

# Kinetics Study on the Formation of Resol with High Content of Hydroxymethyl Group

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**ABSTRACT:** The application of resol as a crosslinking agent with polyacrylamide has become widespread, but it is not clear for forming mechanisms of extraordinarily high activity of the resol. In this research, the major components of the resol and their mass percentage are investigated by Liquid chromatography-mass spectrograph, the mechanism of forming the components is exploited. The evolution of formaldehyde, phenol, and first formed addition products were quantitatively traced by titration and high-performance liquid chromatography, furthermore the kinetics of synthesis is studied based on the analyzing results. The results show that the resol is composed of nine compounds

and the sum of percentage for each integral area is more than 99%. In addition, the constant of overall reaction rate  $k$  consists of three values of  $5.667 \times 10^{-5}$ ,  $7.236 \times 10^{-5}$ , and  $23.05 \times 10^{-5} \text{ s}^{-1}$ , which means that the reaction can be separated to three stages of hydroxymethylphenol (HMP) producing stage, dihydroxymethylphenol (DHMP) and trihydroxymethylphenol (THMP) producing stage and condensation stage. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3157–3162, 2008

**Key words:** resol; hydroxymethyl group; kinetics; cross-linking agent; liquid chromatography-mass spectra

## INTRODUCTION

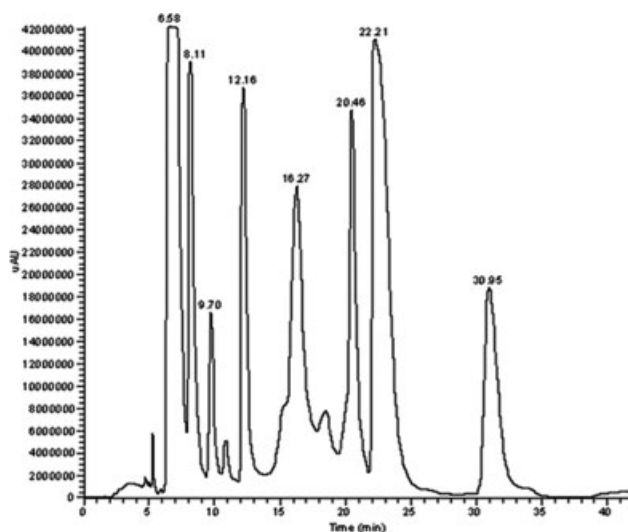
Phenolic-formaldehyde (PF) resins synthesized by phenol and formaldehyde under a basic catalyst have been utilized in a variety fields as electric, construction, automobile, and even aviation and spaceflight industry, owing to their excellent heat-resistance and fire-retardant. The resol, an oligomer derived from the first-step of forming the resin, has been used as adhesive owing to self-crosslinking for long.

The reaction of preparing resol aroused scientists' interests early in the middle of 20th century, but until recent time still a lot of literatures reported some new developments about it. Grenier-Loustalot et al.<sup>1–5</sup> studied the reaction mechanism of phenol, formaldehyde, and the model compounds by high-performance liquid chromatography (HPLC) and <sup>13</sup>C NMR spectroscopy. Astarloa-Aierbe et al.<sup>6–10</sup> analyzed the first step of the condensation reaction, taking account of the influence of many parameters such as pH, type of catalyst, formaldehyde/phenol (F/P) molar ratio by HPLC, gas chromatography, and <sup>13</sup>C NMR spectroscopy. With FTIR spectroscopy using multicomponent spectroscopic analysis of a software package QUANT+, Holopainen et al. pre-

dicting reliably quantitative results such as the amount of free phenol and the F/P molar ratio.<sup>11</sup> In addition, employing a multiple parameter regression method, Riccardi et al. and Manfredi et al.<sup>12,13</sup> carried out the modelling of the phenolic resol resin.

Recently, an extraordinarily active resol has been widely used in the oil production field as a cross-linking agent because of its good water-solubility and high cross-linking reactivity. The cross-linking reaction occurs between amide groups on polyacrylamide and hydroxymethyl groups on resol. It is evident that the activity is closely related with the amount of hydroxymethyl group in each component, so the higher content of hydroxymethyl group is, the higher cross-linking reactivity will be. Although the gelling property of the resol with polyacrylamide has been studied by many researchers, such as Li et al. and Kong and Song,<sup>14,15</sup> few study on components and forming mechanism of the resol with multi-hydroxymethyl groups has been reported. On the other hand, liquid chromatography-mass spectra (LC-MS) technology is hardly employed for analyzing the composition of resol yet. The LC-MS taking the electrospray ionization (ESI) was an efficient way of qualitative and quantitative analysis, testing under low temperature avoids changing the structure of samples, which often takes place during the vapourization in gas chromatography-mass spectra. The qualitative analyzing method can supply a good

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**Figure 1** LC-MS chromatogram of resol by UV detector.

deal of precise information for determination on molecular weight of the high reactive oligomer formed in the organic synthesis.<sup>16</sup>

In the present article, the major components of the resol with great content of hydroxymethyl group and their mass percentage were studied. To understand the evolution procedure of the reaction well, the contents of formaldehyde, phenol, and first formed addition products were quantitatively analyzed and the kinetics of the reaction was constructed, gaining some interesting results.

## EXPERIMENTAL

### Materials

Phenol (>99%), formaldehyde (37% aqueous solution), and sodium hydroxide are from Chongqi Maoye, China. Besides, methanol was from Shandong Yuwang, China and water was from Sichuan University.

### Synthesis of resol

Resol was synthesized by mixing phenol (P) and formaldehyde (F) in a molar ratio of F/P = 2–5, the pH was then adjusted to 9.0 with alkaline catalyst. The mixture was heated to the reaction temperature for 7 h and stirred during the reaction. Samples were taken at regular intervals. The time when mixture reached the reaction temperature was defined as zero, and then the reaction was stopped by putting the reactor in a cold water bath (20°C). The samples were kept at –18°C before test.

### Liquid chromatography-mass spectra

LC analysis was performed using a HPLC system (America) coupled to a Finnigan LCQ<sup>DECA</sup> mass spec-

trometer, equipped with a Z-spray ESI interface (Waters). Chromatographic separation was achieved with a ThermoQuest C<sub>18</sub> (5 μm, 250 mm × 4.6 mm, America) column set at 20°C. For the analysis, a mobile phase of methanol/water (v/v) was used an elution of 30–50% methanol. The flow rate was set at 0.5 mL/min.

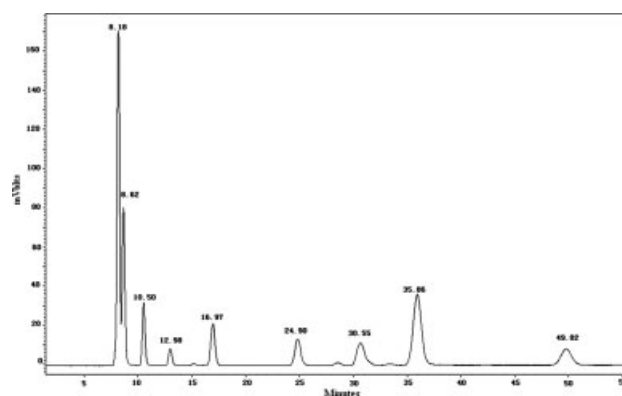
### High-performance liquid chromatography

Analyses were conducted with a HPLC system consisting of a Waters HPLC equipped with the Waters 515 HPLC pump and 2487 detector. The analytical column was a VP-ODS column (5 μm, 250 mm × 4.6 mm, Shimpack, Japan) set at 20°C. A mobile phase of methanol/water (v/v) was used an elution of 30–50% methanol. The flow rate was set at 0.5 mL/min. The eluate was monitored at 254 nm.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the LC-MS and HPLC chromatograms of the same resol sample detected by UV detectors, respectively. Among them, the resol is composed of nine compounds and the sum of percentages for each integral area account for 99%. The  $t_R$  of each peak in LC-MS and HPLC has some deviations between both chromatograms because of the different column effectiveness. However, the order and integral areas of the peaks are corresponding in the two chromatograms.

The information from LC-MS test is shown in Table I. The molecular ion peak and quasi molecular ion peak are strong in LC-MS test owing to the “soft” ionization technology, which can avoid further disintegration of the molecular ion peak, so the molecular weight of the sample is easily ascertained due to the weak peaks of the fragment ions.<sup>16</sup> Figure 3 is the mass spectrum of peak 1, in which the molecular ion peak of  $m/z = 183$  is the base peak, so the molecular weight of the compound corresponding the peak is 184. Combining the mechanism of



**Figure 2** HPLC chromatogram of resol by UV detector

**TABLE I**  
LC-MS Information of Resol

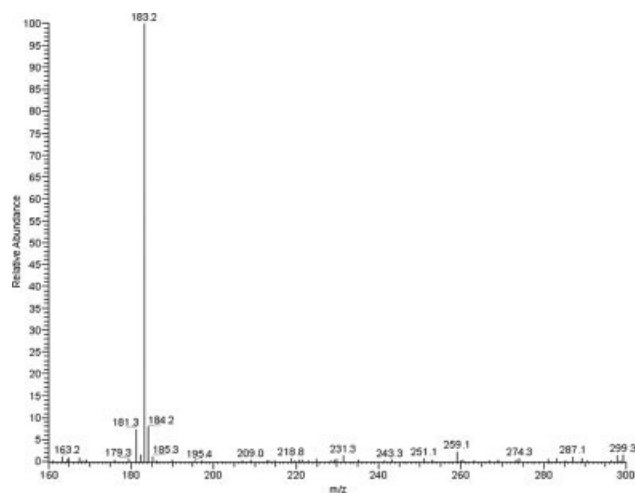
Peak no.	$t_R$ (min)	MS information ( $m/z$ )
1	6.58	183(M-1), 184
2	11.11	289, 301, 319(M-1), 320
3	12.16	389, 407, 425(M-1), 426
4	16.27	299, 301, 319(M-1), 320
5	20.46	153, 271, 289(M-1), 290
6	22.21	299, 301, 319(M-1), 320
7	30.95	271, 289(M-1), 290

the addition reaction between phenol and formaldehyde with the information of the test, this compound can be determined to be 2, 4, 6-trihydroxymethyl phenol (2, 4, 6-THMP).

According to the information such as  $m/z$ ,  $t_R$  of the LC-MS test, and different polarity between *para*-hydroxymethyl and *ortho*-hydroxymethyl, molecular formulas of most compounds are obtained. The MS spectrums of the peaks whose  $t_{RS}$  are 8.11 and 9.70 are not detected because of the sensitivity and detectability of the detector, but it can be deduced that the compounds corresponding the two peaks are 2, 4-dihydroxymethylphenol and 4-hydroxymethylphenol from the former research results.<sup>1-10</sup> In Table II, the molecular formulas of each components obtained by LC-MS and HPLC information are shown as follows.

Among all the resulting nine components, there is no phenol reactant. It is pronounced that the content of THMP is the highest in the resol, while the sum percentages of integral areas of the dimers occupies about 40% and the tripolymer include only one component whose content is very low. To understand the reaction course distinctly, the kinetics of the reaction with high F/P molar ratio was studied.

Generally speaking, the reaction between phenol and formaldehyde in the alkaline pH range can be



**Figure 3** MS chromatogram of peak 1.

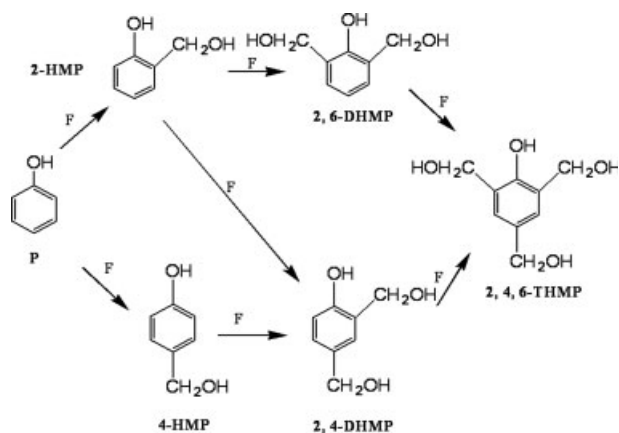
**TABLE II**  
Molecular Formulas of Components Conjectured by LC-MS and HPLC Information

Molecular formula	$t_R$ (min)	Integral area (%)
	6.58	31.23
	11.11	1.98
Tripolymer	12.16	6.34
	16.27	5.51
	20.46	6.38
	22.21	20.27
Dimer	30.95	6.04

divided to two steps: addition reaction of hydroxymethyl groups to the *ortho* and *para* free positions of phenol (Fig. 4) and condensation reactions between hydroxymethyl group and one free position in phenol giving rise to methylene bridges or two hydroxymethyl groups forming methylene ether bonds.

In the past, most studies about kinetics mechanism of resol synthesis focused on the resol, which has the property of self-setting and the low F/P molar ratio, which is helpful to obtain the self-setting PF with high crosslinking density.<sup>17</sup> In present research, the resol synthesized has excellent crosslinking reactivity with polyacrylamide because of high content of hydroxymethyl group derived from high F/P molar ratio.

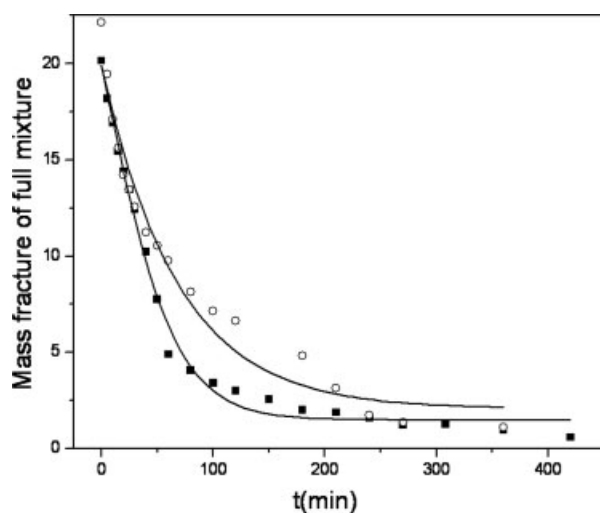
The disappearance of the free formaldehyde and free phenol content versus reaction time is depicted in Figure 5. It can be seen that even though the F/P molar ratio is high in the reaction, formaldehyde still reacts sufficiently in the whole synthesis, while concentration of free formaldehyde finally goes down to around 1%, which demonstrates that high F/P ratio has no effect on the reactive extent of formaldehyde. The concentration of free formaldehyde is assumed to be linear decreased in the beginning 100 min. After that, the velocity of consumption is falling down and the concentration of formaldehyde is almost kept at a certain level. The situation of free phenol is similar with that of free formaldehyde,



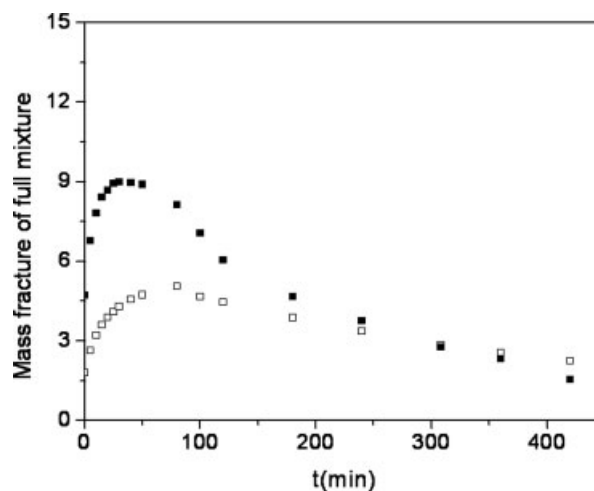
**Figure 4** Reaction mechanism for addition of formaldehyde to phenolic rings.

at beginning 150 min the concentration of phenol drops fast and then hardly changed.

2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP) are not only products but also reactants in the synthesis of the resol, the evolutions of them are shown in Figure 6. At the beginning the concentration of 2-HMP is much higher than that of 4-HMP, because in the addition reaction catalyzed with NaOH, the para-position in phenol shows a slightly higher relative reactivity towards formaldehyde than the ortho-position. However, 2-HMP is produced at a higher rate due to the fact that two ortho-positions are available. The ortho/para (o/p) ratio was found to be 1.7.<sup>18</sup> The concentration of 2-HMP is lower than that of 4-HMP in the end of reaction because 2-HMP is found to be twice as reactive as 4-HMP with respect to either position.<sup>18</sup> Increased reactivity is also found with higher methylolated phenols to be produced, especially



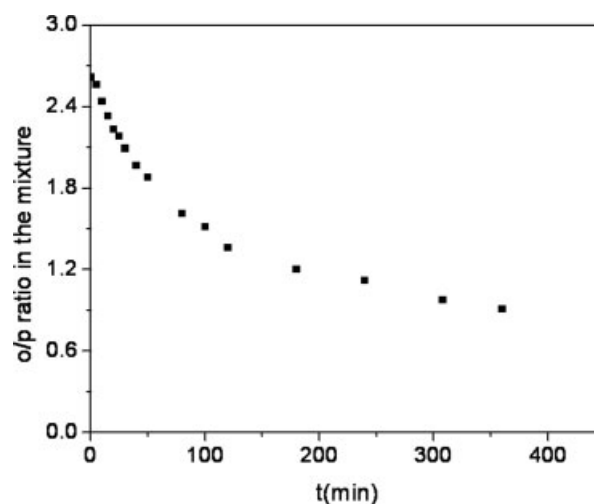
**Figure 5** Disappearance of formaldehyde and phenol. ■ formaldehyde, ○ phenol.



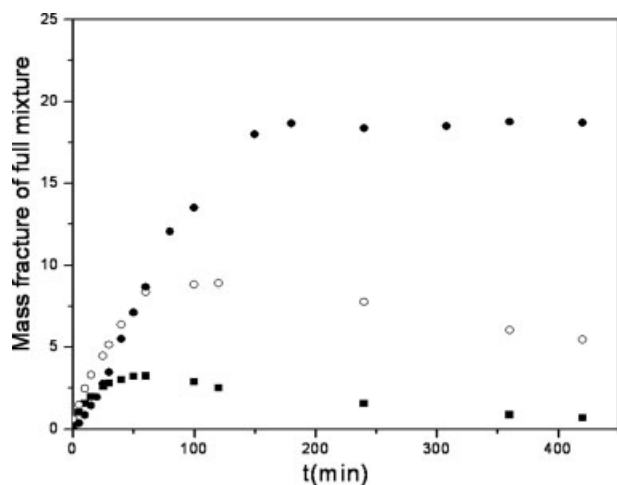
**Figure 6** Evolution of HMP by HPLC during synthesis. ■ 2-HMP, □ 4-HMP.

remarkable with 2, 6-dihydroxymethylphenol. The ratio variation of the concentration of 2-HMP and 4-HMP (o/p) in this system is shown in Figure 7, which corroborates the para directing characteristic of NaOH discussed above. Though the o/p value is over 2.0 at the beginning because the lower catalyst concentration is used,<sup>13</sup> it descends quickly as reaction time increasing in the most of reaction time the o/p value is less than 1.8.

Similarly, both the concentrations of 2, 4-dihydroxymethylphenol (2, 4-DHMP) and 2, 6-dihydroxymethylphenol (2, 6-DHMP) rise at first and then descend in the procedure of reaction, which means that they all play a role of intermediate products in the reaction system. The evolutions of the two compounds can be illustrated in Figure 8. Because of the coaction of high reactivity of *ortho*-hydroxymethyl phenol and the effect of para directing, the concen-



**Figure 7** Ortho/para ratio of the resol.



**Figure 8** Evolution of DHMP and 2, 4, 6-THMP by HPLC during synthesis. ■ 2, 6-HMP, ○ 2, 4-HMP, ● 2, 4, 6-THMP.

tration of 2, 6-DHMP is much lower than that of 2, 4-DHMP except for the beginning of the reaction.

The concentration of 2, 4, 6-trihydroxymethylphenol (2, 4, 6-THMP) does not take on the downtrend in the whole reaction, which means it continuously keeps at a high level in the reaction system (see Fig. 8). After 150 min of the reaction, the concentration of 2, 4, 6-THMP reaches to the highest value and keeps it to the end of the reaction. This period coincides with the time at which the concentration of free phenol goes down to the lowest value. It means that formaldehyde attacks to the free positions of substituted phenol rapidly to forming 2, 4, 6-THMP whose concentration is the highest in the resol. Consequently there are half reactants transformed to 2, 4, 6-THMP at the end of the reaction due to the high F/P ratio at the beginning of the reaction and the low reaction temperature.

The reaction rate is correlative with concentrations of phenol and formaldehyde because the addition reaction between them belongs to second-order reaction. The rate expression for the formation of the products is

$$dy/dt = k(a - x)(b - y) \quad (1)$$

where  $a$  and  $b$  are the initial concentrations of formaldehyde and phenol, while  $x$  and  $y$  are the concentrations of formaldehyde and phenol reacted at time  $t$ , respectively.  $k$  is the constant of overall reaction rate.

Hypothesizing  $y = mx$ , substituting the value of  $y$  in eq. (1) and integrating, we get

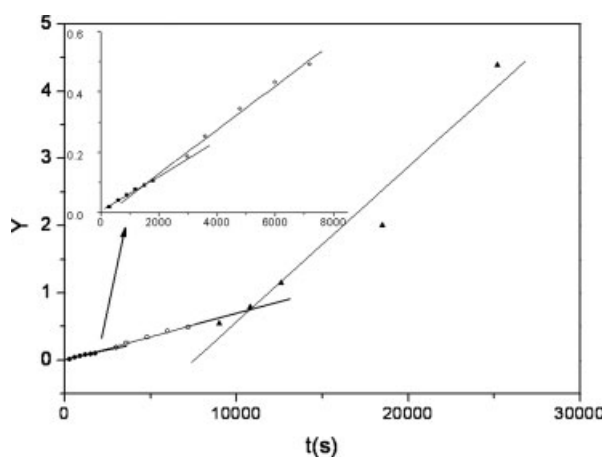
$$kt = \frac{m}{(b - ma)} \ln \left( \frac{a(b - mx)}{b(a - x)} \right) \quad (2)$$

Hypothesizing

$$Y = \frac{m}{(b - ma)} \ln \left( \frac{a(b - mx)}{b(a - x)} \right) \quad (3)$$

introduced the data of concentration to the eqs. (2) and (3) and the fitted results show in Figure 9, the slope of it is the value of  $k$ .

It can be observed from Figure 9 that  $Y$  and  $t$  is not simply linear relation in the researched range but instead of three stages of perfect linear relation, while the slopes of the three lines are  $5.667 \times 10^{-5}$ ,  $7.236 \times 10^{-5}$ , and  $23.05 \times 10^{-5} \text{ s}^{-1}$  increased in sequential, an interesting phenomenon. It means that the constant  $k$  changes following the composition of the products, and the whole reaction can be expressed by three  $k_s$ . The phenomenon could be attributed to the fact that the whole reaction experience three stages of HMP-producing stage, DHMP and THMP-producing stage and condensation stage. The fluctuation of concentration in the reaction system can prove this statement. As shown in Figure 9, the first stage is from zero time to 30 min of the reaction. In this period HMP concentration reaches the highest value (from Fig. 6), it means that HMP plays the role of product, whose concentration is the highest in the whole system. After 30 min, most of HMP starts to occur the addition reaction with formaldehyde, which results in descent of the HMP concentration. The second stage lasts from 30 to 150 min of the reaction. In this stage, HMP in the reaction system react with formaldehyde, DHMP and THMP are formed, the addition reactive rate increase. Compared with the rate of first stage, both concentrations of 2,4- DHMP and 2, 4, 6-THMP arrive to the highest value (see Fig. 8). Here the reaction transit to the last stage from 150 min to the end of reaction. The consumptions of phenol and formaldehyde become lower, but  $k$  value increase rapidly, where DHMP and THMP, the major components in the reaction



**Figure 9** Linear dependence of  $Y$  on time.

system, condensate to form the dimers and tripolymer. The consumption of THMP and DHMP make the reaction equilibrium shift to the product direction, which induce the increment of the  $k$  value.

### CONCLUSIONS

A resol with high content of hydroxymethyl has been synthesized; most of the addition products and low molecular weight condensation compounds in it are identified by LC-MS. The graphs obtained by LC-MS can be corresponded with that from HPLC preferably. On the basis of results from the analysis, kinetics of the synthesis is studied. The constant of overall reaction rate  $k$  consists of three values of  $5.667 \times 10^{-5}$ ,  $7.236 \times 10^{-5}$ , and  $23.05 \times 10^{-5} \text{ s}^{-1}$ , which means that the reaction can be separated to three stages of HMP-producing stage, DHMP and THMP-producing stage and condensation stage.

### References

1. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Leca, J.-P.; Bedel, D. *Polymer* 1994, 35, 3046.
2. Grenier-Loustalot, M.-F.; Larroque, S.; Grande, D.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 1363.
3. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 939.
4. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 955.
5. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 639.
6. Astarloa-Aierbe, G.; Echeverria, J. M.; Egiburu, J. L.; Ormaetxea, M.; Mondragon, I. *Polymer* 1998, 39, 3147.
7. Astarloa-Aierbe, G.; Echeverria, J. M.; Martin, M. D.; Mondragon, I. *Polymer* 1998, 39, 3467.
8. Astarloa-Aierbe, G.; Echeverria, J. M.; Mondragon, I. *Polymer* 1999, 40, 5873.
9. Astarloa-Aierbe, G.; Echeverria, J. M.; Vazquez, A.; Mondragon, I. *Polymer* 2000, 41, 3311.
10. Astarloa-Aierbe, G.; Echeverria, J. M.; Riccardi, C. C.; Mondragon, I. *Polymer* 2002, 43, 2239.
11. Holopainen, T.; Alvila, L.; Rainio, J.; Pakkanen, T.T. *J Appl Polym Sci* 1998, 69, 2175.
12. Riccardi, C. C.; Astarloa-Aierbe, G.; Echeverria, J. M.; Mondragon, I. *Polymer* 2002, 43, 1631.
13. Manfredi, L. B.; Riccardi, C. C.; de la Osa, O.; Vazquez, A. *Polym Int* 2001, 50, 796.
14. Li, G.; Xu, J.; Mao, G.; Dai, B.; Zang, S.; Lu, K. *Oilfield Chem* 2000, 17, 310.
15. Kong, B.; Song, Z. *Acta Petrolei Sinica* 2000, 21, 70.
16. Niessen, W. M. A. *J Chromatogr A* 1999, 856, 179.
17. Manfredi, L. B.; de la Osa, O.; Galego Fernández, N.; Vázquez, A. *Polymer* 1999, 40, 3867.
18. Knop, A.; Pilato, L. *Phenolic Resins*; Springer-Verlag: Berlin, 1985.