

Polymerization of Resole Resins with Several Formaldehyde/Phenol Molar Ratios: Amine Catalysts Against Sodium Hydroxide Catalysts

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ABSTRACT: Triethylamine and sodium hydroxide catalyzed phenol/formaldehyde resole resins were investigated in terms of their behavior during both addition and polymerization reactions. Amine-catalyzed prepolymers were mainly ortho-substituted structures, whereas the sodium hydroxide catalyst directed the addition reaction to para reactive sites. During polymerization, triethylamine led to dimethylene ether bridges as the principal linkages between aromatic structures, increasing their final concentration as the starting hydroxymethyl group concentration increased. In contrast, the use of sodium hydroxide reduced dramatically the dimethylene ether bridge concentration, favoring methylene bridge formation. The influence of hydroxyl ions on the stabil-

ity of quinone methide intermediates could be the reason for those differences. Despite the formation of dimethylene ether bridges, at higher curing temperatures, more oxidized groups started to appear in cured resoles when the formaldehyde/phenol molar ratio was higher. The presence of infrared bands associated with quinones, aldehydes, and/or carbonyl groups, mainly in high-formaldehyde-content resins, could indicate a direct oxidation process from dimethylene ether bridges and/or residual hydroxymethyl groups, without the formation of methylene bridges. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2623–2631, 2006

Key words: catalysts; FTIR; polycondensation; resins

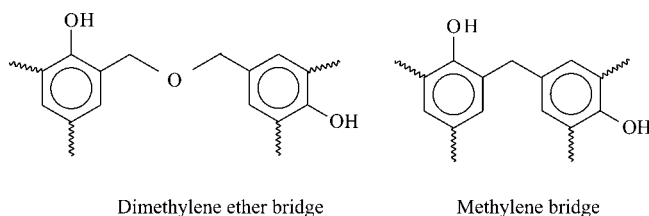
INTRODUCTION

The need for new materials with specific properties has led to the development of better and cheaper polymer composites. Besides, the development and application of polymeric composite materials filled with nanosized compounds (essentially inorganic silica fillers or natural microfibers)^{1–3} have attracted both scientific and industrial interest and renewed interest in the chemistry and final behavior of phenol–formaldehyde resins as matrices in those nanocomposites. To achieve constancy in resole properties, the processing control of the materials becomes of interest; this requires accurate knowledge of the polymerization mechanism as a function of the applied conditions. A resole resin is formed from the reaction of phenol with formaldehyde, usually under basic conditions, with formaldehyde/phenol (F/P) ratios higher than 1. Under such conditions, exothermic reactions occur, both parallel and consecutively,

and give initially monohydroxymethylphenols and then dihydroxymethylphenols and trihydroxymethylphenols as well as their hemiformal derivatives. These products undergo condensation reactions that yield diphenylmethane derivatives containing a higher number of aromatic rings connected by means of methylene bridges or dimethylene ether bridges^{4,5} (Scheme 1). However, other kinds of reactions have been proposed in terms of the synthesis and polymerization conditions.⁶ Although recently work related to the initial reaction of formaldehyde with phenol has been published,^{7,8} little information is available on the processes occurring during the subsequent curing of the resin.^{9–11} Quinone methides have been proposed as key intermediates in the curing (condensation) of phenol–formaldehyde polymers.^{4,12,13} The intramolecular dehydration of methylol or its dimeric anhydro form leads to quinone methides as resonance hybrids between quinoid and benzenoid structures (Scheme 2). The most common catalysts of phenol–formaldehyde resole synthesis are sodium, potassium, and lithium hydroxides; rarely, hydroxides of divalent metals are used. Also, carbonates (sodium carbonate) and oxides (calcium or magnesium oxides) can be used. Tertiary amines, in particular triethylamine, were recently claimed as catalysts for the resole synthesis.^{14,15}

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Scheme 1 Principal bridge types of polycondensation-cured resoles.

In this work, triethylamine as a catalyst for resole synthesis, compared with sodium hydroxide, is analyzed. The differences between the two catalysts in terms of the addition reaction pathway and formation of main linkages between aromatic rings, methylene or dimethylene ether, are studied.

EXPERIMENTAL

The synthesis of the prepolymers was carried out at Bakelite Ibérica S.A. (Hernani, Spain). Phenol (99% purity) and formaldehyde in a 50% aqueous solution were the commercial products employed for the synthesis of the prepolymers. The concentration of the formaldehyde solution was reduced to 37% for better stability of the solution. The resoles with different F/P ratios (1.0–2.2) were synthesized with a fixed quantity of triethylamine (99%) as the catalyst, with a constant catalyst/phenol ratio. This fact produced a decrease in the initial pH for the highest F/P ratio resins because of the acidification effect of the formaldehyde in the initial mixture. However, the effect of different pHs in a narrow range on the synthesized resins was quite small.¹⁵ These prepolymers are named RT(F/P) in this study. Another prepolymer was synthesized with sodium hydroxide (50%) as the catalyst, with the pH of the initial mixture fixed at 8.0 and with an F/P ratio of 1.8. This prepolymer is named RN1.8. The different prepolymers were condensed at 80°C until they showed 1/1 (g/g) dilutability in water. Then, they were distilled *in vacuo* at 45–48°C until a solid concentration of 72–79%. The samples were stored at –20°C until they were analyzed.

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet Nexus spectrometer (Thermo Electron Corp., Alcoberdas, Madrid, Spain). The acquisition conditions were a spectral range of 400–4000 cm^{-1} , 10 scans, and a resolution of 4 cm^{-1} . The neat resin samples were extended in KBr pellets. The curing process was carried out with resin samples between two KBr pellets, to avoid evaporation, at 110, 130, and 150°C. The free phenol concentration in the resoles was measured with an HP 5890 series II gas chromatograph (Las Rozas, Madrid, Spain) with an HP 3396A integrator. The detector was a flame-ionization detector, and helium was the carrier gas. HP 20M (Carbowax 20M) high-performance columns were used

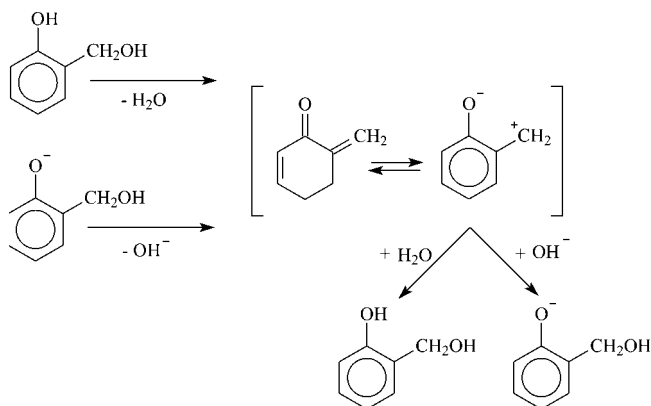
(0.2 μm wide and 50 m long with a 0.2-mm internal diameter). The samples were prepared in a methanol solution with *p*-cresol as the internal patron. The prepolymers were analyzed in a PerkinElmer gel permeation chromatograph (Tres Contos, Madrid, Spain). Ultraviolet (LC 295) and refraction-index detectors (LC-30) (Perkin-Elmer, Tres Contos, Madrid, Spain) were used with a 250 pump and a 900 interphase. The solvent was tetrahydrofuran at 0.5 mL/min. Three alpha TSKgel columns prepared for 10^2 – 10^6 g/mol molecular weight detection were used.

RESULTS AND DISCUSSION

Characterization of the prepolymers

Table I shows the results of the physicochemical analysis of the synthesized and distilled prepolymers. The viscosity ($\eta_{25^\circ\text{C}}$), refraction index (n_D), density ($\rho_{20^\circ\text{C}}$), solubility in water, pH, and water and solid contents are shown. Figure 1 shows the residual contents of phenol and formaldehyde of the different prepolymers. With an increasing F/P molar ratio, the free phenol percentage decreases, whereas the formaldehyde concentration increases. The use of sodium hydroxide as a catalyst increases the concentrations of free phenol and formaldehyde in the prepolymer for the same F/P ratio. It seems that in triethylamine resins, the addition reaction is favored, in contrast to the NaOH resole resin.

FTIR spectra of the synthesized prepolymers are shown in Figure 2. FTIR spectroscopy was used for a complete characterization of the prepolymers. Table II lists the characteristic vibration bands of the resole resins. The band at 1610 cm^{-1} corresponds to the tension vibration of C=C double bonds in aromatic rings. Depending on the type and level of substitution in the aromatic ring, the shoulder at 1595 cm^{-1} appears more or less intense. Because of these changes, the area under the whole C=C signal was preferred to be used as reference (A_R) for the different calculations.



Scheme 2 Quinone methide or phenoxide ion intermediates as a function of the reaction conditions.

TABLE I
Properties of the Synthesized Prepolymers

	RT1.0	RT1.4	RT1.8	RT2.2	RN1.8
$\eta_{25^\circ\text{C}}$ (mPa s)	165	432	550	621	560
n_D	1.5522	1.5592	1.5612	1.5587	1.5553
$\rho_{20^\circ\text{C}}$ (g/cm ³)	1.183	1.212	1.214	1.206	1.228
Water solubility	1.48	1.82	1.94	2.21	1.85
pH	7.70	7.53	7.50	7.45	7.79
H ₂ O (wt %)	8.67	8.75	5.48	6.64	9.123
Solid content (wt %)	72.2	78.8	78.4	73.8	78.1

The bands associated with the tension vibration of the C—O bond in hydroxymethyl reactive groups in the resole resin (A_M) appear between 1100 and 950 cm⁻¹, depending on the number and position of the substitutions and the hydrogen bond created between them or with the phenolic hydroxyl group.^{16,17} Figure 3 shows the calculated relative areas of the hydroxymethyl groups attached to different reactive sites of the synthesized prepolymers, with the 1610-cm⁻¹ band area used as a reference. An increase in the F/P molar ratio leads to an increase in the concentration of hydroxymethyl groups attached to the aromatic ring, as previously reported by Holopainen et al.¹⁸ The resole resin catalyzed with sodium hydroxide, RN1.8, presents fewer reactive groups than RT1.8. The bands corresponding to the deformation vibration of aromatic C—H studied in the 900–650-cm⁻¹ range (Fig. 4) show that an excess of formaldehyde in the mixture leads to a decrease in the peak area (A) of the disubstituted *o*-hydroxymethylphenol and *p*-hydroxymethylphenol compound concentrations [2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP)]. An increase in the amount of 2,4,6-trihydroxymethylphenol reveals a more substituted aromatic structure in the prepolymer synthesized with the highest F/P molar ratio. The use of triethylamine as the catalyst favors the formation of ortho-substituted rings in com-

parison with the para preference in the case of the sodium hydroxide catalyst.¹⁵ Figure 5 shows the ratio of the hydroxymethyl groups in the ortho and para positions. Increasing the initial formaldehyde concentration in the mixture increases the addition in the ortho reactive position. Holopainen et al.¹⁸ in their study on sodium hydroxide prepolymers also concluded that a higher F/P molar ratio leads to an increase in the addition in ortho positions, whereas the addition in para positions is not affected. The catalyst-type effect is clearer regarding the differences in the ortho/para ratio between RT1.8 and RN1.8 resole resins. Kaředkowski and Hetper¹⁹ concluded that the triethylamine catalyst favors the second addition at the ortho position, leading to the formation of 2,6-hydroxymethylphenols.

Gel permeation chromatography was used for the molecular weight study of the different triethylamine prepolymers. Because of the interaction with the solvent and the inter and intra hydrogen bonds created, a complete characterization of the resole resin molecular weight is extremely difficult.²⁰ However, a qualitative approximation of the polydispersity index for each prepolymer is possible¹⁷ (Fig. 6). The results show that the polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] increases with the F/P molar ratio until a maximum

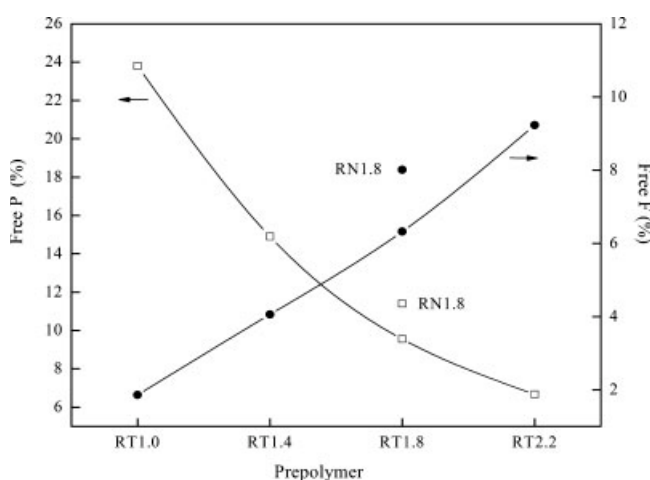


Figure 1 Free phenol (P) and formaldehyde (F) in the prepolymers.

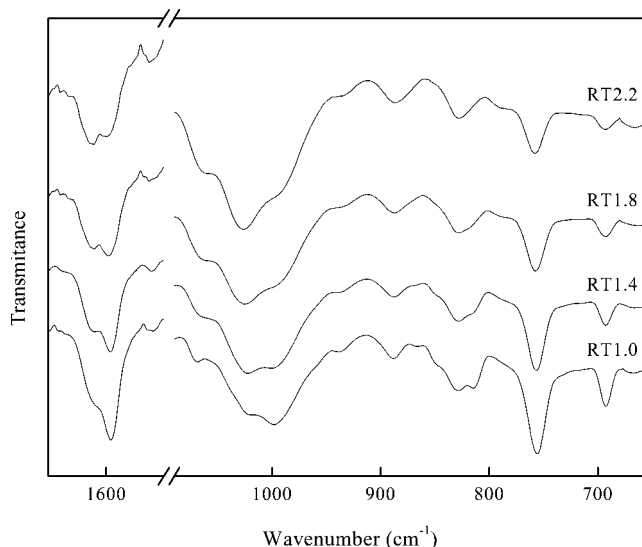


Figure 2 FTIR spectra of the different prepolymers.

TABLE II
FTIR Characteristic Vibration Bands in the Resole Prepolymers

Wave number (cm^{-1})	Vibration	Functional Group
3550–3450	ν (OH), free	Phenol and hydroxymethyl
3400–3300	ν (OH), bonded	Phenol and hydroxymethyl
3060	ν (CH)	Aromatic
3020	ν (CH)	Aromatic
2980	ν_{ip} (CH_2)	Aliphatic
2860	ν_{op} (CH_2)	Aliphatic
1610–1595	ν (C=C)	Aromatic ring
1500	ν (C=C)	Aromatic ring
1470	d (CH_2)	Aliphatic
1450	ν (C=C)	Aromatic ring
1370	d_{ip} (OH)	Phenolic
1240	ν (C–O)	Phenolic
1160	d_{ip} (CH)	Aromatic
1100	d_{ip} (CH)	Aromatic
1060	ν (C–O)	Dimethylene ether bridge
1025–998	ν (C–O)	Hydroxymethyl
888	d_{op} (CH)	H (tri)
826	d_{op} (CH)	2H (para)
790	d_{op} (CH)	3H
757	d_{op} (CH)	4H (ortho)
691	d_{op} (CH)	5H (phenol)

value of $F/P = 1.4$ – 1.8 for the resole. A further increase in the formaldehyde concentration reduces the prepolymer heterogeneity.^{17,18,21}

Polymerization of the prepolymers

The polymerization of the synthesized polymers was studied with FTIR spectroscopy. Figure 7 presents the evolution during the polymerization of FTIR spectra of the RT1.8 prepolymer. With $t_0 = 0$ min and $t_f = 120$ min of reaction at 110°C , during the polymerization, primary alcohols disappear (998 and 1025 cm^{-1}), and dimethylene ether type linkages appear (1060 cm^{-1}). At the same time, substitution bands change during

the reaction as a result of both the formation of methylene bridges and new addition reactions of the liberated formaldehyde. It is worth noting the disappearance of ortho-substituted species at 757 cm^{-1} . For determining the value of the signal of the C–O linkage of primary alcohols, the areas of the bands at 998 and 1025 cm^{-1} were added, and we were sure to take into account the different types of hydroxymethyl groups (A_M^1 and A_M^2). Deconvolution was used for the evaluation of the area of the dimethylene ether bridge band (A_E) because of the proximity of this band to reactive hydroxymethyl group bands. As shown in Figure 8, bands 1 and 2, associated with hydroxymethyl groups, decrease during polymerization, appearing as a single signal at the

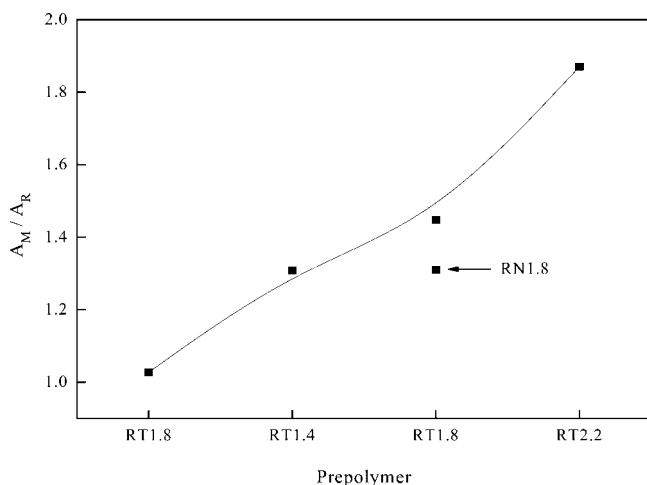


Figure 3 Hydroxymethyl group concentration as a function of the F/P ratio and catalyst type.

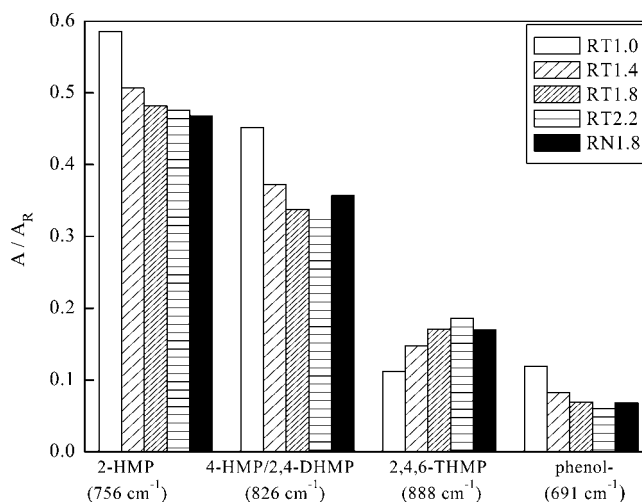


Figure 4 Substitution degree of resoles calculated by FTIR spectroscopy.

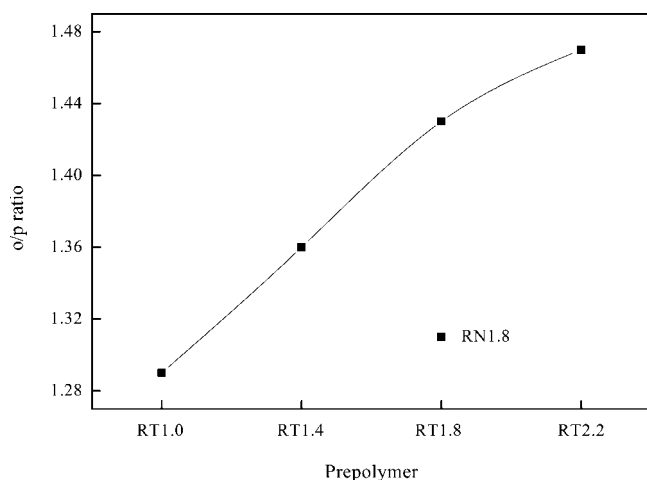


Figure 5 Ortho/para (o/p) ratio for the synthesized resole resins.

end of the reaction (5). The signal of the dimethylene ether linkage vibration (3) increases during the reaction without any displacement in the wave number (4). Derived from the deconvolution and with the band near 1610 cm^{-1} as a reference, the concentrations of dimethylene ether ($[E]_t$) and hydroxymethyl groups ($[M]_t$) versus the reaction time can be calculated as follows:

$$[E]_t \propto \left[\frac{A_E(1060\text{ cm}^{-1})_t}{A_R(1610\text{ cm}^{-1})_t} \right] \quad (1)$$

$$[M]_t \propto \left[\frac{(A_M^1(998\text{ cm}^{-1})_t + A_M^2(1025\text{ cm}^{-1})_t)}{A_R(1610\text{ cm}^{-1})_t} \right] \quad (2)$$

Figure 9 presents the disappearance of hydroxymethyl groups during the polymerization at 110°C for the different prepolymers synthesized with tri-

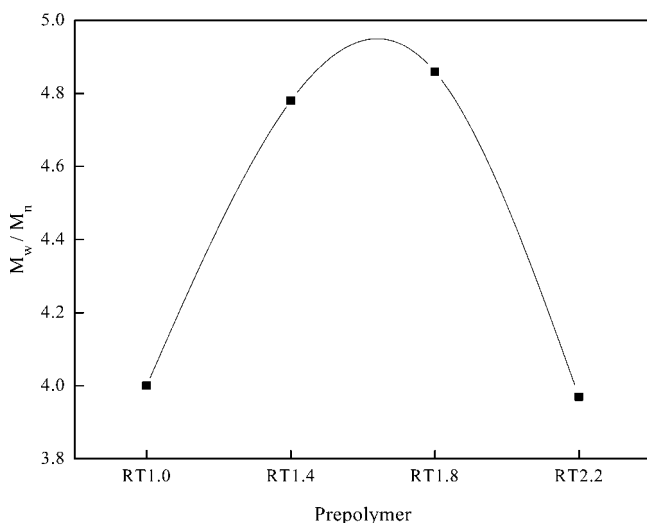


Figure 6 Polydispersity index as a function of the F/P ratio.

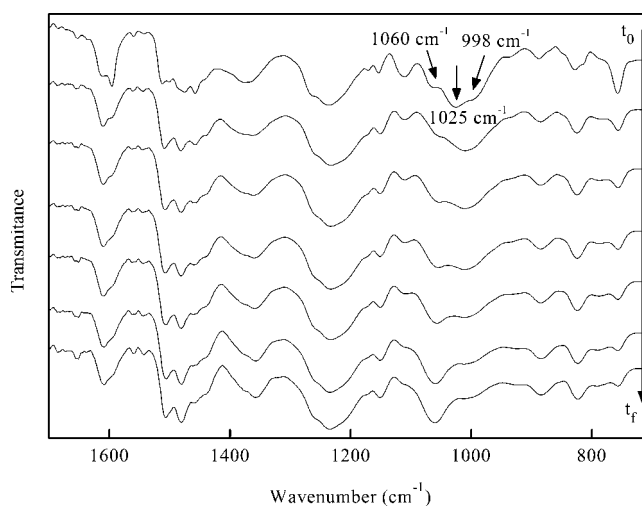


Figure 7 Evolution of the FTIR spectrum during the polymerization of RT1.8 at 110°C .

ethylamine and with several F/P molar ratios. As mentioned previously, the initial concentration of the hydroxymethyl groups increases in the presence of an excess of formaldehyde. For prepolymers with the lowest F/P molar ratio (RT1.0 and RT1.4), the concentration of reactive alcohols slightly increases during the earlier stages of the reaction. It seems that phenol and reactive aromatic sites are available in the mixture to form new reactive hydroxymethyl groups by addition at the relatively low polymerization temperature used. Despite free formaldehyde existing in the prepolymers with higher formaldehyde contents, for them this does not occur because of the absence of free phenolic reactive sites. Indeed, for high F/P molar ratios, the main reaction is condensation without further addition reactions.

The formation of dimethylene ether type bridges during the polymerizations of different prepolymers

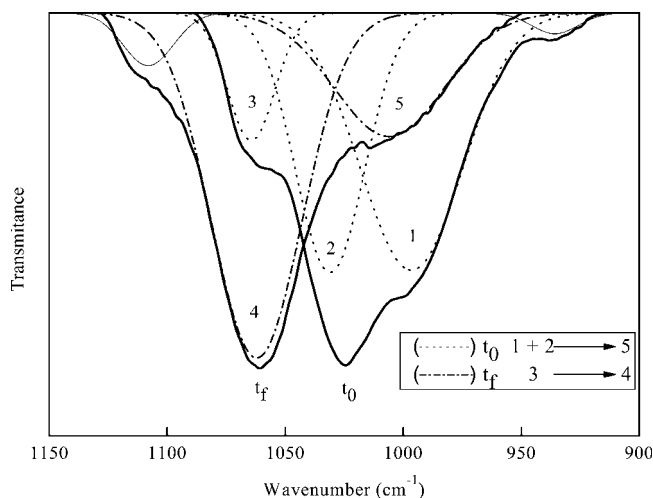


Figure 8 Deconvolution of the ether and hydroxymethyl signals in FTIR.

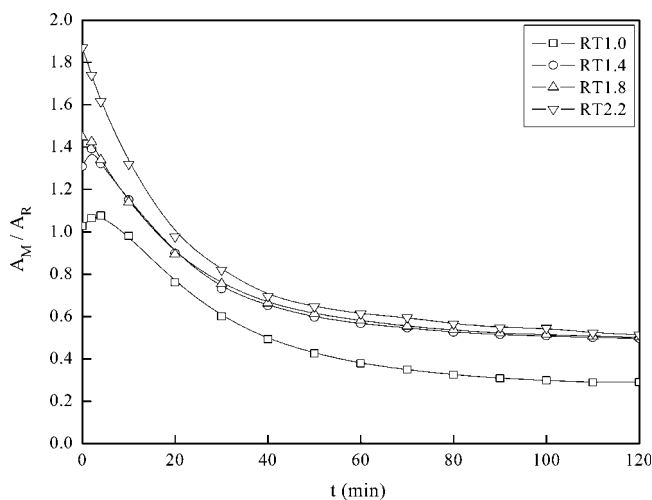


Figure 9 Disappearance of hydroxymethyl groups during polymerization at 110°C for different triethylamine-catalyzed prepolymers.

was studied with the area of the band at 1060 cm^{-1} , and it is presented in Figure 10. The initial concentration of reactive hydroxymethyl groups does not appear to affect the rate of formation of dimethylene ether linkages. Indeed, resoles with an F/P molar ratio above 1.0 show similar rates of formation of dimethylene ether linkages. It seems that above a minimum concentration of hydroxymethyl reactive groups, the formation of dimethylene ether bridges is a quick reaction, and small differences in the hydroxymethyl group concentration do not affect the reaction rate. In the case of the RT1.0 prepolymer, the low concentration of formaldehyde affects the rate of reaction. Only a few results have been reported about the formation of dimethylene ether linkages in resole resins because of the complexity of the process.^{15,22} Lenghaus et al.²² studied the condensation reaction of a 2-hydroxymethyl-4,6-dimethylphenol model compound at 120°C by $^1\text{H-NMR}$. The reaction was carried out in the melt without a solvent. They concluded that the dimethylene ether linkage formation occurred at a higher rate than the methylene bridge formation. Furthermore, their results indicate that the hydroxymethyl group concentration does not affect the main reaction rate until a minimum number of methylol groups. However, the concentration of those groups is important for the final concentration of dimethylene ether bridges formed (Fig. 10). As the initial F/P molar ratio increases, the final concentration of dimethylene ether bridges obtained also increases. The formation of dimethylene ether bridges is favored in high-formaldehyde-content prepolymers, in which few free ortho and para positions exist. Those results are in agreement with those reported by Astarloa¹⁵ from a study of dimethylene ether formation during the synthesis of amine-catalyzed resoles. Christjanson et al.²³ studied the melt autocondensation reaction of 2-HMP and 4-HMP model compounds by $^1\text{H-NMR}$, without

any catalyst. They concluded that the hydroxymethyl groups attached at the ortho positions react preferentially to form dimethylene ether type bridges, whereas the *para*-hydroxymethyl groups form mainly methylene bridges. The cocondensation of *ortho*- and *para*-hydroxymethylphenols with phenol leads to a decrease in the dimethylene ether bridge concentration and also to a decrease in the global reaction rate. It can be concluded that in the polymerization of triethylamine-catalyzed resole prepolymers, the formation of dimethylene ether bridges is the main reaction at the temperature and pH conditions used in this work.

The catalyst used for the synthesis of the prepolymers can also affect the polymerization pathway as a result of its influence on the formation of reactive ortho or para free sites. In this work, the effects of the different groups formed during the synthesis have been studied by a direct comparison of the polymerization at 110°C of RT1.8 and RN1.8 prepolymers. Besides, the influence of the catalyst on the polymerization has also been studied by the addition of 50% sodium hydroxide catalyst to the RT1.8 triethylamine prepolymer until pH was 8.5 or 9.0. The resulting resole resins are named RTN(8.5) and RTN(9.0), respectively. The evolution of dimethylene ether type bridges in those prepolymers is presented in Figure 11. The formation of dimethylene ether bridges in the prepolymer catalyzed with sodium hydroxide occurs with a lower reaction rate, and the final concentration of those bridges is clearly reduced with respect to amine catalysis. The effect of the addition of sodium hydroxide to the RT1.8 prepolymer is stronger with an increase in the resulting pH. The achieved concentration of dimethylene ether bridges in resole RTN(9.0) is reduced four times with respect to the value for RT1.8. Sodium hydroxide has been the most often used catalyst for the synthesis of resole resins, and for this reason, the formation of

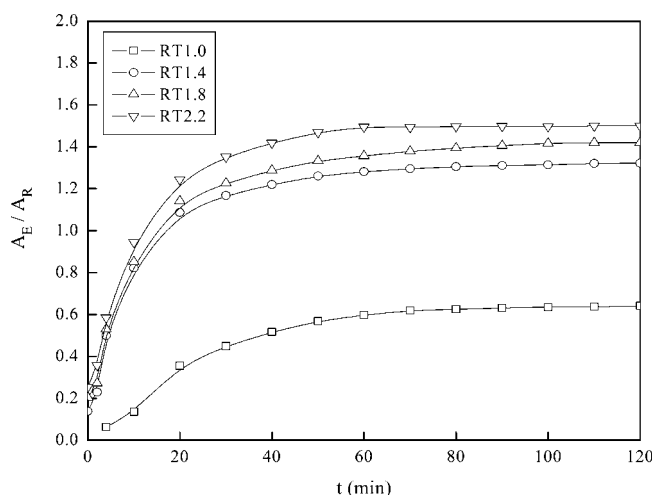


Figure 10 Evolution of dimethylene ether type bridges during polymerization at 110°C for different triethylamine-catalyzed prepolymers.

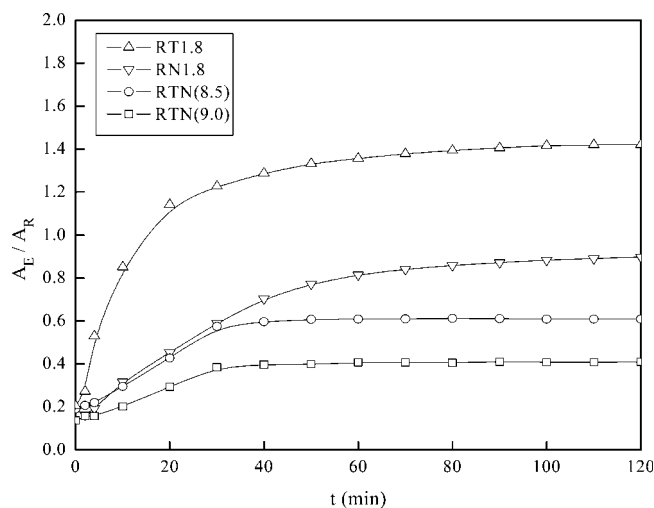


Figure 11 Evolution of dimethylene ether type bridges during polymerization at 110°C for different catalyst-type prepolymers and pH conditions.

dimethylene ether type bridges during polymerization has been not thoroughly studied, as methylene bridge formation appears to be the main reaction. Some authors have studied triethylamine as a resole catalyst, concluding that it favors dimethylene ether formation.^{15,24} Christjanson et al.²³ reported the preference of sodium hydroxide for methylene formation, using model compound autocondensation, in comparison with polymerization in the absence of a catalyst or in the presence of $ZnAc_2$ and C_6H_5COOH .

The aforementioned differences can also be detected in the obtained FTIR spectra for the different prepolymers at the end of polymerization (Fig. 12). The dimethylene ether/methylene final ratio has been calculated by means of the areas of the bands at 1060 and

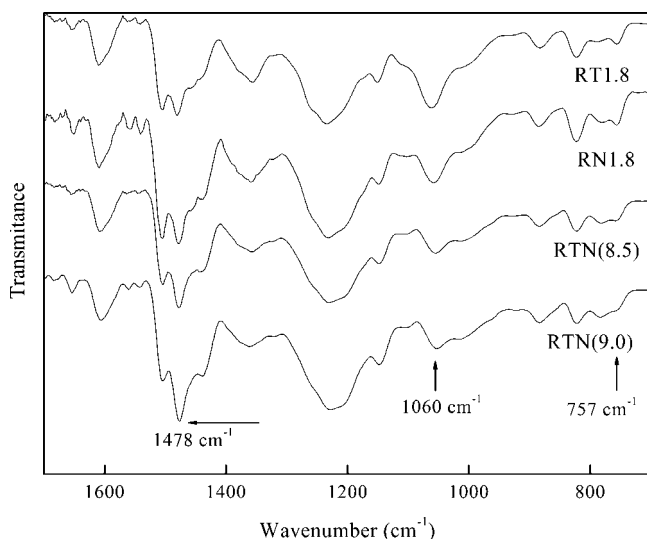


Figure 12 Final FTIR spectra of different prepolymers polymerized at 110°C.

TABLE III
 $A_E/A_{(-CH_2-)}$ Ratios in Resoles Cured at 110°C and Catalyzed with Triethylamine and Sodium Hydroxide

Prepolymer	$A_{(-CH_2-)} / A_R$	$A_E / A_{(-CH_2-)}$
RT1.8	0.24	5.92
RN1.8	0.31	2.89
RTN (8.5)	0.51	1.19
RTN (9.0)	0.59	0.69

1478 cm^{-1} (A_{-CH_2-}) with the 1610-cm^{-1} band as a reference (Table III). The preference of the reaction pathway, defined by the catalyst used, determines the characteristics of the final product. The absorption bands of associated and free hydroxyl groups are shown in Figure 13. Intra- and inter-hydrogen-bonded hydroxyl groups appear in the $3300\text{--}3400\text{-cm}^{-1}$ range. Free hydroxyl groups absorb between 3450 and 3550 cm^{-1} . The prepolymer formed with sodium hydroxide presents a higher concentration of not bonded, free hydroxyl groups. The triethylamine-synthesized prepolymer has a higher capacity for hydrogen bonding as a result of the existence of more dimethylene ether bridges. In other words, triethylamine favors addition in free ortho reactive sites and the posterior reaction to dimethylene ether bridges. Taking into account both that quinone methide intermediates are formed preferentially in ortho positions through an intramolecular loss of water²² and that they more commonly react to form dimethylene ether bridges,²⁵ we believe that this is the reaction pathway in triethylamine-catalyzed prepolymers under the alkalinity and temperature conditions used. In the case of sodium hydroxide, the quinone intermediate would be unstable because of the high concentration of OH^- ions, favoring the phenoxide ion pathway. This pathway is preferred as nucleo-

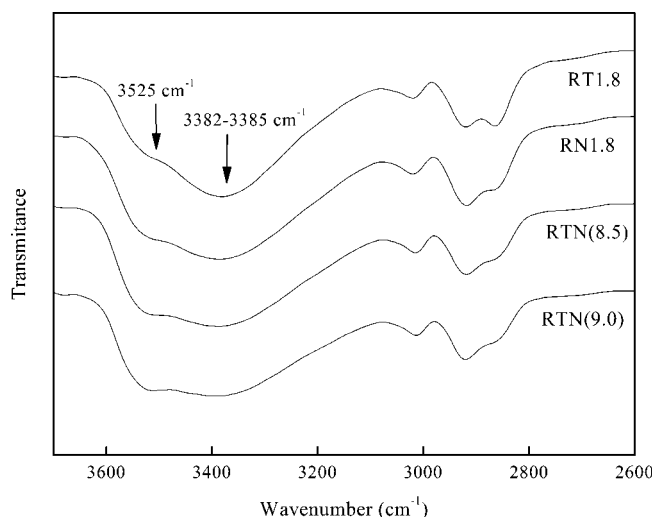


Figure 13 Hydrogen-type bridges in different prepolymers polymerized at 110°C.

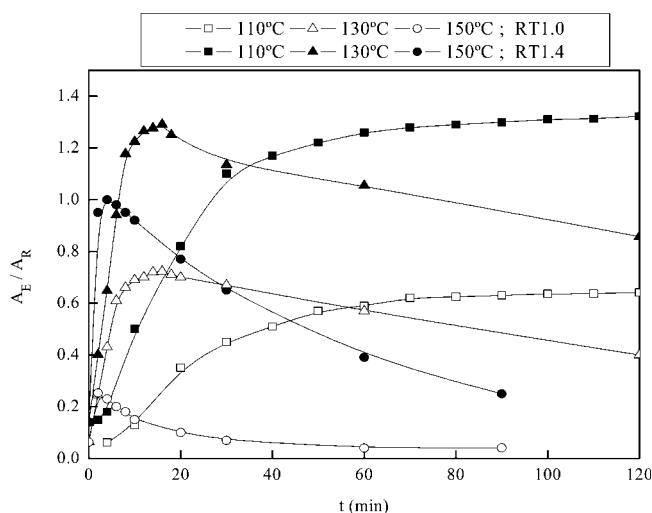


Figure 14 Evolution of dimethylene ether type bridges for RT1.4 and RT1.0 at several polymerization temperatures.

philic phenolic nuclei are strengthened, by the ionization of phenol, to form phenoxide ions. Consequently, under high-alkalinity conditions, the methylene bridge formation is favored by means of the formation of phenoxide ions (Scheme 2).

With the aim of reducing as much as possible gelation and vitrification times, usually the polymerization temperature of resole prepolymers is higher than 110°C when no catalyst is used. The temperature could have a great effect in the formation and further stability of dimethylene ether bridges. Figure 14 shows the evolution of dimethylene ether bridges at several polymerization temperatures for the RT1.4 and RT1.0 resole prepolymers. Dimethylene ether bridge formation occurs at all studied temperatures, the achieved final concentration becoming higher as the F/P molar ratio increases. The reaction rate increases with the temperature. However, the final concentration of dimethylene

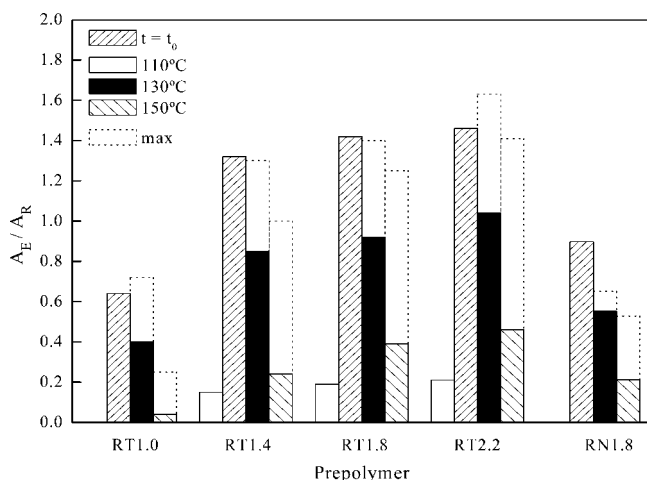


Figure 15 Dimethylene ether bridge concentrations in resoles cured at several temperatures.

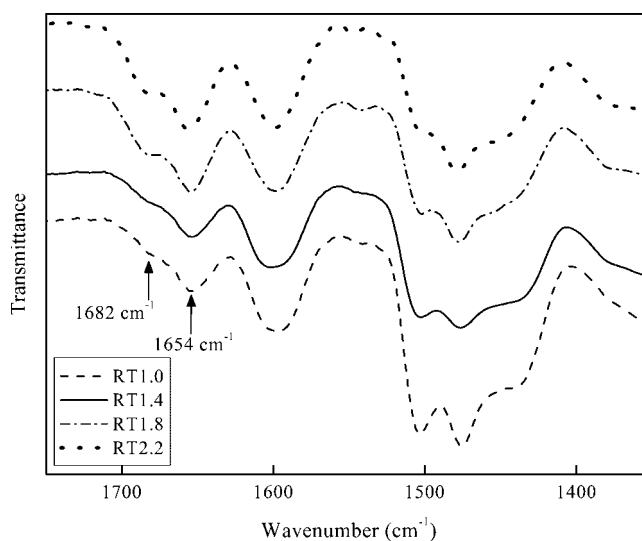


Figure 16 Final FTIR spectra of resoles cured at 150°C.

ether bridges is reduced as the polymerization temperature increases for both F/P molar ratios. Above 110°C, there is a maximum in the concentration of formed dimethylene ether bridges, which thereafter disappears with the polymerization time. The disappearance rate increases as the reaction temperature increases. Figure 15 shows the maximum and final concentrations of dimethylene ether bridges for different prepolymers at several temperatures. Resoles cured at high temperatures do not present significant concentrations of dimethylene ether bridges, above all in prepolymers synthesized with low F/P molar ratios. Despite the lack of publications related to the evolution of dimethylene ether bridges, several authors have maintained that methylene bridges are formed from dimethylene ether bridges at high temperatures, with the liberation of formaldehyde. However, dimethylene ether bridges also could be responsible for the presence of oxidation groups in resoles cured at high temperatures. Figure 16 shows the final FTIR spectra of several resoles. The bands located at 1654 and 1682 cm^{-1} are associated with benzophenone-type bridges derived from the oxidation of methylene groups and quinone, aldehyde, and/or carbonyl groups formed as a result of the cleavage of the main chain, respectively. However, the fact that more oxidized groups appear for higher F/P molar ratio resoles could indicate that a direct transformation of dimethylene ether bridges and/or hydroxymethyl groups to quinone, aldehyde, and/or carbonyl groups occurs, thus preventing methylene bridge formation between aromatic structures.²²

CONCLUSIONS

Both the synthesis of resole prepolymers and the further polymerization reaction have been investigated in

terms of the differences associated with the effects of the initial monomer molar ratio and the catalyst used. A higher initial F/P molar ratio leads to a final higher concentration of free formaldehyde in the prepolymer. The triethylamine catalyst favors the addition reaction toward sodium hydroxide for the same F/P molar ratio resole resin. For the amine catalyst, the addition reaction mainly occurs in ortho reactive sites, whereas NaOH-catalyzed prepolymers present higher addition in para positions. During the polymerization, the effects of both the F/P molar ratio and catalyst are high. Prepolymers catalyzed with triethylamine lead to mainly dimethylene ether type bridges at low temperatures and weak pHs. Even though the rate of reaction does not depend on the starting hydroxymethyl concentration, the final dimethylene ether bridge concentration increases as the hydroxymethyl group concentration does. In contrast, prepolymers catalyzed with sodium hydroxide mainly form methylene-type bridges, leading to high methylene/dimethylene ether ratios. The influence of the hydroxyl ions on the stability of a possible intermediate quinone methide could be the reason for those differences. However, resoles cured at higher temperatures do not present a high concentration of dimethylene ether type bridges because of the evolution of those groups at these temperatures. Under those conditions, oxidized groups start to appear in cured resoles, the oxidation being more evident at high F/P molar ratios. The presence of bands associated with quinone, aldehyde, and/or carbonyl groups mainly in high-formaldehyde-content resins could indicate a direct oxidation process from dimethylene ether bridges and/or residual hydroxymethyl groups, without the formation of methylene bridges.

References

1. Xu, Y.; Brittain, W. J.; Xue, C.; Eby, R. K. *Polymer* 2004, 45, 3735.
2. Azizi Samir, M. A. S.; Alloin, F.; Sanchez, J.-I.; Dufresne, A. *Macromolecules* 2004, 37, 4839.
3. Mamalis, A. G.; Vogtländer, L. O. G.; Markopoulos, A. *Precision Eng* 2004, 28, 16.
4. Knop, P. W.; Pilato, L. A. *Phenolic Resins*; Springer-Verlag: Berlin, 1985.
5. Drumm, M. F.; LeBlanc, J. R. In *Step-Growth Polymerizations*; Solomon, D. H., Ed.; Marcel Dekker: New York, 1972.
6. Maciel, G. E.; Chuang, I.-S.; Gollob, L. *Macromolecules* 1984, 17, 1081.
7. Grenier-Loustalot, M. F.; Larroque, S.; Grenier, P.; Leca, J. P.; Bedel, D. *Polymer* 1994, 35, 3046.
8. Grenier-Loustalot, M. F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 939.
9. Zhang, X.; Solomon, D. H. *Chem Mater* 1999, 11, 384.
10. Solomon, D. H.; Zhang, X. *Chem Mater* 1998, 10, 1833.
11. Gabilondo, N.; Echeverría, J. M.; Martín, M. D.; Mondragon, I. *High Perform Polym* 2002, 14, 415.
12. Solomon, D. H. *The Chemistry of Organic Film Formers*; Krieger: New York, 1977.
13. Jones, R. T. *J Appl Polym Sci* 1983, 21, 1801.
14. Nesterova, O. M.; Akkuratova, O. L.; Plotnikova, L. S. *Rus. Pat.* 2028313 (1995).
15. Astarloa, G. Ph.D. Thesis, Euskal Herriko Unibertsitatea, 1999.
16. Hummel, D. O.; Schöll, F. *Atlas of Polymer and Plastics Analysis*, 2nd ed.; Hanser: Munich, 1998; Part b/I, Vol. 2, p 428.
17. Manfredi, L. B. Ph.D. Thesis, Universidad Nacional de Mar del Plata, 2000.
18. Holopainen, T.; Alvilä, L.; Rainio, J.; Pakkanen, T. T. *J Appl Polym Sci* 1997, 66, 1183.
19. Kałedkowski, B.; Hetper, J. *Polymer* 2000, 41, 1679.
20. Rudin, A.; Fyfe, C.; Martin Vines, S. *J Appl Polym Sci* 1983, 28, 2611.
21. Park, B.-D.; Riedl, B.; Kim, Y.-S.; So, W. T. *J Appl Polym Sci* 2002, 83, 1415.
22. Lenghaus, K.; Qiao, G. C.; Solomon, D. H. *Polymer* 2000, 41, 1973.
23. Christjanson, P.; Köösel, A.; Suurpere, A. *Oil Shale* 1998, 15, 374.
24. King, P. W.; Mitchell, R. H.; Westwood, A. R. *J Appl Polym Sci* 1974, 18, 1117.
25. Pizzi, A.; Stephanou, A. *J Appl Polym Sci* 1993, 49, 2157.