscopy and HPLC measurements showed that the amount of free formaldehyde left in solution depends on the initial formaldehyde concentration: almost no formaldehyde is left for R/1.0, whereas R/2.6 shows a concentration higher than 8%. The phenol disappearance is also influenced by the initial F/P ratio. There were two limiting initial F/P values for phenol consumption: underneath F/P = 1.0, and due to the lack of formaldehyde, high amount of free phenol is left in the prepolymer, and beyond F/P = 2.0, almost total phenol consumption occurs and free formaldehyde is left in excess.

As a consequence of the variation in formaldehyde concentration and amount of catalyst the formation of monosubstituted species vary for all the prepolymers. Although resols with F/P > 1.8 needed less catalyst than R/1.0, R/1.4, and R/1.8, the former resols reached the maximum concentrations earlier due to the high amount of formaldehyde made the formation of these species and their consumption to happen simultaneously.

The maximum concentrations of di- and trisubstituted products were independent of F/P ratio, except for that corresponding to R/1.0 which was a little lower due to formaldehyde was consumed, thus it was under the low limiting F/P value for phenol to be consumed. Low formation of 2,6-DHMP was observed whereas the maximum concentrations of 2,4-DHMP and 2,4,6-THMP and further consumption in condensation reactions were of the same magnitude.

Phenolic rings bonding bridges (methylene and ether) increase with F/P ratio as a consequence of the higher concentration of present hydroxymethyl groups, which favors interactions between these groups and free phenolic sites. R/2.6 resol differs from the rest of prepolymers in free sites left hydroxymethyl groups and methylene and ether bonds. It seems that the low amount of catalyst added gave rise to a lower advance of polymerization respect to the other prepolymers.

Acknowledgements

One of the authors wishes to thank Ministerio de Educación y Ciencia for the grant IN92-D15376286 supplied for this project which it is being carried out with the collaboration of Bakelite Ibérica.

References

- [1] Knop A, Pilato LA. Phenolic resins. Berlin: Springer, 1985.
- [2] Böttcher A, Pilato LA. SAMPE J 1997;33:35.

- [3] Grenier-Loustalot M-F, Larroque S, Grande D, Grenier P, Bedel D. *Polymer* 1997;37:1363.
- [4] Grenier-Loustalot M-F, Larroque S, Grenier P, Bedel D. *Polymer* 1996;37:939.
- [5] So S, Rudin A. *J Appl Polym Sci* 1990;41:205.
- [6] Fisher TH, Chao P, Upton CG, Day AJ. *Magn Reson Chem* 1991;29:966.
- [7] Grenier-Loustalot M-F, Larroque S, Grenier P. *Polymer* 1996;37:639.
- [8] Astarloa-Aierbe G, Echeverría JM, Egiburu JL, Ormaetxea M, Mondragon I. *Polymer* 1998;39:3147.
- [9] Astarloa-Aierbe G, Echeverría JM, Martin MD, Mondragon I. *Polymer* 1998;39:3467.
- [10] Astarloa-Aierbe G, Echeverría JM, Mondragon I. *Polymer* 1999;40:5873.
- [11] Méchin B, Hanton D, Le Goff J, Tanneur JP. *Eur Polym J* 1986;22:115.
- [12] Grenier-Loustalot M-F, Larroque S, Grenier P, Bedel D. *Polymer* 1994;35:3046.
- [13] Holopainen T, Alvila L, Rainio J, Pakkanen TT. *J Appl Polym Sci* 1997;66:1183.
- [14] King PW, Mitchell RH, Westwood AR. *J Appl Polym Sci* 1974;18:1117.
- [15] Méchin B, Hanton D, Le Goff J, Tanneur JP. *Eur Polym J* 1984;20:333.
- [16] Werstler DD. *Polymer* 1986;27:750.
- [17] Pethrick RA, Thomson B. *Br Polym J* 1986;18:171.
- [18] Fisher TH, Chao P, Upton CG, Day AJ. *Magn Reson Chem* 1995;33:717.
- [19] Luukko P, Alvila L, Holopainen T, Rainio J, Pakkanen TT. *J Appl Polym Sci* 1998;69:1805.
- [20] Vazquez A. *Espumas fenólicas*. Universidad Nacional de Mar del Plata, 1986.