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Pin Gao[a]; Yanfang Zhang[a]; Guangsu Huang[a]; Mengmeng Chen[a]; Jing Zheng[a]
[a] State Key Lab of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu, China

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The Variation of Composition of Resols Under Different Reaction Conditions

PIN GAO, YANFANG ZHANG, GUANGSU HUANG*, MENGMENG CHEN and JING ZHENG

State Key Lab of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu, China

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The multi-hydroxymethyl structure of resol makes it suitable for connecting two or more polyacrylamide chains as a crosslinker in oil recovery applications, but control of the structure and composition of the resol, whether in practice or theory, is still a controversial problem. In the present research, a series of resol prepolymers synthesized with different amounts and types of catalysts, formaldehyde to phenol molar ratio, reaction temperature and charging steps were characterized by high-performance liquid chromatography. It is found that the compositions of the resols barely changed with almost all the varying conditions, but the contents of each component were greatly affected by the variation of reaction conditions. Finally, the best conditions for preparing resol crosslinker were obtained.

Keywords: Resol, alkali catalyst, reaction temperature, charging step

1 Introduction

Resol, an intermediate for preparing thermosetting phenolic resin, is used as industrial impregnation resins and plywood glues (1). In particular, the multi-hydroxymethyl structure of resol characterizes it as a suitable cross-linker in oil recovery applications (2). As a cross-linker, resol can react with partly-hydrolyzed polyacrylamide (HPAM) generating a new crosslinked material which has better thermal stability and anti-degradation. Some researchers, including Li, Shi and co-workers (3–7), synthesized different resol crosslinkers that can satisfy different oil-displacing requirements; these crosslinkers were reported to be outstanding in salt-resistance, thermal stability and shear stability. Therefore the molecular structure and composition of resols should be thoroughly understood for studying the mechanism of the crosslinking reaction and practical application. However, the molecular structure and composition of resols are influenced by many synthesis parameters, such as type and amount of catalyst, formaldehyde to phenol molar ratio (F/P), reaction temperature and charging steps. These parameters have been studied for different resols by many authors, using IR, ^{13}C-NMR, HPLC, etc, as described below. Grenier-Loustalot and co-workers studied the reaction mechanism of phenol, formaldehyde and model compounds by high-performance liquid chromatography and ^{13}C NMR spectroscopy (8-12), and they found that different catalyst types, pH, reaction temperatures and F/P ratios could influence reaction mechanism, kinetics and final structure of resol. Mondragon and co-workers analyzed the first step of the condensation reaction, taking account of the influence of many parameters such as pH, type of catalyst, formaldehyde/phenol molar ratio by high-performance liquid chromatography, gas chromatography and ^{13}C NMR spectroscopy (13-18). In the literature, the conclusion is drawn that the ortho directing properties of the catalyst studied increase in the order triethylamine > barium hydroxide > sodium hydroxide. The researchers also discovered that the final structures of resols varied in amounts of free phenol with the F/P ratios (from 1.0 to 2.6). Using FTIR spectroscopy, ^{13}C-NMR spectroscopy and gel permeation chromatography, Alvila and co-workers researched the effect of several reaction factors on the forming of resols, such as F/P, the amount of catalyst, reaction time and charging method (19-24). The F/P ratios of resol resins were successfully predicted by the recording of infrared (IR) spectra of both calibration and analyzed resins and by a multi-variate analysis technique, and the best models were successful in the quantitative prediction of F/P molar ratios. In addition, their results indicated that a two stage charging method could facilitate control of the initial stages of resol production. However, although there has been some work done in the field of resol synthesis, the variation of molecular structure and composition of resols with respect to synthesis conditions are still not completely understood.

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*Address correspondence to: Guangsu Huang, State Key Lab of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China. E-mail: guangsu-huang@hotmail.com

In this paper, in order to investigate the variation of molecular structure and composition of resols under different reaction conditions, we quantitatively studied the content of each component in resols under different reaction conditions using high-performance liquid chromatography after the composition of resol had been determined by liquid chromatography-mass spectra.

2 Experimental

2.1 Synthesis of Resol

Phenol (>99%), formaldehyde (37% aqueous solution) and sodium hydroxide were from Chongqi Maoye Co. in China.

Resols were synthesized by mixing 0.4–0.8 mol formaldehyde with 0.2 mol phenol; the mixture with 2–4 wt% of reactant content catalyst added (NaOH) was heated to the reaction temperature (50°C∼70°C) for 7 h and stirred at a low velocity during the reaction. The reaction was stopped by putting the reactor in a cold water bath. The samples were kept at –18°C before testing.

2.2 High-performance Liquid Chromatography (HPLC)

Analyses were conducted with a Waters chromatograph equipped with a Waters 2487 UV detector, set at 254 nm. The column was a Shimpack VP-ODS (5 μm). The column temperature was 20°C. The mobile phase was a mixture of 30 wt% methanol and 70 wt% water. Integral areas (%) of each component represent its mass fraction in the product; these can be obtained from the HPLC data directly. All integral area results were the average value of three tests and the repeatability of the data are represented by error bars in the figures. The pH of the samples used for HPLC test were 7.0, obtained by adding HCl; the samples were diluted to 1 wt% with water of chromatographic grade.

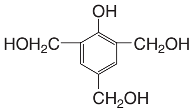
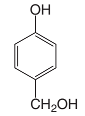
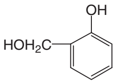
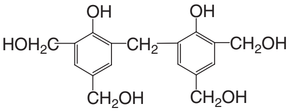
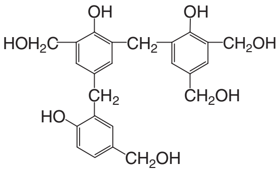
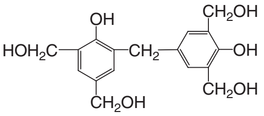
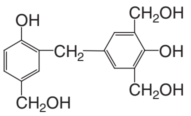
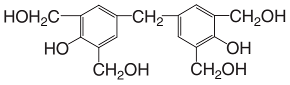
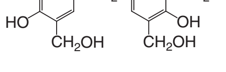
3 Results and Discussion

3.1 The Compositions of Resols

In a previous paper (25),one of the resols used here (formaldehyde phenol ratio 3:1, NaOH 3%, reaction temperature 60°C) was characterized by liquid chromatography-mass spectra (LC-MS). By analyzing the obtained spectra, the composition of resol was determined. The result is listed in Table 1. Peaks 1, 2 and 3 are the products of addition reaction between phenol and formaldehyde without condensation. 4, 6, 7, 8 and 9 are dimer with active hydroxymethyls, and only 5 is trimer.

The multi-hydroxymethyl structure of resol characterizes it as a suitable crosslinker of HPAM in oil recovery applications. Among the nine kinds of components, 2,4,6-trihydroxymethyl phenol (component 1) is the most effective compound (2). As for the other components, the more hydroxymethyls it has, the higher the reactivity will be.

Table 1. The composition of a resol

Peak NO.	t_R*(min) in LC-MS*	*Integral area (%)*	*Molecular formulae*
1	6.58	31.23	
2	8.11	14.73	
3	9.70	6.350	
4	11.11	1.982	
5	12.16	6.339	
6	16.27	5.514	
7	20.46	6.379	
8	22.21	20.27	
9	30.96	6.036	

In addition, the larger the crosslinker molecule, the better the crosslinking effect. Accordingly, components 4, 5, 6, 8, with four hydroxymethyls in their structure, are the most reactive in these resols; also these molecules are larger than the other products. On the other hand, 2 and 3 have the lowest reactivity, and 1, 7, 9, with three hydroxymethyls are intermediate between these two groups. Overall, all components except 2 and 3 have the multi-hydroxymethyl structure, and thus, can be used as crosslinkers for HPAM. To better understand the relationship between reaction

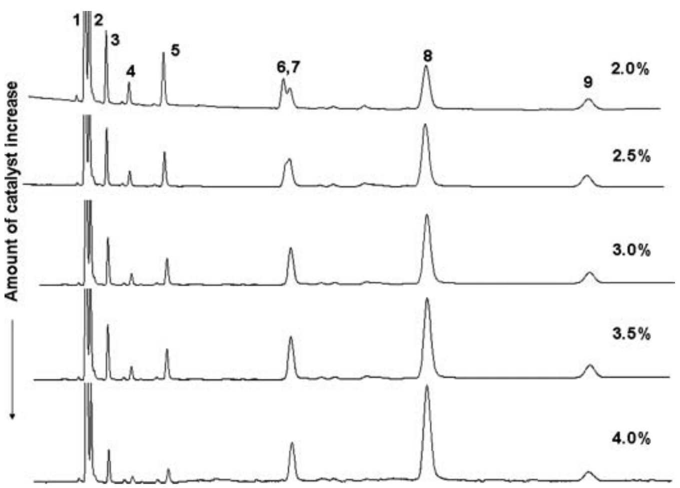


Fig. 1. HPLC chromatogram of resol with different amounts of catalyst using a UV detector.

conditions and product structure and to prepare crosslinkers with more outstanding crosslinking ability, the influence of experimental conditions was studied here by HPLC.

3.2 Amount of Catalyst

In order to study the influence of the amount of catalyst, five resol prepolymers were synthesized with F/P = 3 at 60°C for 7 h, catalyzed with various amounts of sodium hydroxide. Considering the ability of the catalyst and cost analysis, the amount of catalyst was chosen to be 2, 2.5, 3, 3.5 and 4 wt% with respect to the mass of reactant. The content of each component in the synthesized products was quantitatively determined by liquid chromatography.

Figure 1 shows the HPLC chromatograms of the resols synthesized with different amounts of catalyst. The effect of the amount of catalyst on the content of each component in the final prepolymers can be observed. The number and position of each peak remained the same with the increasing of the amounts of catalyst, which means that the components of the resols were unchanged. However, from the HPLC chromatograms, the integral areas of the peaks were changed with the variation of the amount of catalyst, indicating that the content of each component in the resols was altered. The variation of the content of each component is illustrated in Figure 2.

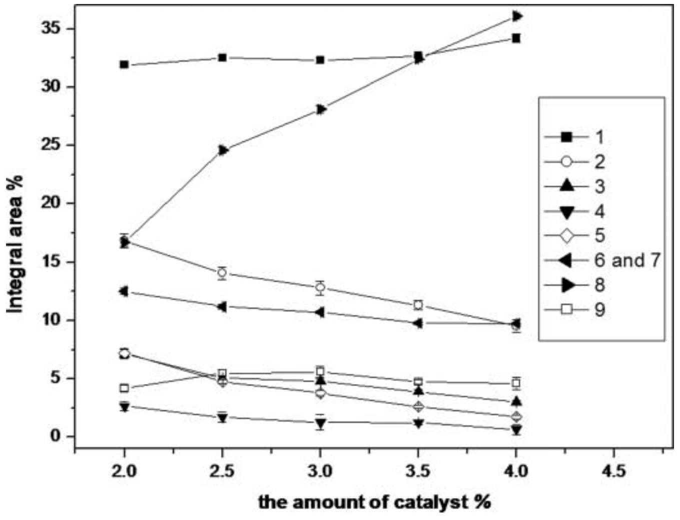


Fig. 2. The constituents' contents with different amounts of catalyst.

As the amount of catalyst was increased, the content of component 1 had a slight increase, whereas that of dimer 8 went up sharply. At the same time, the content of trimer 5 went down, resulting from the para directing property of sodium hydroxide (13, 24).

It must be pointed out that the content of component 1 was almost unchanged as the amount of catalyst was increased and it was the highest among all components when the amount of catalyst was lower than 3.5%; however, as the amount of catalyst was increased, the content of dimer 8 increased sharply and finally exceeded that of component 1 for catalyst greater than 3.5%. As the condensation of para-hydroxymethyl gives rise to dimer 8, the increase of its content means that the increase of the amount of catalyst was propitious to condensation of para-hydroxymethyl. On the contrary, the content of dimer 4 derived from the condensation of ortho-hydroxymethyl underwent a small decrease with the increase of catalyst amount. Therefore, the content of dimer 8 was much greater than that of dimer 4 in the entire reaction because the condensation reactivity of para-hydroxymethyl is higher in comparison with that of ortho-hydroxymethyl when using sodium hydroxide as the catalyst (13). It is well-known that component 1 (2,4,6-trihydroxymethyl phenol) is the most effective crosslinker of all components of the resols (2), so the best amount of catalyst is 3.0–3.5% for which 2,4,6-trihydroxymethyl phenol is the major component, while contents 2 and 3, which have only one hydroxymethyl, are relatively low in the resols.

3.3 Initial F/P

The initial F/P is one of the most important reaction factors. This study covered five initial F/Ps (F/P = 2, 2.5, 3, 3.5, 4) for resol fabrication and the reaction was catalyzed with sodium hydroxide (3.5wt%) at 60°C for 7 h.

The number and positions of the peaks remained the same (Fig. 3) when the initial F/P was increased, which implies that the components of the resols were not changed. From Figure 3, the variation of the content of each component can be quantitatively obtained. The contents of product 1 and dimer 8 increased, whereas that of trimer 5, and dimers 6 and 7 decreased with the increasing of initial F/P. The amount of product 1 increased relatively sharply when the initial F/P was below 3. It leveled off after the initial F/P reached 3.

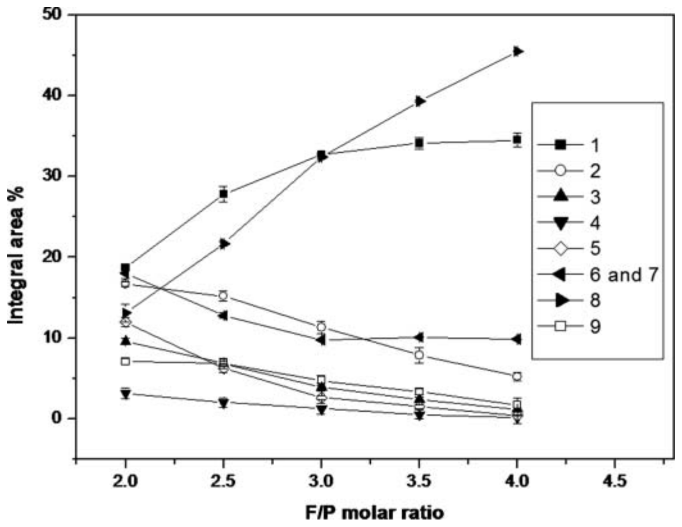


Fig. 3. The constituents' contents with different F/P molar ratio.

This result can be explained according to the reaction mechanism. As shown in Figure 4, the condensation between hydroxymethyls and reactive hydrogen atoms on phenol rings would yield water molecules, so an excessive addition of formaldehyde solution, which also means an excessive addition of water, could shift the reaction balance toward the left and restrain the condensation reaction. This is the reason that the content of trimer 5 decreased as F/P was increased. It should be pointed out that the optimum F/P is 3.0 for which component 1 is the major component in the resols.

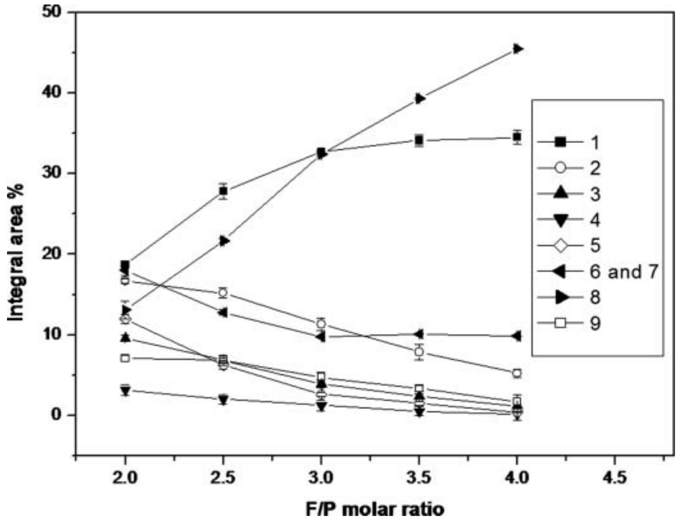


Fig. 4. Reaction mechanism for condensation of addition products.

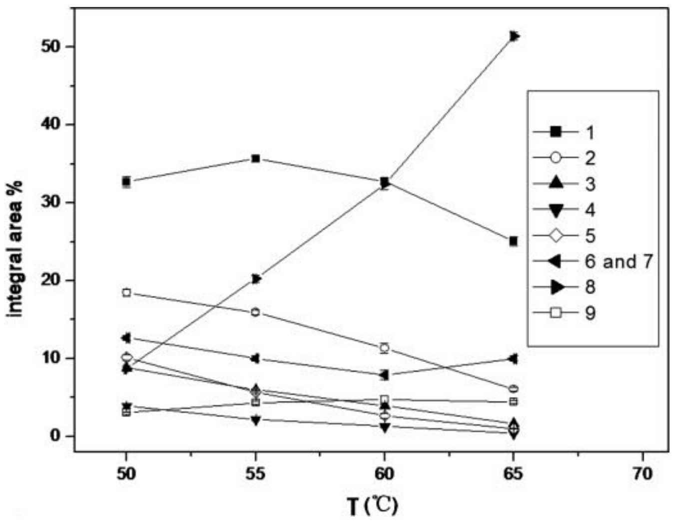


Fig. 5. The constituents' contents with different reaction temperatures.

3.4 Reaction Temperature

In this study, five resols catalyzed with sodium hydroxide (3.5 wt%) were synthesized at 50, 55, 60, 65 and 70°C for 7 h with F/P = 3. Since the resol synthesized at 70°C was not water miscible, only four results were obtained by HPLC. Several of the integral peak areas (Fig. 5) strongly depended on the temperature, indicating that the condensation temperature greatly affects the resol formation. When the reaction temperature was over 55°C, the content of product 1 decreased as the temperature increased because 2,4,6–trihydroxymethyl phenols can easily undergo condensation and form dimers when the condensation temperature reaches 60°C (1). The content of dimer 8 went up, obviously due to the enhancement of para-hydroxymethyl condensation reactivity at high temperature. Therefore, the best reaction temperature for synthesizing an effective crosslinker is 55–60°C.

3.5 Type of Catalyst

The structures of two resols synthesized under the same conditions (F/P = 3, 60°C) but with different types of catalysts, sodium hydroxide (3.5 wt%) and triethanolamine, were investigated by HPLC. The same mol% of the two catalysts were used. The components of the two resols were still the same, but their contents underwent some changes (Fig. 6). The content of trimer 5 in the resol catalyzed with triethanolamine (resol T) was twice as much as that in the resol catalyzed with sodium hydroxide (resol S), which demonstrates that the catalytic efficiency for condensation of triethanolamine was higher than that of sodium hydroxide. As for the content of dimer 8, it had an opposite trend, proving that the condensation reactivity of para-hydroxymethyl in resol T was lower than that in resol S. There was a small change in the content of dimer 6 and 7;

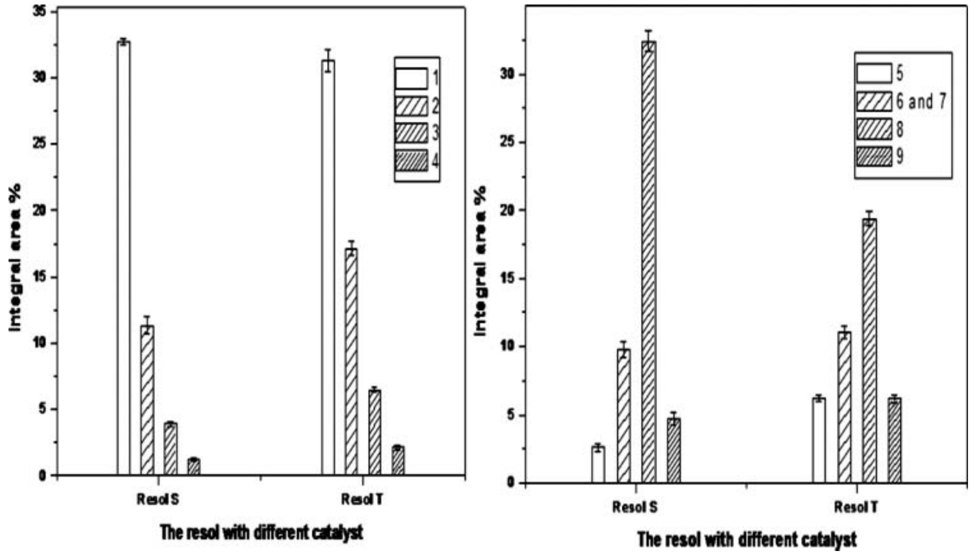


Fig. 6. The constituents' contents with different catalysts.

this can be explained in terms of the fact that the condensation reactivity of ortho-hydroxymethyl in the two types of catalyzed conditions was almost the same. Both kinds of catalysts can be used to catalyze the crosslinker synthesis since the content of product 1 was large in both resol S and resol T, but sodium hydroxide was better as the contents of products 2 and 3 in resol S were smaller than that in resol T.

3.6 Charging Step

The charging step of the reaction was tentatively studied. Two resols were synthesized by one-step charging (all formaldehyde was added to the reaction system at the beginning) and two-step charging (the formaldehyde was added in the reaction system in two steps), by catalyzing with the same amount of sodium hydroxide (3.5%) under the same conditions (60°C, F/P = 3). In Figure 7, it can be seen that the components of resols did not vary with the different charging steps. However, the content of trimer 5 in the two-step resol was twice that in the one-step resol because adding formaldehyde in two steps favors condensation compared with adding it once. Therefore, the content of dimer 8 in the one- step resol increased in comparison with that in the two-step resol. Considering the contents of products 2 and 3, one-step charging is the better choice to prepare crosslinker than two-step charging.

4 Conclusions

The variation of composition of resols with a high content of hydroxymethyl groups under different reaction conditions were characterized and studied by HPLC. The

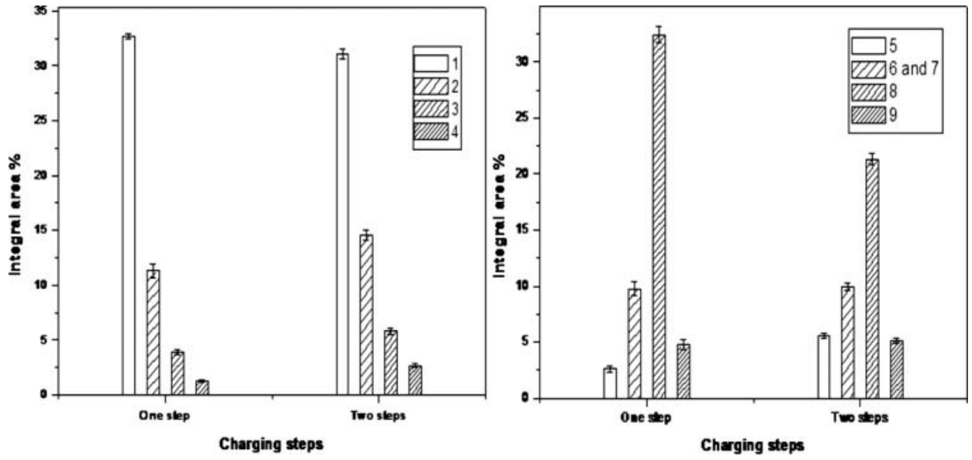


Fig. 7. The constituents' contents with different charging steps.

results show that the composition of resol doesn't change when all used research conditions vary, but the contents of components exhibit differences with reaction conditions. The dimer 8, obtained by condensation between para-hydroxymethyls, was the most sensitive component in the system to all the altering conditions. In addition, the condensation reactivity of para-hydroxymethyl is higher than that of ortho-hydroxymethyl when using sodium hydroxide as catalyst. In conclusion, the best condition to synthesize the desired crosslinker is to use sodium hydroxide as catalyst at 3.0 wt%–3.5 wt% of the reactants, F/P of 3.0 and reaction temperature of 55-60°C with one-step charging.

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