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Influence of the amount of catalyst and initial pH on the phenolic resol resin formation

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Abstract

The influence of the added amount of triethylamine as phenolic resol resin catalyst and that of the initial pH were studied for resols synthesized at 80°C with $F/P = 1.8$. The evolution of phenol and first formed addition products were quantitatively followed by high-performance liquid chromatography (HPLC) and final prepolymers were analyzed by ^{13}C NMR spectroscopy. The catalyst amount kinetically and mechanistically affected the prepolymer formation. The higher the amount of added catalyst the higher reactant consumption rates and product formation rates. The *ortho* directing characteristics of triethylamine for the addition of formaldehyde onto phenolic sites were observed. It could be stated that two mechanisms for the addition of formaldehyde occurred simultaneously. On the one hand, hydroxyl groups favoured the formation of phenolate ions, which would favour addition onto *para* phenolic positions. On the other hand, formaldehyde, phenol, and triethylamine could be involved in the formation of an intermediate transition state, favouring addition onto *ortho* sites, due to the *ortho* directing properties of triethylamine. The influence of the studied pH range did not give rise to significant differences on the resol resin prepolymer formation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Resol formation; Triethylamine; pH

1. Introduction

The widely applicable phenolic resins (resols and novolacs) have been thoroughly studied by many research groups using all kind of techniques. Nowadays, the studies are mainly focussed on the combination of these polymers with different materials in order to reach specific properties. Although there is much work done in the field of the synthesis of phenolic prepolymers, some aspects of the complex reaction mechanisms and kinetics remain unanswered.

The effect of increasing the amount of catalyst (sodium hydroxide) reported in the literature [1–3] by using NMR spectroscopy, differential scanning calorimetry, FT-IR spectroscopy and liquid chromatography, basically affects the activation and rate of polymerization reaction, thus reaching higher polymerization degrees on the prepolymer formation. Due to the lack of studies on the influence of the amount of triethylamine as catalyst of resol resins on the formation of prepolymers we studied three resols with varying amounts of catalyst.

The phenolic prepolymer synthesis is affected by several parameters such as type and amount of catalyst, initial formaldehyde to phenol (F/P) molar ratio, condensation temperature and time, and initial pH. Following the analysis of the influence of the synthesis parameters on the formation of resol prepolymers [4–7], this paper presents the study carried out on the influence of the amount of catalyst and initial pH on the formation of prepolymers catalyzed with triethylamine and synthesized at 80°C with $F/P = 1.8$. Disappearance of formaldehyde was followed by chemical assay. Disappearance of phenol and evolution of first formed addition products were quantitatively followed by high performance liquid chromatography (HPLC) and final prepolymers were analyzed by ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR).

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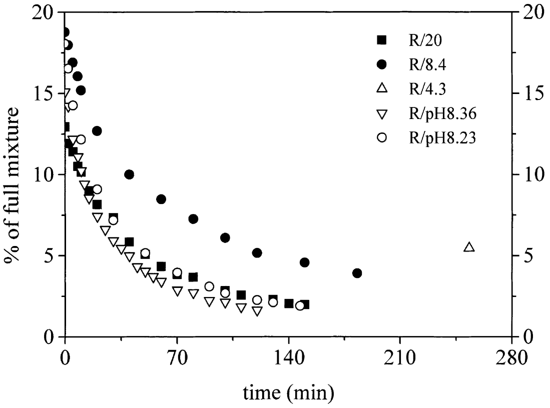

Fig. 1. Disappearance of free formaldehyde during synthesis of resols.

2. Experimental

2.1. Synthesis of resols

Phenol (>99%) and triethylamine were commercial products used without further purification. Formaldehyde (37% aqueous solution) was prepared from a 50% commercial solution, and the pH was adjusted to 7.0 with sodium hydroxide (1 M), except for resol R/20.

Prepolymers were synthesized in the Bakelite Ibérica factory by mixing phenol and formaldehyde in a molar ratio of F/P = 1.8. The pH was then adjusted to 8.0 with triethylamine ($(CH_3CH_2)_3N$) for resols R/20, R/8.4, and R/4.3, where 20, 8.4, and 4.3 indicate the amount of triethylamine (g) added. In order to study the influence of the initial pH, resols R/pH8.23 and R/pH8.36 were synthesized by adding 20.0 g of triethylamine reaching an initial pH value of 8.23 and 8.36, respectively. The mixture 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 the time taken by the mixture to reach 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.

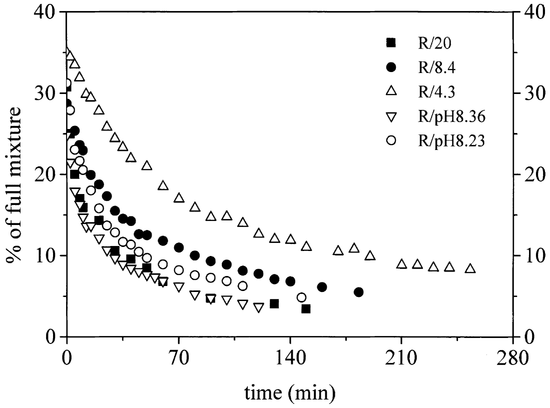

Fig. 2. Disappearance of free phenol during synthesis of resols.

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 13 nuclear magnetic resonance spectroscopy

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

3. Results and discussion

In order to study the influence of the initial pH and the amount of catalyst, five resol prepolymers were synthesized with F/P = 1.8, and catalyzed with triethylamine at 80°C. The disappearance of free formaldehyde during synthesis was followed by chemical assay [8], while the disappearance of phenol and formation of addition products were quantitatively followed by liquid chromatography.

The first observed influence of the amount of catalyst is reflected on the condensation time needed to reach the final prefixed point of 1/1 g/g dilutability in water. The condensation time decreases with the added amount of catalyst. The influence of the initial pH on the synthesis time is not so clearly marked.

The influence of the initial pH and amount of catalyst can be observed on the disappearance of reactants and evolution of products and final prepolymers. The disappearance of free formaldehyde for the five prepolymers during synthesis is depicted on Fig. 1. Only the final value for R/4.3 is shown. Condensation times are longer as the catalyst amount is reduced, final concentrations becoming higher. The rate of formaldehyde consumption increased with the amount of triethylamine. These results follow trends similar to the values obtained by Grenier-Loustalot et al. [9] for resols catalyzed with sodium hydroxide. On the contrary, the resols prepared with the same amount of catalyst (20.0 g) but varying initial pH show similar final concentrations and evolutions during synthesis. It seems that the addition of

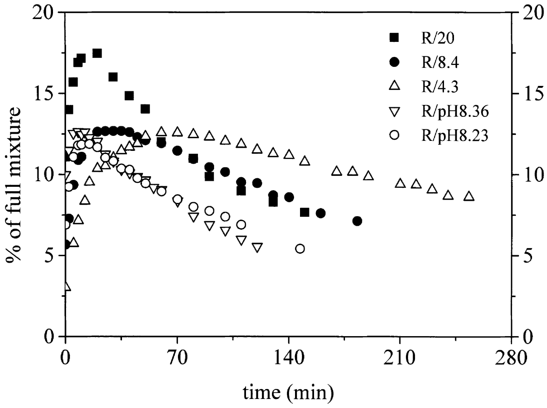

Fig. 3. Evolution of 2-hydroxymethylphenol (2-HMP) during synthesis of resols.

formaldehyde onto phenolic rings is controlled by the amount of catalyst.

The evolution of the other reactant, phenol, can be seen in Fig. 2. Similar to the behavior followed by the free formaldehyde, the final concentrations reached by phenol decreased with the amount of triethylamine, whereas resols with varying pH did not show significant differences in the final concentrations. Again, the consumption of the reactant is decreased with longer condensation times. The phenol disappearance rates increased with the amount of catalyst. The influence of the amount of catalyst on the addition of formaldehyde is reflected in the disappearance of formaldehyde and phenol for every resol analyzed.

As a consequence of the consumption of reactants, several addition products were formed. The evolution of 2-hydroxymethylphenol (2-HMP) during synthesis is shown in Fig. 3. An increase of the amount of triethylamine accelerates the rates of reactants consumption and therefore the rates of 2-HMP formation. Increasing the amount of catalyst, the formation of 2-HMP became faster. Every prepolymer, except R/20, reached similar maximum concentration values, but afterwards the consumption was controlled by the amount of catalyst. R/4.3 shows the higher final concentration, and R/pH8.36 and R/pH8.23 the lowest, the latter two showing similar evolutions. It is worth noting the different behavior of R/20, whose formaldehyde solution was not adjusted to pH = 7.0 by sodium hydroxide before synthesis as for the rest of the resols.

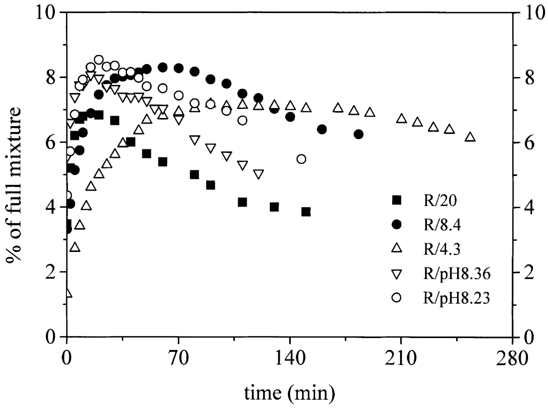

Fig. 4. Evolution of 4-hydroxymethylphenol (4-HMP) during synthesis of resols.

Thus, although R/20 shows similar formation rate and time needed to reach the maximum concentration as the ones shown by resols with the same amount of catalyst but varying initial pH, the maximum and final concentrations were higher. The first formaldehyde addition is more *ortho* directed in comparison to the other resols. The absence of hydroxyl groups coming from the sodium hydroxide could give rise to triethylamine participating in the addition reaction forming an intermediate state with phenol and formaldehyde, as it is known to be formed with other catalyst types [10–16].

It can be stated for R/pH8.36 and R/pH8.23, that the effect of the same amount of triethylamine (20.0 g) is reduced by the presence of OH groups, which could form phenolate ions favoring the addition onto the *para* sites of the rings.

The 4-hydroxymethylphenol (4-HMP) evolution curves showed in Fig. 4 are similar to those analyzed for 2-HMP. The higher the amount of catalyst added, the shorter the condensation time needed to reach maximum concentration and faster the formation rates. The maximum concentrations reached for all the resols were similar, except for R/20, which reached a lower value. Both R/pH8.36 and R/pH8.23 showed the lowest final concentrations due to the higher amount of catalyst present gave rise to further consumption of 4-HMP. Among these three prepolymers synthesized with 20.0 g of triethylamine, R/20 showed the lower maximum concentration. As discussed above, the *ortho* directing properties of triethylamine and absence of OH groups gave rise to the lower addition onto the *para* site.

The evolution of second and third formaldehyde addition products was also followed by liquid chromatography and their evolutions are depicted in Figs. 5 and 6. The curves corresponding to the evolution of 2,6-dihydroxymethylphenol (2,6-DHMP) can be analyzed in Fig. 5. The kinetic effect of the amount of catalyst is clearly marked. The formation of 2,6-DHMP for R/4.3 and R/8.4 did not start at zero time, it was delayed for several minutes. Again, R/20 showed the higher maximum concentration indicating the *ortho* directed addition occurring for this resol. R/pH8.36 also showed a high maximum value attributable to the high amount of triethylamine employed. Anyway, the well known high reactivity of the *para* position left free on 2,6-DHMP, made its formation very low and the further consumption almost complete.

The evolution of 2,4-dihydroxymethylphenol (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) during synthesis is shown in Fig. 6 by a unique curve because both compounds eluted together under the chromatographic conditions used.

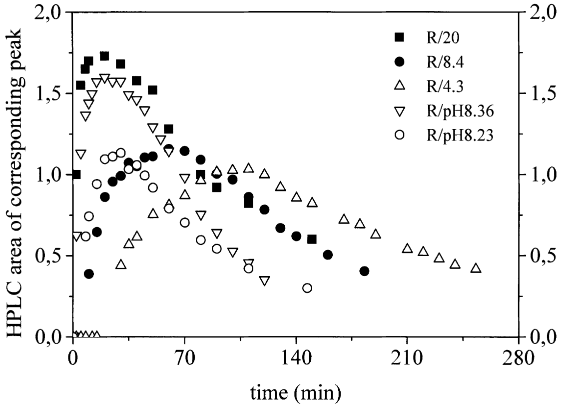

Fig. 5. Evolution of 2,6-dihydroxymethylphenol (2,6-DHMP) during synthesis of resols.

The three resols synthesized with 20.0 g of catalyst showed curves with similar rates of formation, time needed to reach the maximum concentrations, and final concentrations. There was no influence of the variation of the initial pH in the studied range. On the contrary, when the amount of catalyst added was lower the maximum concentrations delayed and became lower and the final concentrations decreased. The increase of catalyst amount favored and accelerated the addition reactions and even the condensation times were shortened. The variation of initial pH studied did not bring a drastic influence on the formation of addition products.

The final prepolymers were analyzed by ^{13}C NMR spectroscopy in DMSO-d$_6$ and acetone-d$_6$. The characteristic peak group areas or peak areas of groups were normalized by the area of the peak group corresponding to the carbon containing the phenolic hydroxyl group, i.e. *ipso* region. The residual formaldehyde left on the prepolymers is shown in Fig. 7. The free formaldehyde present decreased with the added amount of triethylamine, corroborating the chromatographic values discussed above. The highest formaldehyde concentration shown in Fig. 7 corresponds to R/4.3, followed by R/8.4, and afterwards by the prepolymers synthesized with 20.0 g of catalyst. With respect to the influence of the initial pH, only a slight decrease of formaldehyde concentration with pH was observed.

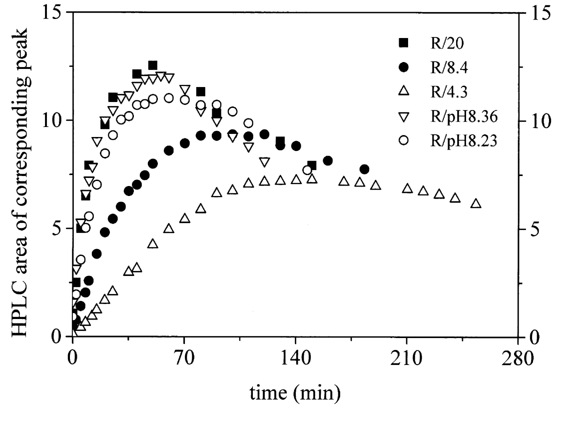

Fig. 6. Evolution of 2,4-dihydroxymethylphenol (2,4-DHMP) and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) during synthesis of resols.

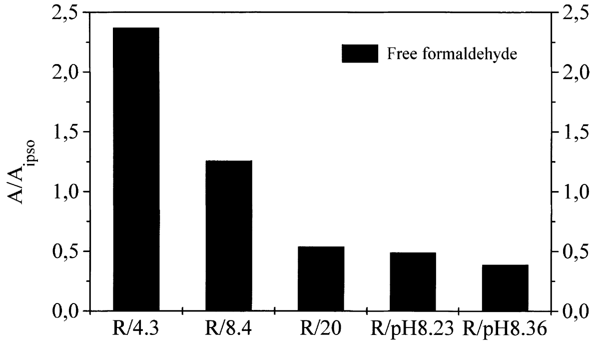

Fig. 7. Formaldehyde (80–95 ppm) in prepolymers.

The relative amount of *ortho* and *para* phenolic positions left free can be analyzed in Fig. 8. As a consequence of the higher addition reactions that occurred increasing the amount of catalyst, the free *ortho* and *para* sites were reduced. Therefore, prepolymers with higher substitution were formed. The amount of free reactive positions observed for resins prepared with varying initial pH did not show any evident trend, thus no influence can be concluded. In order to complete the work presented here, further studies covering a wider pH range, as it was published in the literature for other catalysts [8,9], would be necessary.

4. Conclusions

The influence of the initial pH and the amount of added triethylamine as catalyst in the synthesis of resol resins were analyzed by two techniques (HPLC and ^{13}C NMR) obtaining complementary results. The amount of catalyst kinetically and mechanistically influences the formation of the resol prepolymers. Shorter condensation times, faster reaction rates, and higher advancement in polymerization are reached increasing the amount of triethylamine used.

With respect to the analyzed range of pH, the study did

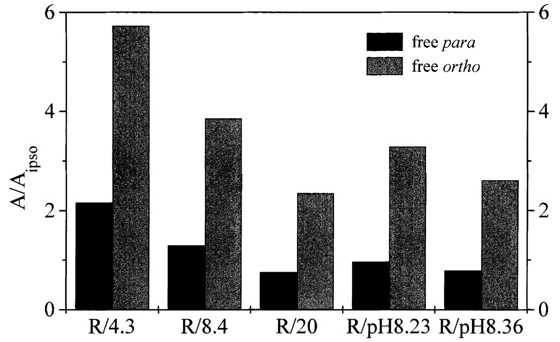

Fig. 8. Free *ortho* and *para* positions left unreacted in prepolymers.

not show clear differences either in the reactants and products evolution or in the final prepolymers. In order to complete the work presented here, further studies covering a wider pH range would be necessary.

The special synthesis conditions employed in the preparation of R/20 have allowed us to obtain interesting conclusions. R/20 showed mechanistic differences attributable to the absence of OH groups coming from NaOH for the other resols in the formaldehyde solution used in the synthesis. It could be stated that two mechanisms for the addition of formaldehyde occurred simultaneously. On the one hand, hydroxyl groups added for the pH adjusting of formaldehyde were used for neutralizing the formic acid contained in the formaldehyde solution, as well as for the formation of phenolate ions which would favor addition onto *para* phenolic positions. On the other hand, formaldehyde, phenol, and triethylamine could be involved in the formation of an intermediate transition state, favoring addition onto *ortho* sites, due to the *ortho* directing properties of triethylamine.

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