PII: S0032-3861(97)10055-6

Polymer Vol. 39 No. 14, pp. 3147–3153, 1998
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0032-3861/98/$19.00+0.00

Kinetics of phenolic resol resin formation by HPLC

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(Accepted 11 July 1997)

The kinetics of phenolic resol resins catalysed by sodium hydroxide and triethylamine have been studied by HPLC. Prepolymers were synthesized under controlled conditions: 80°C, F/P = 1.8, and initial pH = 8.0. Resol catalysed by triethylamine showed higher addition of formaldehyde onto *ortho* positions of phenolic rings, whereas in the presence of sodium hydroxyde addition onto *para* sites was favoured. Although preferences existed towards addition of formaldehyde to phenol, both resins showed finally similar composition of compounds. Reaction products were identified by ^{13}C n.m.r. spectroscopy. Mainly, *para,para*-DPMs, and later on, and to a lesser extent *ortho,para*-DPMs were formed. No *ortho,ortho*-DPMs were detected. As a result of reheating the resin, an increase in high molecular weight compounds was observed, as well as one phenolic ring species which kept on decreasing. *Para,para*-DPMs were still formed while *ortho,para*-DPMs started disappearing due to the higher reactivity of the unbonded *para* position towards condensation reactions. Addition and condensation reactions can occur simultaneously due to the presence of free formaldehyde in the mixture arising from cleavage of the hemiformal species or condensation reactions between hydroxymethyl groups. Another resol synthesized under the same conditions but in the presence of triethanolamine was also analysed. It took much longer to reach the final prefixed point, and showed mainly low molecular species © 1998 Elsevier Science Ltd. All rights reserved.

(**Keywords: phenolic resol resin; kinetics; HPLC**)

INTRODUCTION

Phenol/formaldehyde resins are thermosetting polymers useful in a wide range of applications as thermal and sound insulation, moulding compounds, foundry resins and composite wood materials[1]. The molecular structure and properties of the resins depend on many factors, related to the prepolymer formation and curing reactions, such as: formaldehyde/phenol ratio (F/P), type and amount of catalyst, pH and temperature. In an acidic medium and F/P molar ratio of 0.75–0.85, reaction leads to the formation of little branched long-chain polymers, called novolacs. In basic catalysis and excess of formaldehyde (F/P > 1), highly branched and substituted chains resols are obtained[1].

In order to study the complex structures and kinetics of resols, many analytical techniques have been used over the years: high performance liquid chromatography (HPLC)[2–6], gel permeation chromatography (GPC)[7,8], carbon and proton nuclear magnetic resonance spectroscopy (^{13}C and ^{1}H n.m.r.)[9,10], differential scanning calorimetry (DSC)[11,12], thermogravimetric analysis (TGA)[13], dynamic mechanical analysis (DMA)[14]. The influence of variation of many parameters during synthesis and cure[5,7,10,15] has been analysed in these investigations. Studies on self-condensation of first-formed reaction products[16], formation of hemiformals[9] and ether bridges and reactivity of monomers[6] have also been carried out.

Due to the lack of information on resols catalysed by amine type substances, it is our purpose in this study firstly to use triethylamine and triethanolamine as catalysts, and later on, to complete the study with other types of more useful catalysts, in order to compare them and to state the structural and kinetic differences between the prepolymers formed.

In this paper, we study the kinetics of two resols synthesized under the same conditions but with different types of catalyst: sodium hydroxide and triethylamine. For comparison, a third prepolymer catalysed by triethanolamine, was prepared. The major components of the prepolymer were identified by ^{13}C n.m.r. spectroscopy and their evolution during synthesis at 80°C followed by HPLC.

EXPERIMENTAL

Synthesis of resols

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

Prepolymers were synthesized in the IQU-Bakelite factory by mixing phenol and formaldehyde in a molar ratio of F/P = 1.8. The pH was then adjusted to 8.0 with a 50% aqueous solution of sodium hydroxide (NaOH) for resol S, triethylamine ($(CH_3CH_2)_3N$) for resol T and triethanolamine ($(HOCH_2CH_2)_3N$) for resol Te. The mixture was heated to 80°C (heating rate: 2.5–3.5°C/min)

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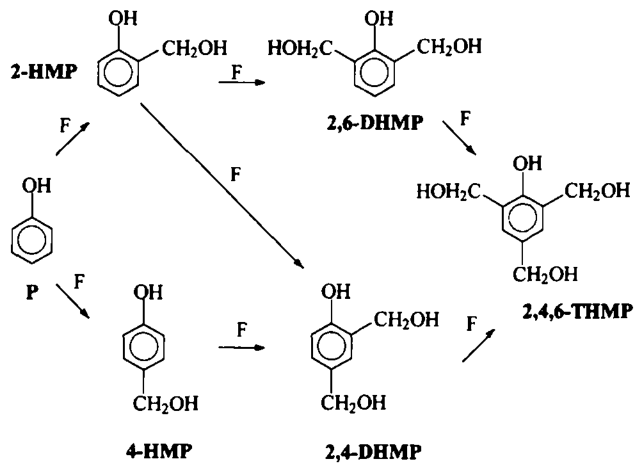


Figure 1 Reaction mechanism for addition of formaldehyde to phenolic rings

and stirred during reaction. Samples were taken every 10 min. Zero time was defined as time when the mixture reached the condensation temperature. The reaction was stopped by putting the reactor in a cold water bath, when the resin showed a 1/1 g/g solubility in water. Samples were kept at − 4°C.

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 columns were Spherisorb ODS-2 (5μm). In order to decrease the viscosity of the solvents, the columns were thermostatted 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. The equipment was used in two ways:

- Analytical: 25 × 0.46 cm column with 1.0 ml/min flow rate.
- Semi-preparative: 25 × 1.0 cm column with 3.0 ml/min flow rate.

Successive collection cycles were carried out until enough sample was obtained to be analysed by ^{13}C n.m.r. spectroscopy. For this objective, solvent was removed in a vacuum oven at 60°C.

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 spectrometer. 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 s and data points = 29952.

Fractions collected from semi-preparative chromatography were redissolved in deuterated dimethylsulfoxide (DMSO-d$_6$). ^{13}C chemical shifts were measured with respect to tetramethylsilane (TMS) as internal standard $\{\delta(\text{DMSO-d}_6) = 39.5\ \text{ppm}\}$.

RESULTS AND DISCUSSION

The reaction between phenol and formaldehyde in the alkaline pH range is based in two types of reactions: addition (*Figure 1*) of hydroxymethyl groups to the *ortho* and *para* free positions of phenol (no *meta* addition has been detected) and condensation (*Figure 2*) reactions between one hydroxymethyl group and one free position in phenol giving rise to methylene bridges or two hydroxymethyl groups forming methylene ether bonds. As a result of condensation reactions water and formaldehyde are released.

In some papers, the influence of catalyst type on addition reactions between phenol and formaldehyde has been already reported. Indeed, Peer[17] found that using hydroxides of the transition metals Cu, Cr, Mn, Ni and Co in aqueous solution at pH = 4-5 and boric acid, addition reactions occur mainly at the *ortho* position; Solomon and Rudin[7] demonstrated that methylolation at the *para* position increases in the order: $Ba(OH)_2 < NaOH < Na_2CO_3$; and Grenier-Loustalot *et al.*[5] studied the influence of KOH, NaOH, LiOH, $Ba(OH)_2$ and $Mg(OH)_2$ in the addition and condensation reactions.

In the past, most of the studies presented have been carried out using sodium hydroxide as catalyst. In this research, three resols synthesized by using different catalysts under controlled temperature, pH and F/P ratio, are compared. The kinetics of formation of Resol S, obtained by using sodium hydroxide and resol T catalysed by triethylamine are discussed. A resol formed using triethanolamine as catalyst (Resol Te) was also synthesized under the same conditions, and the final resin was compared to the other two resols.

Prepolymers were heated until a 1/1 g/g solubility in water was reached. As it has been suggested in the literature the observed better solubility of resol S in the presence of sodium hydroxide as catalyst could correspond to formation of phenolate ions[1]. Resol S took 270 min to reach the

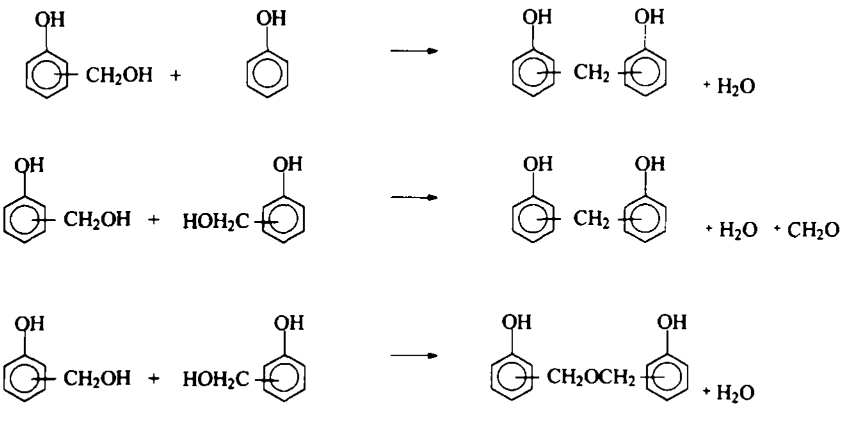


Figure 2 Reaction mechanisms for condensation

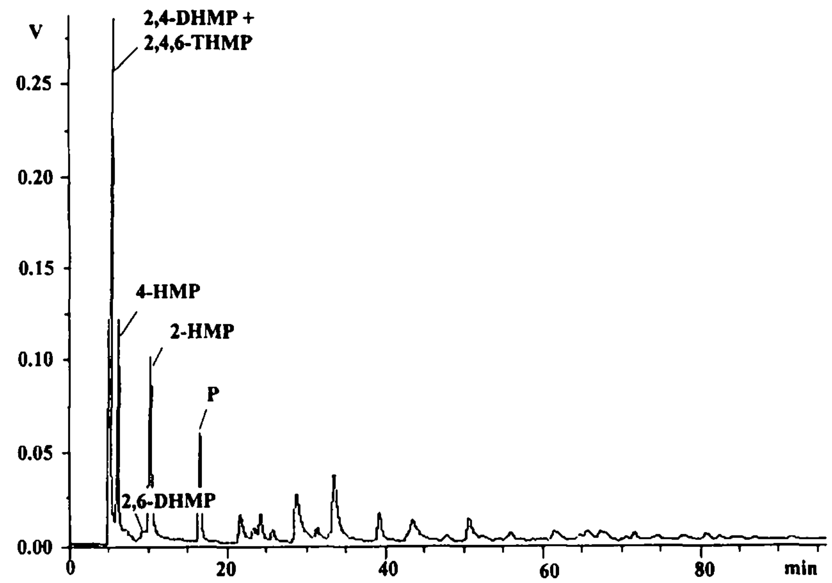


Figure 3 HPLC chromatogram of resol S

prefixed final point, whereas, resol T needed only 150 min. The colour that the mixture was taking while condensation was going on is another characteristic evidence that the mechanism of resol formation depends on the type of catalyst added. Phenolate ions usually give resol S dark red colour. Resol T and Te were yellow, like the novolacs cured with hexamethylenetetramine[1]. It has been shown that ammonia catalysed resols contain benzylamines[10,18–20] and benzoxazine[18–20] structures. By studying the reaction of hexamethylenetetramine with phenol, Sojka has shown[21] that the substitution pattern of the benzylamines formed is exclusively *ortho* and he suggested the apparent intermediacy of benzoxazine which rearranges to the amines.

Chromatography was used to quantitatively follow the evolution of phenol and the first formed products: 2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP). As is shown in the chromatogram of resol S (*Figure 3*), addition species (*Figure 1*) are first eluted at low retention times followed by higher molecular condensation compounds. Free formaldehyde was measured by acid/base titration, based on the formation of the corresponding oxime and hydrochloric acid, when hydroxylamine chlorhydrate was added.

The disappearance of free formaldehyde *versus* condensation time is depicted in *Figure 4*. The concentration of free formaldehyde in resol S keeps very close to that for resol T at initial condensation times but becomes higher beyond 20 min of reaction. Even though the condensation of resol S took 125 min longer, the concentration of free formaldehyde at the prefixed final point remained higher with respect to that for resol T.

Figure 5 shows for both prepolymers the disappearance of free phenol quantitatively followed by HPLC. As soon as the mixture started reacting, a marked difference in the concentration of phenol in both resols was observed. As stated above for formaldehyde, resol T also showed faster consumption of phenol. After 80 min of reaction, resol T had already reached the final concentration value of resol S (5%), and kept decreasing until the final 3%, at the prefixed solubility.

As can be seen in the figures corresponding to the evolution of the addition products, faster consumption of reactives led to a higher concentration of substituted phenols, except for 4-HMP.

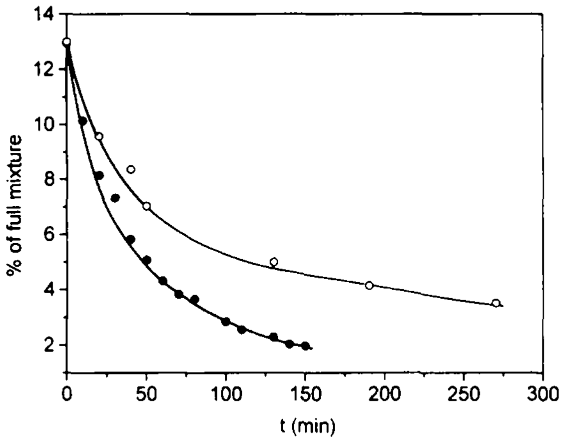


Figure 4 Disappearance of formaldehyde by the titration method. ○ resol S; ● resol T

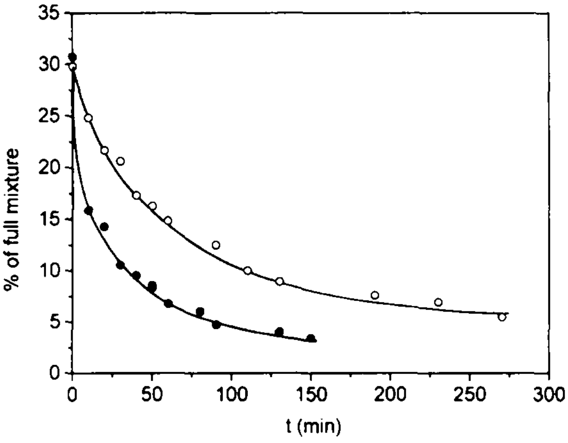


Figure 5 Disappearance of phenol by HPLC. ○ resol S; ● resol T

The evolution of first formed addition products 2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP) for both condensates is shown in *Figures 6 and 7*, respectively. The formation of 2-HMP is more favoured in resol T than in resol S. The latter shows higher concentration of 4-HMP than the former. Although two of the three reactive positions of phenol are *ortho* and only one *para*, resol S shows similar concentration of 2-HMP and 4-HMP: 11%, which means that the reactivity per site of the *para* position is double with respect to the *ortho* position. On the other hand, due to the *ortho* directing character of the triethylamine, resol T shows a maximum concentration of 2-HMP (17%) higher than that of 4-HMP (7%); thus, higher reactivity per site of the *ortho* position.

Figure 8 corroborates the *ortho* directing properties of triethylamine discussed above. Only at the prefixed final point of reaction resol T shows a 2-HMP/4-HMP weight ratio (O/P), lower than 2, whereas resol S does not reach the value of equal reactivity of sites (O/P = 2). As has been stated elsewhere[7], sodium hydroxide has *para* directing properties.

The evolution of di- and tri-substituted phenols, 2,4-dihydroxymethylphenol (2,4-DHMP), 2,6-dihydroxymethylphenol (2,6-DHMP), and 2,4,6-trihydroxymethylphenol (2,4,6-THMP), can be followed in *Figure 9*. 2,4-DHMP and 2,4,6-THMP did not separate under the chromatographic conditions used. Their evolution is presented by one curve. Again, compounds in resol T form faster and reach higher concentration values than in resol S. In the case of 2,6-DHMP, important differences are observed: in resol S this compound is not formed until after 20 min of reaction while in resol T it already exists at time 0, so it is formed before the temperature reaches 80°C. The fact that a second hydroxymethyl group can be added to the second free *ortho* position instead of to the *para* position corroborates the *ortho* directing character of the amine. In resol S, very little 2,6-DHMP is formed due to the preference of the free *para* position. The higher consumption of phenol and formaldehyde in resol T, discussed above, is reflected in the higher formation of addition products as 2,6-DHMP and 2,4,6-THMP (*Figure 9*), as well as 2-HMP (*Figure 6*).

^{13}C n.m.r. solution studies revealed the presence of hemiformals in the three resols (80–92 ppm). At the prefixed final point hemiformal species, as shown in *Figure 10*, corresponding to the addition reaction products, have been detected in other investigations for resols catalysed by sodium hydroxide[9] and ammonia[10]. Formaldehyde is also consumed to form hemiformals which constitute a potential source of formaldehyde. The oxymethylene unit bonded to the phenolic ring is stable. The other oxymethylene units are unstable. They can cleave

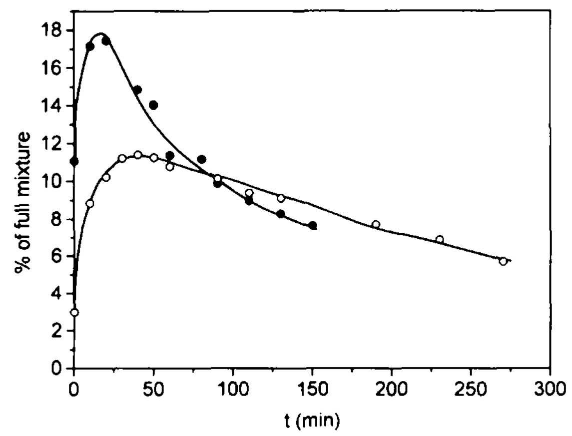


Figure 6 Evolution of 2-hydroxymethylphenol (2-HMP) during synthesis. ○ resol S; ● resol T

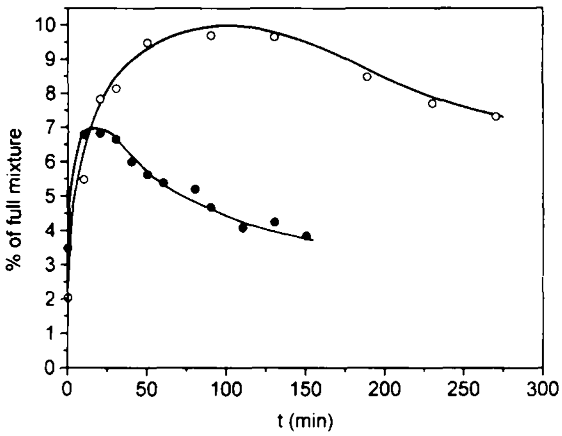


Figure 7 Evolution of 4-hydroxymethylphenol (4-HMP) during synthesis. ○ resol S; ● resol T

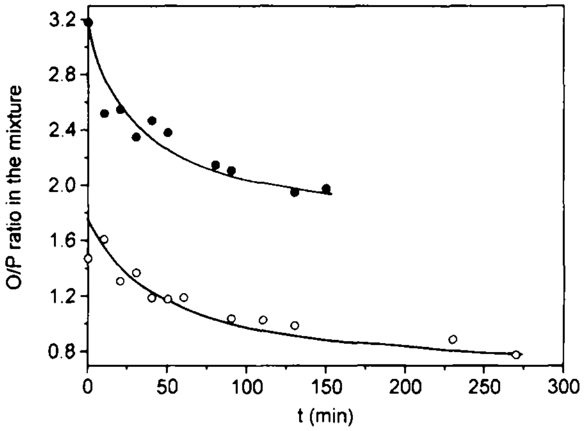


Figure 8 *Ortho/para* ratio of Resol S and Resol T. ○ resol S; ● resol T

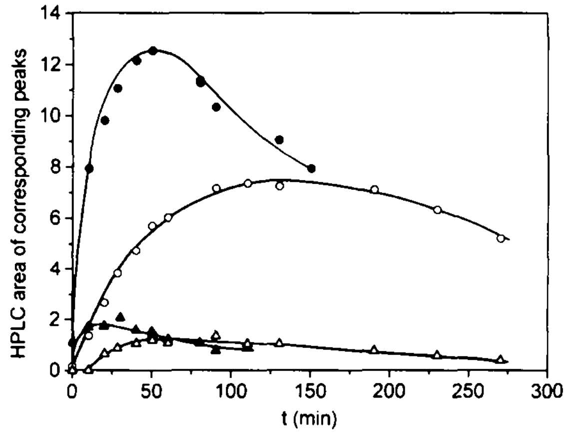


Figure 9 Evolution (HPLC area) of 2,4-DHMP, 2,6-DHMP, and 2,4,6-THMP. 2,4-DHMP and 2,4,6-THMP: ○ resol S; ● resol T. 2,6-DHMP: △ resol S, ▲ resol T

from the structure and react with other phenol rings[9]. Due to the continuous presence of free formaldehyde in the mixture addition reactions can occur simultaneously with condensation reactions. Free phenol, if left, or free phenolic positions can be occupied by hydroxymethyl groups.

The formation of the major condensation products of resol S was followed by HPLC. Collection of samples using a semi-preparative column were made in order to analyse them by ^{13}C n.m.r.. The results achieved were not always clear enough, for several reasons: poor separation of some peaks, reaction and evaporation of solutes during evaporation of mobile phase, and too low concentration of sample left to be detected by the ^{13}C n.m.r. spectrometer.

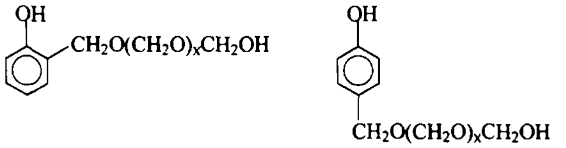


Figure 10 Hemiformal compounds detected in sodium hydroxyde[9] and ammonia[10] catalyzed resols

However, the main diaryl compounds were identified and their retention times are now known (*Figure 11a*). The compounds formed were diphenylmethanes (DPM), mainly *para,para*-DPMs (1–4) ($\approx$ 40 ppm) and to a less extent *ortho,para*-DPMs (5) ($\approx$ 35 ppm). No *ortho,ortho*-bonds ($\approx$ 30 ppm) were detected either in the collected samples or in the spectra of the resols (*Figure 12*).

For both resins in the first 30 min, no condensation products were observed. Afterwards, 2,6,6′-trihydroxymethyl-p,p′-dihydroxyDPM (1), 2,6-dihydroxymethyl-p,p′-dihydroxyDPM (2), 2,2′6,6′-tetrahydroxymethyl-p,p′-dihydroxyDPM (3), and 2,6′-dihydroxymethyl-p,p′-dihydroxyDPM (4) compounds appeared and they did not stop growing during reaction (*Figure 11a* and *Figure 13*). These condensation products began to be formed before a decrease in the concentration of addition products was noticed. At this stage, addition and condensation reactions competed to occupy the free positions left in the phenolic rings. *Ortho,para*-DPMs were not observed until 90 min of reaction. Once again, the higher reactivity of the *para*

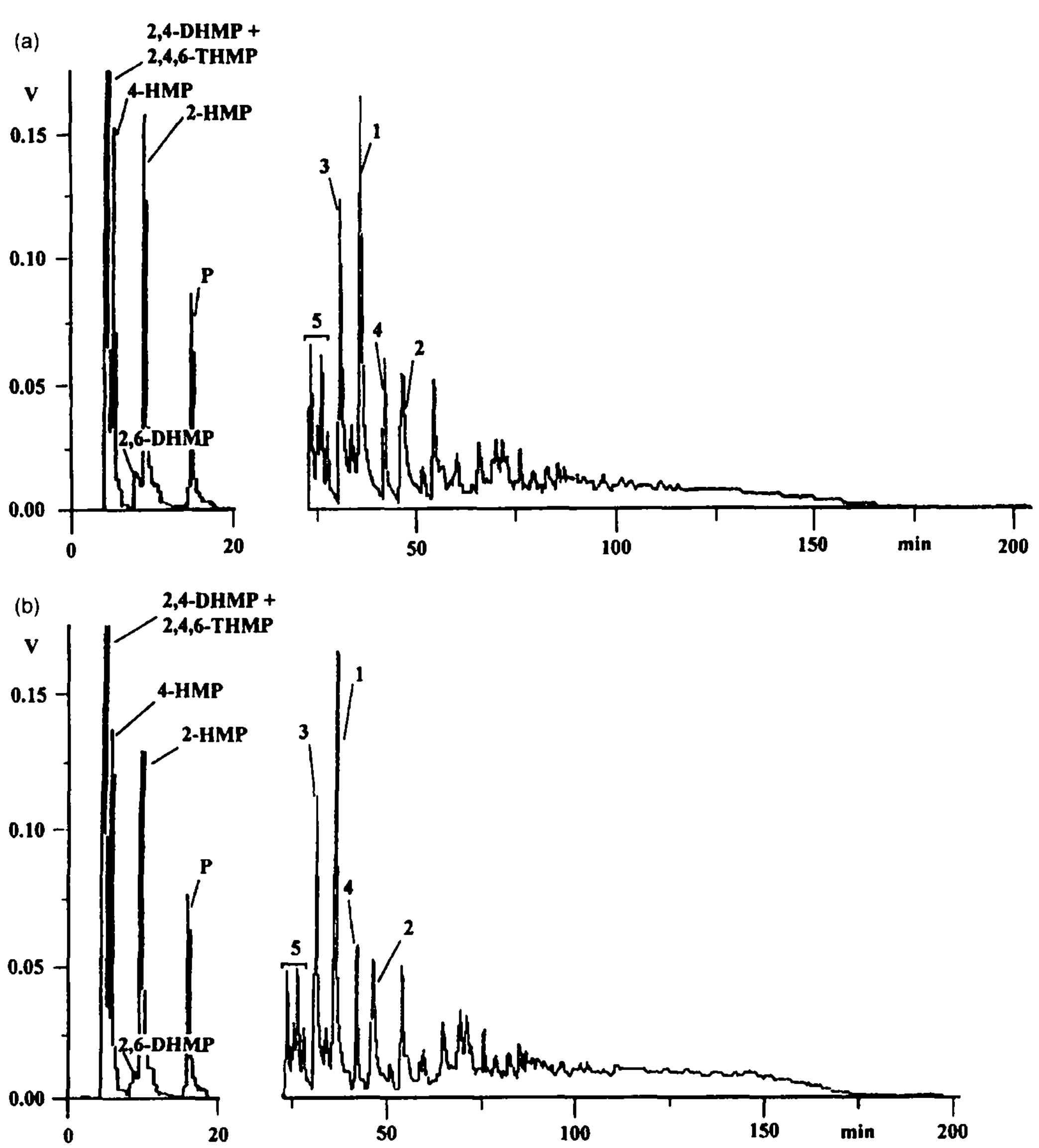


Figure 11 HPLC chromatograms of resol S. (a) 1/1 g/g solubility in water, (b) 0.1/1 g/g solubility in water

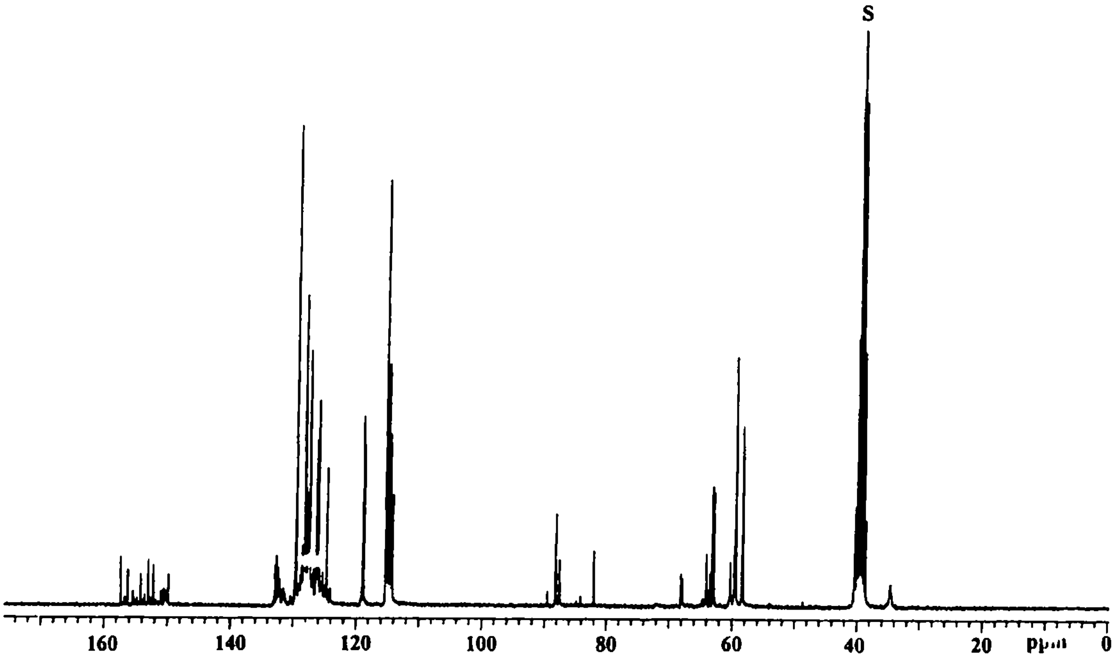


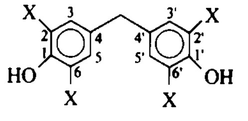
Figure 12 ^{13}C n.m.r. spectrum of resol S (S = dmso-d_6)

position is demonstrated. Due to steric restrictions and interactions between benzylic and phenolic OHs, hydroxymethyl groups in *para* attack first free *para* positions to form *para,para*-DPMs, and after these positions are occupied, free *ortho* positions are attacked forming *ortho,para*-DPMs.

In order to study the structural changes of the resin, resol S was reheated until 0.1/1 g/g solubility in water was reached (*Figure 11b*). As expected higher molecular weight compounds were formed and phenol and methylolated phenols kept on decreasing. *Figure 11b* shows that the amount of species at high retention times has increased with respect to that for a 1/1 g/g solubility, as a result of the condensation reactions occurring amongst the low molecular weight compounds which have consequently decreased in concentration. *Para,para*-DPMs increased with condensation time while *ortho,para*-DPMs decreased. The higher reactivity of the *para* position towards condensation is responsible of the continuous formation of *para,para*-DPMs, whereas *ortho,para*-DPMs are later and less formed and disappear faster because they have one unbonded *para* site. Thus, hydroxymethyl groups of other rings can react with these positions to form longer chains. It is more difficult for this mechanism to occur in the *ortho* positions due to steric and chemical restrictions. Identification of species formed by three or more phenolic units was problematic, because their separation in order to collect samples was not good enough.

Although triethylamine has *ortho* directing properties for addition reactions, resol T shows the same condensation products as resol S: no qualitative differences have been observed by HPLC nor by ^{13}C n.m.r., which agrees with the studies of Knop[1] who stated that tertiary amines lead to prepolymers which are similar to sodium hydroxide catalysed resols in their structure, except for higher *ortho* orientation.

The synthesis of resol Te until the prefixed final point took much longer than the other two resols (631 min). The ^{13}C n.m.r. *ipso* region (150–160 ppm) (*Figure 14*) shows that bands corresponding to phenol (157.4 ppm) and low molecular species (2-HMP 154.2 ppm, and 4-HMP 156.3 ppm) dominate and condensation was not as favoured as in the other resols (trisubstituted phenols 150.0–153.0 ppm). Although it finally became red, its yellowish colour lasted for much longer than in resol T. The presence of hydroxyl groups in the catalyst suggests that the interaction of these groups with the reactives is responsible for the slow advancement of this resin.



X: CH_2OH or H

Figure 13 Main diphenylmethane compounds observed in the resols

CONCLUSIONS

High performance liquid chromatography is a useful technique to follow the evolution of phenolic resins during the formation of the prepolymer. The concentration changes of the addition products formed and low molecular weight condensation compounds can be studied.

Comparison of resols catalysed by triethylamine and sodium hydroxide indicates that the former catalyst has *ortho* directing properties and the latter favours the addition to the *para* position. Formation of 2-HMP and 2,6-DHMP in resol T is much higher than in resol S. During synthesis of the prepolymer the latter shows an O/P ratio higher than 2, while resol S does not reach this value.

Condensation products were analysed by ^{13}C n.m.r.. The main products formed were firstly *para,para*-DPMs, and later on, and to a lesser extent, *ortho,para*-DPMs. *Ortho,ortho*-DPMs were not detected. In order to study the changes in concentration of species in resol S, the resin was reheated until 0.1/1 g/g solubility in water. Increase in

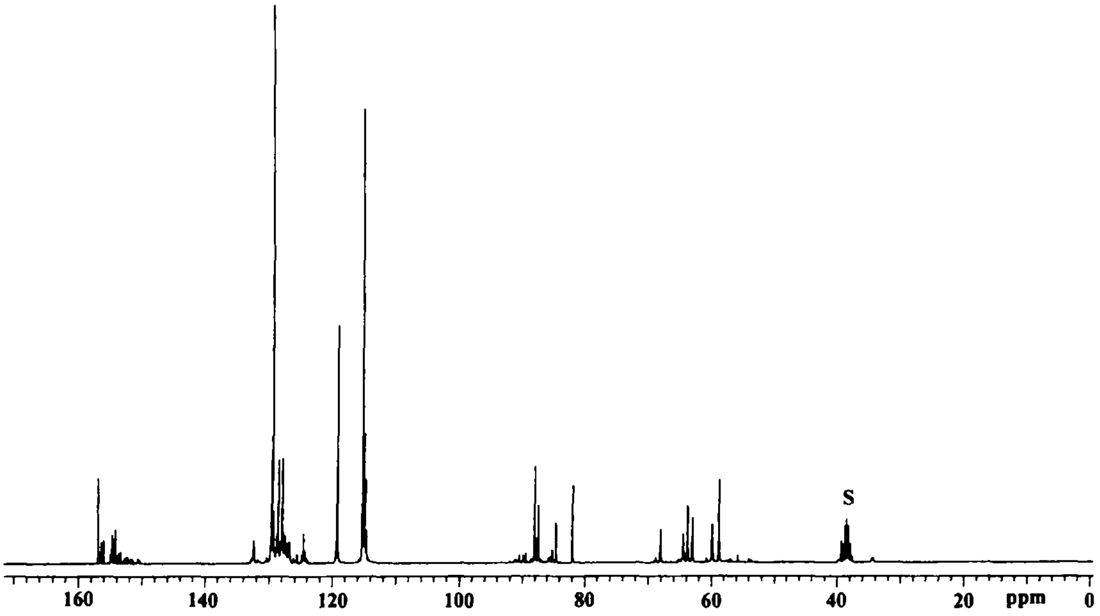


Figure 14 ^{13}C n.m.r. spectrum of resol Te (S = dmso-d_6)

concentration of *para,para*-DPMs and decrease of *ortho,-para*-DPM as well as one phenolic ring compounds were observed. *Para* position showed higher reactivity than *ortho* towards condensation in both resols.

Resol Te took a much longer reaction time, probably, due to the interaction between the hydroxyl groups of the catalyst and those of the phenolic units. As can be seen in the ^{13}C n.m.r. spectrum of resol Te, lower molecular weight species predominate in the mixture. Triethanolamine showed poor catalysing properties for phenolic resins.

Hemiformal species and dibenzyl ether bridges were also detected in the resins. Due to the possibility of formaldehyde being released from these compounds, addition reactions can occur simultaneously to the formation of high molecular weight species by condensation reactions. Both types of reactions can compete for occupying free *ortho* and *para* positions in the phenolic rings.

ACKNOWLEDGEMENTS

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

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