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Influence of the temperature on the formation of a phenolic resol resin catalyzed with amine

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Abstract

The influence of the condensation temperature on the phenolic resol resin prepolymer formation was studied by liquid chromatography and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy. Four resols catalyzed with triethylamine and with initial pH = 8.0 and F/P = 1.8 were synthesized at 60, 80, 95 °C, and reflux (98–102 °C). On increasing the condensation temperature, reactant consumption rates and first formed addition products increased, condensation times decreased as well. Prepolymer synthesized at refluxing temperatures showed higher formaldehyde addition onto *ortho* positions with respect to the other resols. Different types of phenolic rings connecting bonds were observed: *para*, *para* and *ortho*, *para* bridges as well as ether bonds were detected. No *ortho*, *ortho* bonds were observed for the condensation with the catalyst used. ^{13}C NMR measurements did not show qualitative differences between prepolymers. Anyway, residual phenol and formaldehyde concentrations and the amount of free unreacted *ortho* and *para* positions decreased with temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Resol; Prepolymer; Triethylamine

1. Introduction

Phenolic resol prepolymer formation is influenced by many synthesis parameters, such as formaldehyde to phenol molar concentration ratio (F/P), type and amount of catalyst, pH and condensation temperature. Every parameter has been studied for different resols by many authors using all kind of techniques [1–8]. Previously, the influence of the type of catalyst [9–11], and the influence of the initial formaldehyde to phenol concentration ratio [12], as well as the influence of the amount of catalyst and initial pH [13] on the formation of phenolic resol resins were studied by our group.

The studies concerning the influence of the temperature cover a wide temperature range combined with varying synthesis parameter values. Some studies were carried out employing fixed synthesis temperatures [2,5,6,8,14–17] and others combined temperature steps during synthesis of the resin [7,18,19]. As a result of the variation of so many synthesis parameters several aspects still remain to be studied. In this paper, we report the study of the influence of the condensation temperature on the formation of triethylamine catalyzed resols with F/P = 1.8 synthesized at 60, 80, 95 °C, and reflux (98–102 °C).

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 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 of the formaldehyde/phenol = 1.8 mixture was then adjusted to 8.0 with triethylamine. The mixture (25–30 °C) was heated to the

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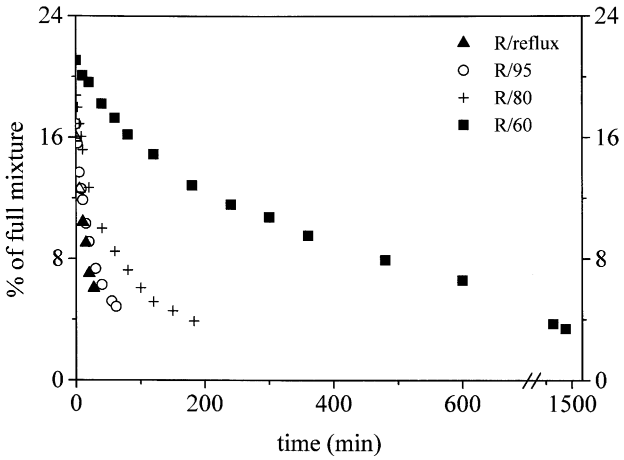

Fig. 1. Disappearance of free formaldehyde during synthesis of resols.

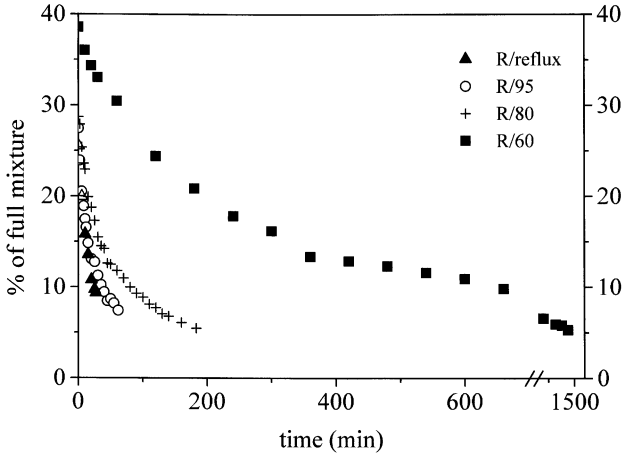

Fig. 2. Disappearance of free phenol during synthesis of resols.

condensation temperature: 60 °C (R/60), 80 °C (R/80), and 95 °C (R/95), with a heating rate of 2.5–3.5 °C/min, and stirred during reaction. Samples were taken during synthesis. Zero time was defined as the time when the mixture reached the condensation temperature. The reaction was stopped when the resin showed a 1/1 g/g dilutability in water.

For resol synthesized at reflux (R/reflux) a 15 kg formaldehyde/phenol mixture was prepared and its pH adjusted to 8.0 with triethylamine. One kilogram samples were taken from the mixture and placed in the flask. The sample was heated until reflux. Zero time was defined as the sample started to reflux and was stopped immediately. Then another sample was taken and the same procedure was followed until 5 min of reflux were gone, the mixture was cooled down and sample was stored. This procedure was followed until a mixture reached the 1/1 g/g dilutability in water. Samples were kept at 4 °C before analysis.

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 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.

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

3. Results and discussion

The first observed influence of the condensation temperature on the formation of the resol prepolymers is related to the time needed to reach the final value of 1/1 g/g dilutability in water. The higher the condensation temperature the shorter the synthesis time. As it can be observed in the following figures, the analyzed temperatures can be classified into three groups. R/60 followed very slow evolution and the condensation time was 1420 min. Prepolymers synthesized at 95 °C and reflux reached the prefixed final point much faster, while 80 °C condensation temperature cooked resol spent 3 h, approximately. The rates of reactant consumption also reveal the influence of the temperature (Figs. 1 and 2). Increasing temperature increases the consumption rates of the raw materials.

Fig. 1 shows the evolution of free formaldehyde during synthesis. Increasing temperature concentrations at zero time decreased whereas final concentrations increased, the latter being a consequence of the shorter time for formaldehyde to be added onto the reactive phenolic sites. The higher the condensation temperature, the longer the heating period from room temperature to condensation temperature, and, therefore, more free formaldehyde was consumed during the heating process of the initial mixture of reactants.

As depicted in Fig. 2, the evolution of free phenol followed by high performance liquid chromatography (HPLC) shows similar curves with respect to the evolution of free formaldehyde. The phenol consumption at zero time for R/60 is very low while its final concentration shows lower value with respect to other resols due to the longer condensation time needed to reach the final point of synthesis. The rest of the curves show higher final concentrations

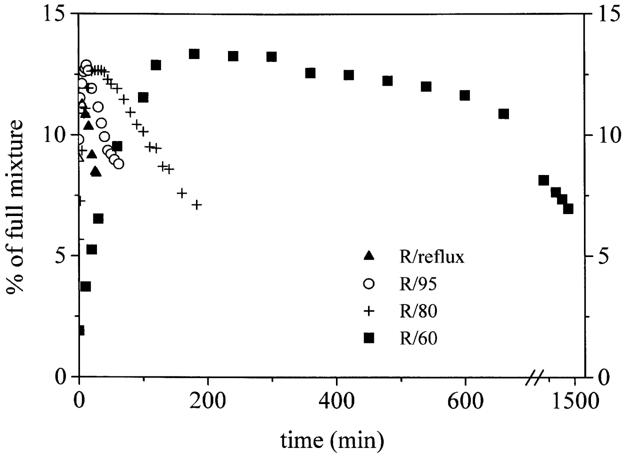

Fig. 3. Evolution of 2-hydroxymethylphenol (2-HMP) during synthesis of resols.

as temperature was increased. As shown for formaldehyde, the reaction rates for the formation of all prepolymers increased with the temperature.

Among other phenolic resol resin synthesis parameters such as the type and amount of catalyst, F/P ratio and initial pH, studied in our group [9–13], the temperature is the factor that mostly influence the process of prepolymer fabrication kinetically. The effect of the condensation temperature on the condensation time, similar to the effect of the added catalyst concentration, gives rise to varying reactants consumption and, thus, to the variations in first formed addition product concentrations.

Fig. 3 shows the evolution of 2-hydroxymethylphenol (2-HMP) during synthesis. Again, temperature dictates the rates of 2-HMP formation. At zero time concentration differences are clearly stated, increasing temperature increases the initial concentrations. However, similar maximum concentrations are observed, except for R/reflux which was formed in a lower quantity. With respect to the final concentrations, R/60 and R/80 showed similar values around 7%, while the resols synthesized at higher temperatures (R/95 and R/reflux) showed concentrations higher than 8%. However, these differences are into the experimental error limits, therefore, it can be stated that final similar concentrations were left for 2-HMP in every case.

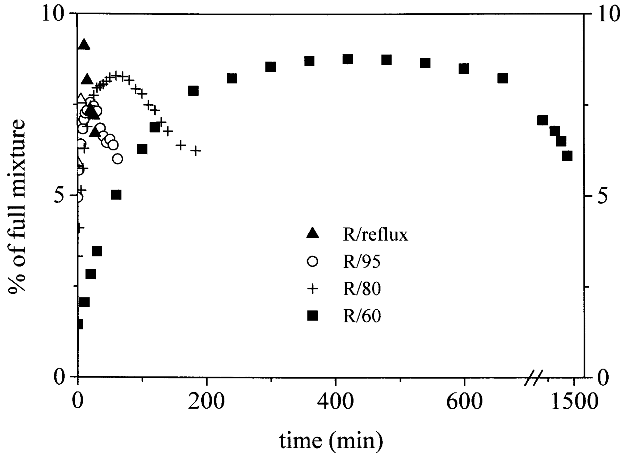

Fig. 4. Evolution of 4-hydroxymethylphenol (4-HMP) during synthesis of resols.

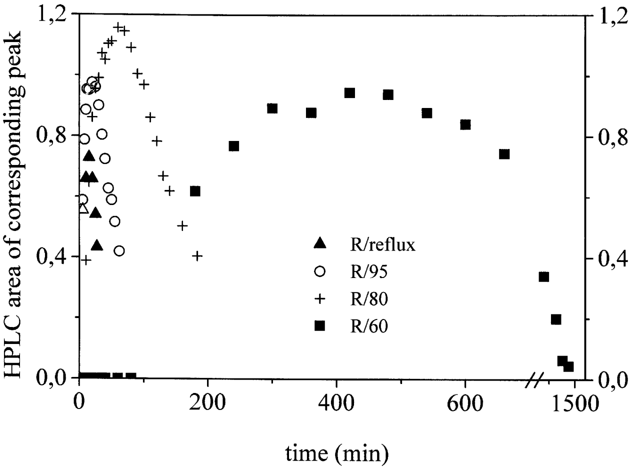

Fig. 5. Evolution of 2,6-dihydroxymethylphenol (2,6-DHMP) during synthesis of resols.

The formaldehyde addition onto the *para* position of phenol giving rise to the formation of 4-hydroxymethylphenol (4-HMP) shows similar concentration relations for R/60, R/80, and R/95 (Fig. 4). Increasing synthesis temperature increased the concentrations at zero time, but no differences can be observed in the maximum and final concentrations. It has to be pointed out that the higher maximum concentration reached by R/reflux, opposite to the lower concentration reached by this resol for the formation of 2-HMP. It seems that addition of formaldehyde is more directed onto *para* sites than onto *ortho* positions for refluxing in comparison to resols synthesized at lower temperatures.

As expected from previous results with triethylamine catalyzed resols [9–13], the addition of a second formaldehyde molecule onto the free *ortho* site of 2-HMP did not occur in high concentrations. Fig. 5 shows the HPLC peak evolution corresponding to 2,6-dihydroxymethylphenol (2,6-DHMP). Due to the high reactivity of the *para* free position left on 2,6-DHMP, its consumption after the maximum was reached, was the higher when relatively compared to the rest of compounds. The lower the temperature the higher concentration was formed for R/reflux, R/95, and R/80. Independently of the maximum concentrations those resols ended with the same concentration of 2,6-DHMP left ($\approx$0.4). In contrast with this behavior, appearance of 2,6-DHMP for R/60 was delayed until 90 min of reaction and its final concentration was almost nil. Besides, the maximum concentration was lower in comparison with the rest of resols, which reached higher maximum concentrations as condensation temperature decreased. The long condensation time of R/60 allowed formaldehyde to add onto the free

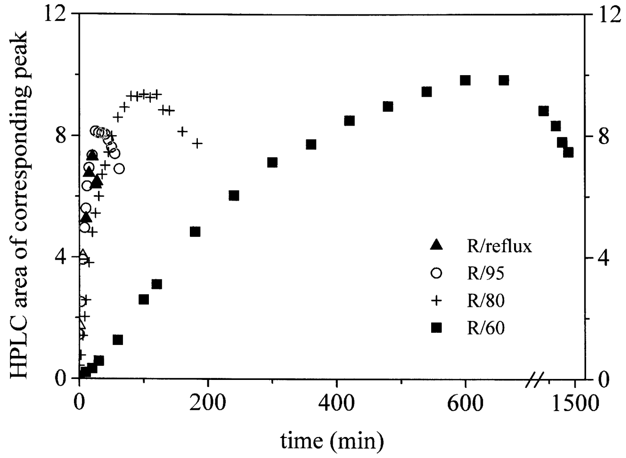

Fig. 6. Evolution of 2,4-dihydroxymethylphenol (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) during synthesis of resols.

para site left, giving rise to 2,6-DHMP being formed and consumed during synthesis and its complete disappearance after 1420 min of reaction.

Evolution of 2,4-dihydroxymethylphenol (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) is depicted by a unique curve in Fig. 6 because they did not separate under the chromatographic conditions used. In this case, the four resols followed the fact that maximum concentration decreased with condensation temperature. The lower the temperature, the longer the condensation time was and, therefore, highly substituted compounds were easier to be formed. Similarly to 2,6-DHMP, consumption beyond the maximum concentration decreased with temperature due to the differences in the condensation times.

Final prepolymers were redissolved in dmso-d_6 and acetone-d_6, and analyzed by ^{13}C NMR spectroscopy. No qualitative differences were observed. In order to carry out a comparable study of these spectra, the peak area or group of peaks area were normalized with respect to the area corresponding to the *ipso* region, i.e. carbon bearing the oxygen atom of the phenolic hydroxyl group.

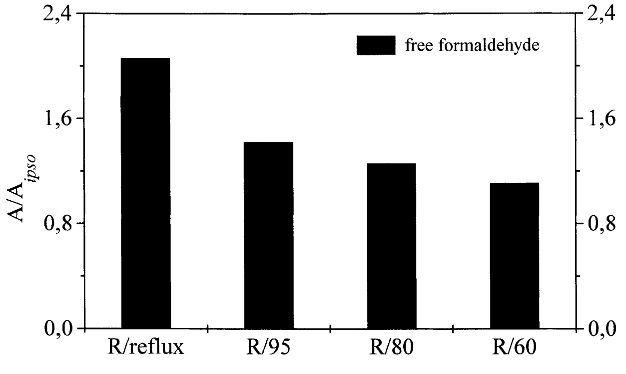

Fig. 7. Formaldehyde (80–95 ppm) in prepolymers in acetone-d_6 by ^{13}C NMR.

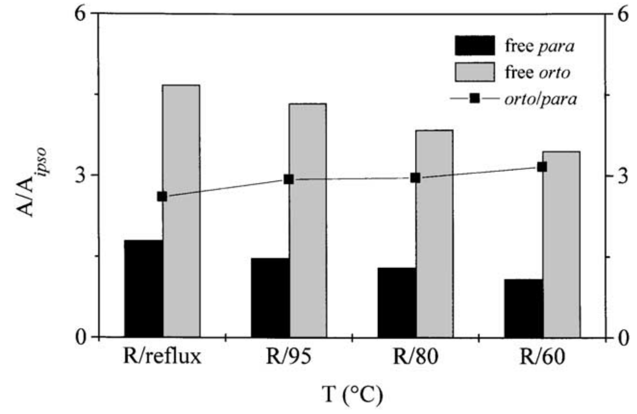

Fig. 8. Free *ortho* and *para* positions left unreacted in prepolymers and *ortho*/*para* ratio positions in acetone-d_6 by ^{13}C NMR.

Fig. 7 shows the free formaldehyde on its several polymeric forms left on the prepolymers. ^{13}C NMR spectroscopy corroborates the chromatographic results discussed earlier; the final formaldehyde values increased with condensation temperature. As the temperature increased the lower condensation time needed for reaching the final point avoided the formaldehyde consumption, thus increasing its residual concentration.

As a consequence of the lower formaldehyde addition onto phenolic rings the free *para* and *ortho* positions left on the prepolymers increased with temperature (Fig. 8). Again the higher reactivity of the *para* position is demonstrated by the *ortho*/*para* free sites ratio, which is around 3 for every resol.

In every resol three types of phenolic rings connecting bonds were observed (Fig. 9). On one hand, methylene type bonds in the 45–25 ppm region of the ^{13}C NMR spectra corresponding to *para*, *para*- and *ortho*, *para*-methylene bonds. No *ortho*, *ortho*-methylene bridges were detected. On the other hand, ether type bonds around 70 ppm, which at higher temperatures can be rearranged to methylenic bonds releasing formaldehyde, were observed [1].

4. Conclusions

The influence of the condensation temperature on the resol prepolymer formation was analyzed by HPLC and ^{13}C NMR spectroscopy.

The condensation temperature influences the kinetics of prepolymer formation. Firstly, the condensation time decreases with the condensation temperature, and secondly, the rates of reactants consumption and products formation slow at lower temperatures. As condensation time was decreased, the residual concentrations of free formaldehyde and free phenol increased as a consequence of the shorter condensation time.

First formaldehyde addition reaction for R/reflux is more *para* directed with respect to addition onto *ortho* position. At reflux temperature, prepolymer formation is carried out

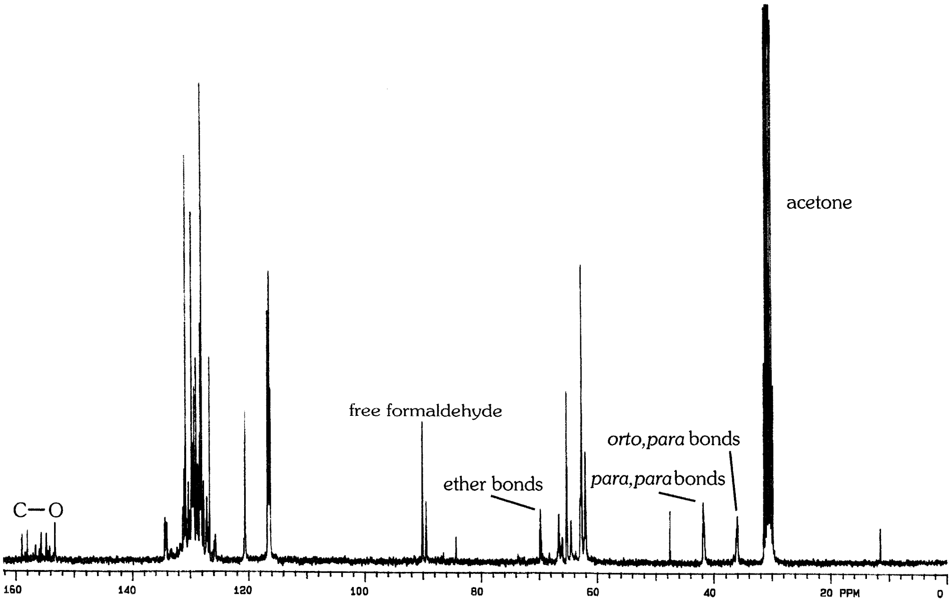

Fig. 9. ^{13}C NMR spectrum of R/60 in acetone-d_6 by ^{13}C NMR.

fastly giving rise to formaldehyde preferentially being added onto the *para* site due to its higher reactivity. At 95 °C and reflux condensation, addition reactions occur very fast giving rise to products disappearing as they are formed because they are involved in several addition and condensation reactions. However, no qualitative differences were observed between prepolymers although residual reactants concentrations and the amount of free unreacted *ortho* and *para* positions decreased with temperature.

The condensation temperature controls the condensation time and the rates of reactant consumptions and product formations but final prepolymers did not show qualitative differences.

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