ELSEVIER

Polymer 40 (1999) 5873–5878

polymer

# Kinetics of phenolic resol resin formation by HPLC. III: Zinc acetate

G. Astarloa-Aierbe[a], J.M. Echeverría[b], I. Mondragon[a,*]

[a]*Escuela Univ. Ingeniería Técnica Industrial, Dpto. Ingeniería Química y Medio Ambiente, Universidad País Vasco/Euskal Herriko Unibertsitatea, Av. Felipe IV, 1B. 20011 Donostia, Spain*

[b]*Bakelite Ibérica. Ctra. a Navarra. Epele, 39. 20120 Hernani, Spain*

Received 18 November 1997; received in revised form 17 November 1998; accepted 17 November 1998

**Abstract**

Zinc acetate was used as catalyst in the synthesis of a phenolic resol resin. The evolution of the addition and condensation reactions was quantitatively followed by high performance liquid chromatography. The addition of formaldehyde to phenol was almost exclusively *ortho* directed. Very low advancement in polymerization was observed, and diaryl compounds were only slightly formed. $^{13}C$ NMR studies did not show *para, para* methylene bridges as a result of the poor addition of hydroxymethyl groups onto the *para* phenolic sites. The change in concentration of free phenol as a parameter of the evolution of the resin during storage was followed by gas chromatography. Disappearance of free phenol did not stop at any of the analysed storing temperatures (room temperature, 4°C, and −20°C). © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Phenolic resol resin; Kinetics; Catalyst

## 1. Introduction

The final properties of phenolic resins catalysed under basic conditions depend on many factors as, synthesis temperature and time, formaldehyde (F) to phenol (P) molar ratio, and catalyst type and amount [1]. The latter influences mechanistic and kinetically the addition of formaldehyde onto phenolic rings, and consequently condensation reactions between the formed products.

In order to study the influence of different catalyst types on the kinetics of prepolymer formation, this report presents the results obtained with zinc acetate as catalyst of phenolic resol resins. This work is the last of a series of studies reported elsewhere [2,3] carried out by analyzing, by liquid chromatography and carbon nuclear magnetic resonance spectroscopy, the kinetics of resols catalysed with four types of catalysts: sodium hydroxide, triethylamine, barium hydroxide and zinc acetate.

## 2. Experimental

### 2.1. Synthesis of resol

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

Prepolymer was synthesized in Bakelite-Ibérica factory by mixing formaldehyde and phenol in a molar ratio of F/P = 1.8. Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as catalyst was used (11.7 g, 0.01 mol/mol of phenol). The mixture was heated to 80°C (heating rate: 2.5–3.5°C/min) and stirred during reaction. Samples were taken throughout condensation reaction. Zero time was defined as time to the mixture reached 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°C−23°C) in order to study by Gas Chromatography the evolution of free phenol as a parameter of stability of these resins.

### 2.2. 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 Spherisorb ODS-2 (25 × 4.6 cm), and 5 μm particle size. 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% to 80% of methanol in 180 min, and 80% to 100% in 5 min. Flow rate: 1 ml/min.

* Corresponding author. Tel.: +34 43 455022; fax: +34 43 471097.
*E-mail address:* iapmoegi@sp.ehu.es (I. Mondragon)


PII: S0032-3861(98)00816-7

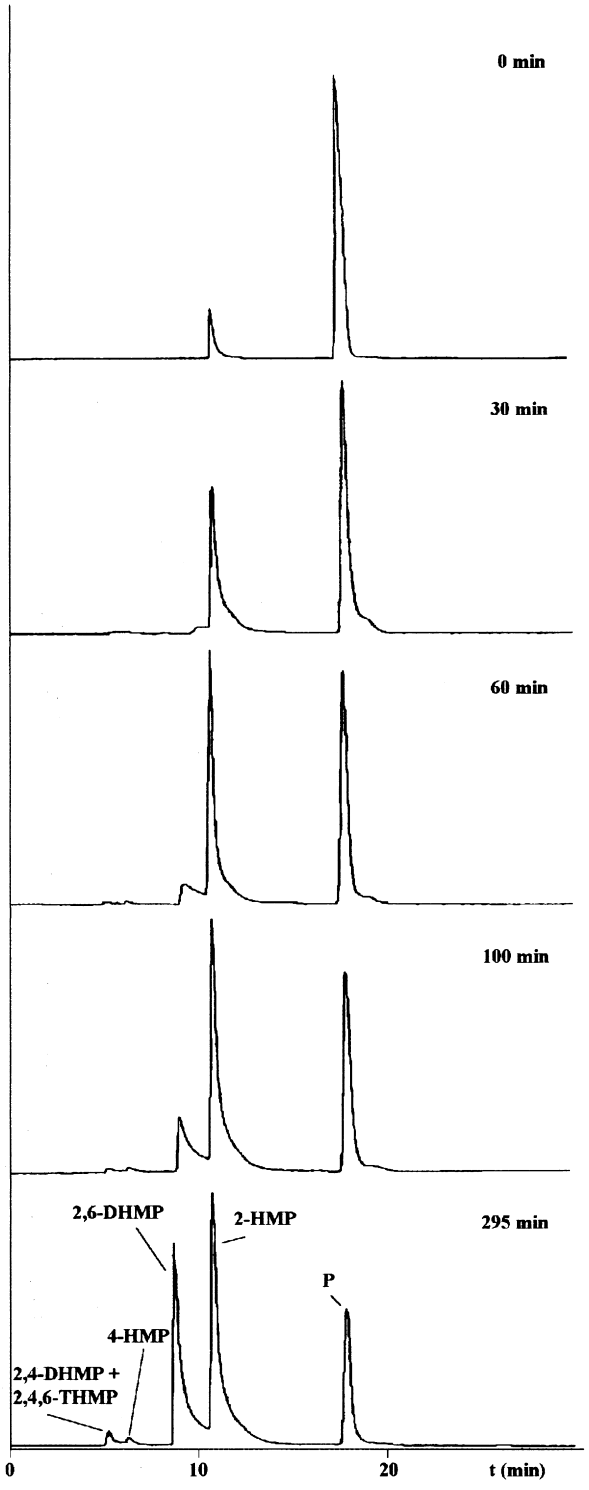


Fig. 1. HPLC chromatograms at different synthesis times.

### 2.3. Gas chromatography (GC)

Samples were analyzed in a HP5890 Series II chromatograph connected to a HP3396A Integrator equipped with flame ionization detector (FID) using helium as carrier gas (flow rate: 130 ml/min and head pressure: 20 psi.). A 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.

### 2.4. Carbon nuclear magnetic resonance spectroscopy ($^{13}C$ NMR)

High resolution $^{13}C$ NMR spectra in liquids were recorded with a Varian VXR-300 spectrophotometer. The following conditions were used: sweep width = 16501.7 Hz, pulse width = 14.8 μs (90°), pulse delay = 1.0 s, acquisition time = 0.908, and data points = 29952.

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 {$\delta$(DMSO-$d_6$) = 39.5 ppm, $\delta$(acetone-$d_6$) = 29.8 and 205.7 ppm}.

## 3. Results and discussion

The influence of three types of catalyst on the addition and condensation reactions of resol formation have been reported earlier [2,3]. The rate of addition products formation and disappearance was controlled by the catalyst type used. Sodium hydroxide and barium hydroxide showed similar evolution through the synthesis, respect to orientation of addition groups and rates of reaction, whereas triethylamine favoured addition onto *ortho* positions of the phenolic ring and the prefixed final point was reached much faster than for the other two catalysts. However, the final condensation products observed in all the three resols by HPLC and $^{13}C$ NMR spectroscopy were similar, no qualitative differences were detected.

In order to cover a wider field of catalyst types studied by many authors [2–5], a resol catalysed with zinc acetate under the same controlled temperature, formaldehyde to phenol ratio (F/P) and final point as in the previous experiments [2,3] was synthesized and its kinetics followed by HPLC. In this case, because of the acidic condition of the catalyst utilized the initial mixture was not adjusted to pH = 8.0. Instead, a similar amount of catalyst per mol of phenol (cat/P = 0.01) respect to the previous resols cooked was added. The mixture was heated up to 80°C and taken at this temperature until it reached a 1/1 g/g dilutability in water.

The presence of hydroxyl groups in the catalysts involved the formation of phenolate ions as a first step in the addition of methylol groups onto phenol. In the case that these ions were formed, the prepolymer took a reddish characteristic colour, whereas in the resin catalysed with the amine, as well as in the case of the salt studied in this report, the colour of the resols were lighter and yellowish in the case of the triethylamine.

The final prepolymer needed 295 min to reach the

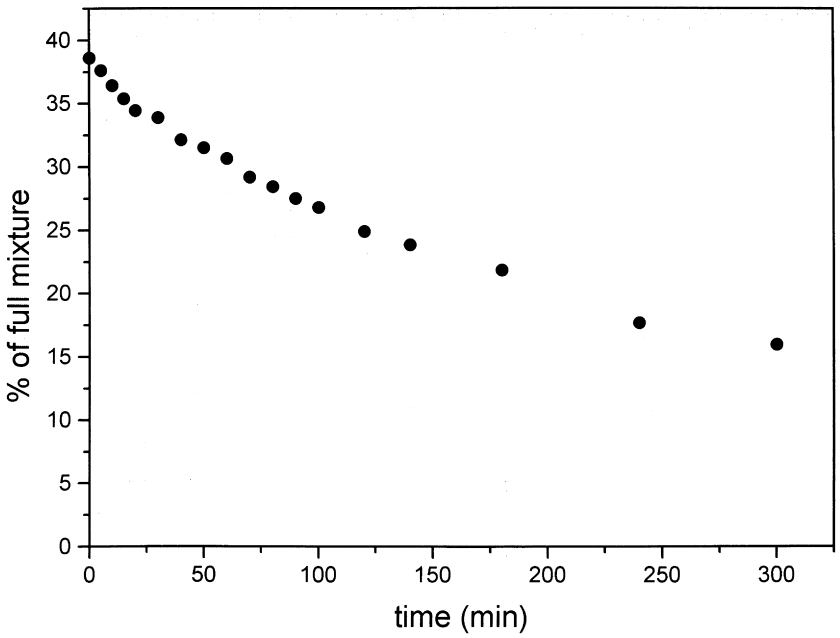


Fig. 2. Disappearance of phenol during synthesis.

prefixed final point and showed very low viscosity and lighter colour than for the other resols synthesized along the investigation of these products. Besides, a strong formaldehyde smell was detectable as a first indication of the low addition reactions and evolution performed by the reactives.

The evolution of free phenol and addition products formed were quantitatively followed by liquid chromatography (HPLC). Fig. 1 shows chromatograms of samples taken at different times during synthesis. The disappearance of formaldehyde in the previous resols [2,3] was followed by chemical assay but in the case of the prepolymer studied in this report, this was not possible owing to the high amount of free formaldehyde left in the mixture was out of range of the standard. Only the final value was achieved (14%). Even at the final point the amount of formaldehyde was high. The consumption of formaldehyde was lower respect to the prepolymers catalysed with other catalysts.

The evolution during synthesis of free phenol (Fig. 2) suggests a low degree of polymerization was reached. The rate of decrease in concentration was very similar during the

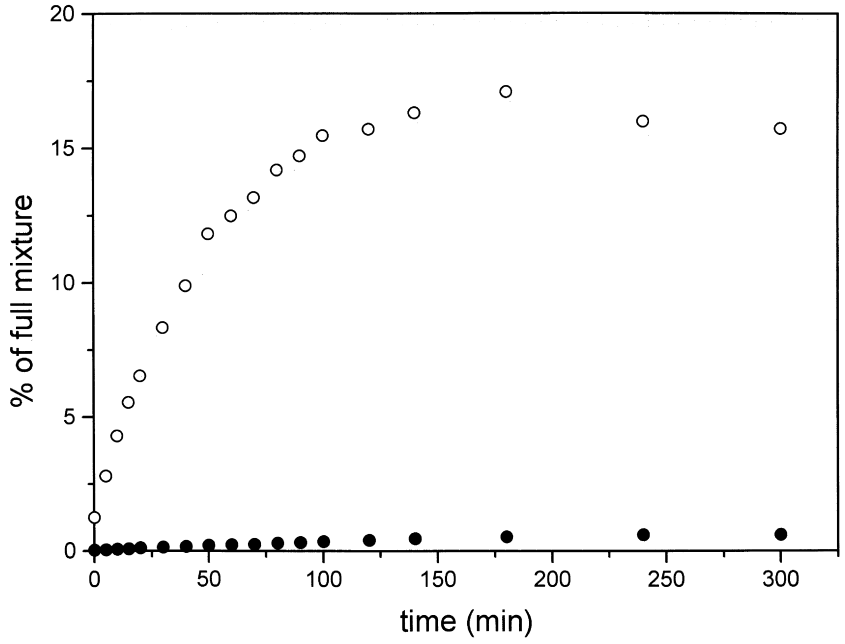


Fig. 3. Evolution of 2-hydroxymethyphenol (○) and 4-hydroxymethylphenol (●) during synthesis.

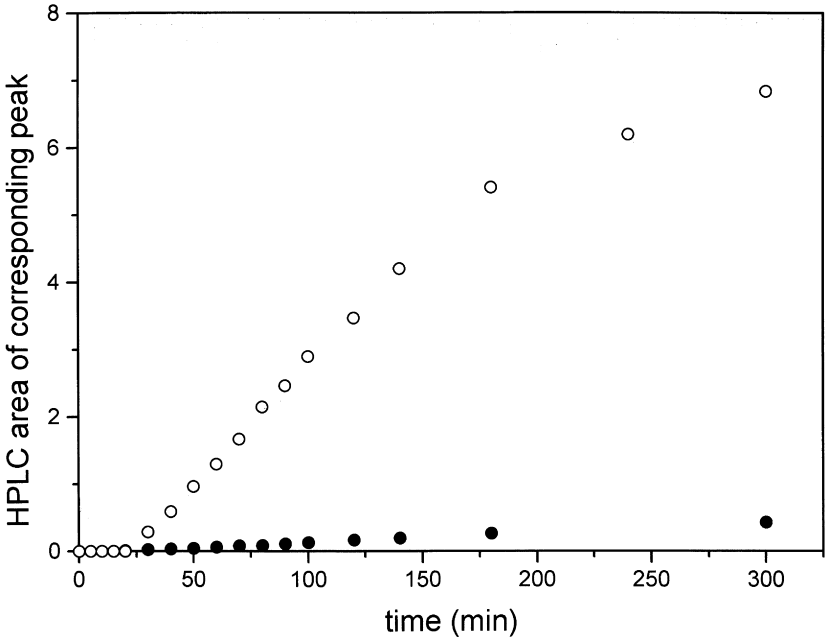


Fig. 4. Evolution (HPLC area) of 2,6-hydroxymethylphenol (○) and 2,4-hydroxymethylphenol + 2,4,6-hydroxymethylphenol (●) during synthesis.

whole process, except at the first 25 min when it was slightly higher, and for the last 35 min of reaction, when the disappearance of free phenol almost stopped. The high final value (15.7%) as well as the free formaldehyde left in the final mixture suggests that the degree of polymerization of the prepolymer was low and condensation products might have not been formed.

The evolution of 2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP) are depicted in Fig. 3. Before the cooking temperature was reached the only product formed was 2-HMP (1.2%) and very little of 4-HMP (0.04%). In comparison to the other three catalyst used earlier, zinc acetate shows worse catalytic properties, making the addition of formaldehyde onto phenolic species very slow. The *ortho* directing properties of zinc acetate as catalyst are demonstrated in these two evolution curves. 2-HMP was formed until 17.3% was reached in 180 min, whereas the appearance of 4-HMP did not exceed a 0.62% concentration (240 min) and afterwards started to decrease. The rate of 4-HMP formation was much slower with respect to that of 2-HMP, the last being almost the only product formed during the first 20 min of reaction, as will be discussed later with the analysis of disubstituted and trisubstituted phenols. The *ortho* orientation of the hydroxymethyl groups is almost exclusive, the addition onto this position is preferred respect to that onto *para* site of the phenolic ring. In the previous articles [2,3] the 2-HMP/4-HMP ratio (O/P) was presented as a valid parameter of the addition orientation properties of the catalyst. In the case of the resol catalysed with zinc acetate it is not possible to determine the O/P ratio because of the exclusive formation of 2-HMP.

The analysis of the evolution curves of 2,4-dihydroxymethylphenol (2,4-DHMP), 2,6-dihydroxymethylphenol (2,6-DHMP) and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) shown in Fig. 4 corroborates the *ortho* directing properties of the catalyst. Under the used chromatographic conditions 2,4-DHMP and 2,4,6-THMP did not separate, and so their evolution is shown by only one curve. The formation of these two species was almost inhibited with respect to that for 2,6-DHMP, as it is observed in the large difference between both curves. The formation of 2,4-DHMP can happen by addition of an hydroxymethyl group onto one of the free *ortho* positions of 4-HMP or addition onto the free *para* site of 2-HMP. The very low formation of 4-HMP makes the first route to give poor results. However, the *ortho* directing properties of the catalyst favoured the addition of a second hydroxymethyl group onto the *ortho* free site left in 2-HMP and disadvantaged the second way of 2,4-DHMP formation. As a result of these difficulties, the formation of 2,4,6-THMP was also problematic. Owing to the poor catalytic effect of the zinc acetate employed, the beginning of the formation of disubstituted and trisubstituted species were delayed for 15 and 25 min of reaction for 2,4,6-THMP + 2,4-DHMP and 2,6-DHMP, respectively. At the prefixed final point both curves showed an upward orientation; species were still being formed, although at a slower rate than at shorter times, specially for 2,6-DHMP.

Among the addition products studied, only the concentration curves for 2-HMP and 4-HMP turned downwards, started to disappear. Reaction was stopped when disubstituted and trisubstituted phenols were still being formed, which is a preliminary step for condensation reactions to happen. As a result of the slow addition of formaldehyde onto phenolic rings, condensation reactions were delayed

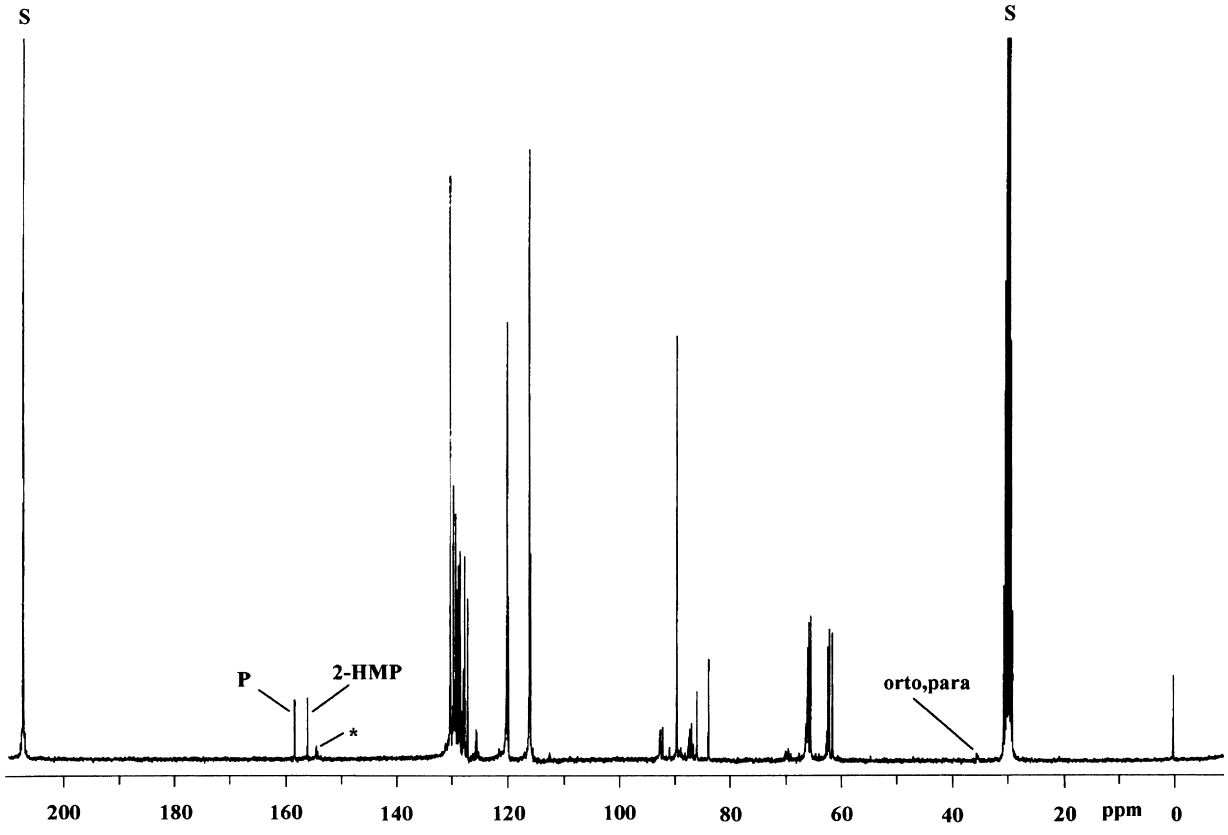


Fig. 5. $^{13}C$ NMR spectrum in deuterated acetone.

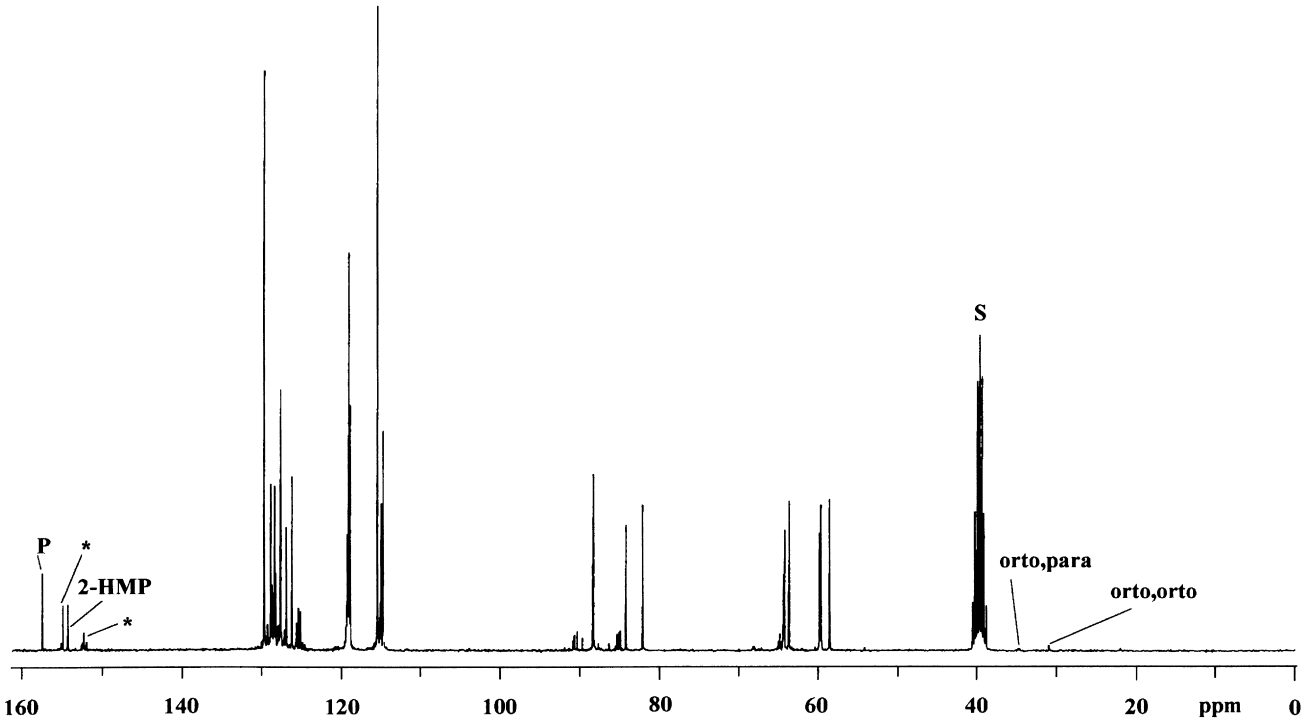


Fig. 6. $^{13}C$ NMR spectrum in deuterated dimethylsulphoxide (S).

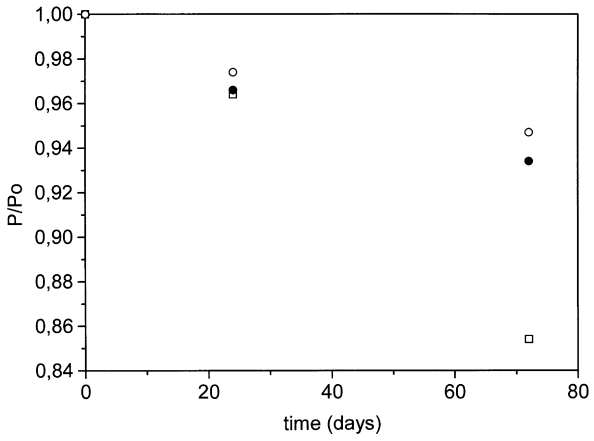


Fig. 7. Evolution of free phenol by gas chromatography during storage at different temperatures. −20°C (○), 4°C (●) and room temperature (□).

and condensation products were very slightly detected at the final point.

For the final products, liquid $^{13}C$ NMR spectroscopy analysis were carried out in two deuterated solvents in order to observe the methylene bridge region (40–30 ppm). In consonance with the stated above, several facts can be observed in Figs. 5 and 6. Firstly, the *ipso* region (160–150 ppm) showed few signals, being the most important the one corresponding to phenol as well as 2-HMP and *ortho*, *ortho* and *ortho*, *para* methylene bridge bonded phenolic rings (* in Figs. 5 and 6). The absence of signals of highly reacted species corroborates the results obtained by HPLC. Secondly, as it was expected, almost undetectable signals of methylene bridges were present in the 40–30 ppm region. The spectrum of the sample dissolved in deuterated acetone (Fig. 5) enables to see there were not *para*, *para* methylene bonds. However, the presence of *ortho*, *ortho* methylene bonds is detected in the sample dissolved in deuterated dimethylsulphoxide (Fig. 6). Both NMR spectra showed also the presence of *ortho*, *para* bonds. *Ortho* hydroxymethyl groups were involved in condensation reactions because of the marked *ortho* oriented addition of formaldehyde, and their high concentration in the mixture, giving rise to chains with no *para*, *para* methylene bridges.

The evolution of the prepolymer during storage of such a little advanced resol did not stopped. Addition and condensation reactions keep on occurring in the mixture as a result of the highly reactive species present. Among other changing parameters, such as consumption of free formaldehyde, rising in viscosity, water dilutability..., the evolution of free phenol can be followed by gas chromatography. Final samples were kept in a freezer (−20°C), fridge (4°C) and at room temperature (17°C–23°C) and their content in free phenol was measured periodically. Fig. 7 shows the change in phenol concentration (P) with respect to the concentration at the final prefixed point (Po) versus storage days. Even at low temperatures as those of the freezer, the evolution of resols did not stop. Differences were observed from the first analysis carried out after 24 days of storage. During this period the evolution of the samples was very similar, although the prepolymer exposed to room temperature evolved the most, followed by the resol kept in the fridge and by the one in the freezer. However, after 72 days of storage, large differences between the prepolymer stored at −20°C and 4°C respect to that kept at room temperature were observed. The change in free phenol concentration of the latter was much larger. Room temperature seems to be too high for storing purposes of phenolic resol resins.

## 4. Conclusions

Zinc acetate shows specific catalytic characteristics in comparison to the other catalysts studied earlier [2,3]. The addition of formaldehyde onto phenol is almost exclusively *ortho* directed. Addition onto *para* position was very low respect to that onto *ortho* position. Besides, condensation products were slightly formed at the final point of reaction. $^{13}C$ NMR studies corroborated the low polymerization degree of the prepolymer observed by HPLC. Low methylene bond signals were measured, corresponding to those for the type *ortho*, *ortho* and *ortho*, *para* substitutions. No *para*, *para* bridges were detected as a result of the poor addition of hydroxymethyl groups onto the *para* sites of the rings. The *ortho* directing properties of the catalysts studied during the whole research including the previously reported [2,3] increase in the order zinc acetate > triethylamine > barium hydroxide > sodium hydroxide.

Disappearance of free phenol during storage followed by gas chromatography was considered as a parameter of control for conservation of the prepolymer properties. Owing to the high amount of reactive species and addition products present in the mixture, evolution did not stop at any of the three storing temperatures. The lower storing temperature the lower change in resin phenol content which will give rise to better conservation of the resin.

## References

[1] Knop A, Pilato LA. Phenolic Resins, Springer-Verlag, Berlin: 1985.
[2] Astarloa-Aierbe G, Echeverría JM, Egiburu JL, Ormaetxea M, Mondragon I. Polymer 1998;39:3147.
[3] Astarloa-Aierbe G, Echeverría JM, Martin MD, Mondragon I. Polymer 1998;39:3467.
[4] Grenier-Loustalot M-F, Larroque S, Grande D, Grenier P, Bedel D. Polymer 1996;37:1363.
[5] So S, Rudin A. J Appl Polym Sci 1990;41:205.