Synthesis of 2,6-dihydroxymethyl-4-methyl phenol and Its Application in Novolac Resins

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DEPT135 was used to study the hydroxymethylation of p-cresol in basic condition. The roles of type and amount of catalyst, reaction temperature, reaction time were investigated to optimize reaction conditions for the synthesis of 2,6-dihydroxymethyl-4-methyl phenol (2,6-DHMMP). Subsequently, a series of novolac resins with extremely high or low Mw, narrow Mw/Mn, as well as alternating co-condensation structure have been produced by the condensation of 2,6-DHMMP and phenol, m-cresol etc. The synthesized p-cresol/phenol resin has a Mw of 20000-30000, and Mw/Mn of 15-20, and also excellent resistance to alcohol and alkali, which meet the needs of photosensitive compositions. The synthesized p-/m-cresol resin has a Mw of 25000, and Mw/Mn of below 15, as well as well resistance to alkali, heat and etching. These novolac resins have good prospects in terms of resist and printing plates.

Key words: DEPT135, p-cresol, hydroxymethyl reaction, novolac resin

1. Introduction

In the late 19th and early 20th century, Lederer1,2) found the hydroxymethyl reaction of phenolic compounds with formaldehyde in basic condition. Meer3) synthesized 2,6-DHMMP by the reaction of p-cresol with excess formaldehyde in 20% of NaOHaq (equal molar of NaOH and p-cresol) at low temperature in 1944. Afterward, the hydroxymethyl reaction of some phenolic compounds with formaldehyde in basic conditions were further studied, however, there is lack of study about p-cresol, particularly no systematic study about the influences of sodium hydroxide amount, reaction temperature and time. Therefore, the method in previous reports for synthesis of 2,6-DHMMP using of p-cresol and formaldehyde is used nowadays4-8). Base on others and our previous work, DEPT135 was used in the present study to investigate the reaction process between p-cresol and formaldehyde in basic conditions. This study is for the purpose of optimizing reaction conditions for synthesis of 2,6-DHMMP under the premise of that condensation reaction does not occur.

we have been involved in the research of novolac resins used in lithographic resist and lithoagraphic printing plate for many years. In recent years, we have pioneered in using continuous stepwise base-acid catalyzed reaction, and synthesized o-cresol novolac and mixed-phenol novolac containing mainly o-cresol, both of which have high Mw, low Mw/Mn, and low contents of monomer and dimer, which solve the problem that existed in the history of novolac resin synthesis for a hundred years9). Later, using this method, we synthesized a series of novolac resins, such as p-/m-cresol resin, p-cresol/phenol resin, and p-/m-cresol/phenol resin, all of which has well application in printing plates. These achievements should be attributed to continuous stepwise base-acid catalyzed reaction. Hydroxymethylation occurs at base catalyzed reaction stage, and
produce 2,6-DHMMP as the main component of the intermediate. At the acid catalyzed stages, 2,6-DHMMP participates in condensation reaction, which produces novolac resins with high $M_W$, low $M_W/M_N$, and low contents of monomer and two nuclear bodies, due to that 2,6-DHMMP has higher reactivity than $p$-cresol. Though 2,6-DHMMP is the main component of the intermediate at the base catalyzed stage, there may be also a small amount of oligomer, single hydroxymethylated $p$-cresol, and $p$-cresol, all of which influence the condensation reaction at the acid catalyzed stage. The use of 2,6-DHMMP instead of intermediate product, can not only avoid some of the drawbacks exists in continuous stepwise base-acid catalyzed reaction, but also greatly simplify the process, shorten the production time, as well as uniform microstructure of resins. This will be another breakthrough in the synthesis of novolac resins, and the key is to explore a simple method for synthesis of 2,6-DHMMP.

2. Experimental

2.1 Materials

Formaldehyde solution (37%) was purchased from Kermel (Tianjin, China). Phenolic compounds were purchased from Jingchun Biochemical Technology Co., Ltd (Shanghai, China).

2.2 Detection of hydroxymethylation of $p$-cresol by DEPT135 spectrum

With stirring, the $p$-cresol, 20% NaOHaq, and 37% formaldehyde solution were added into the reaction flask, and the temperature was rapidly raised to the set reaction temperature. A small amount of the reaction mixture was taken at intervals, and neutralized with hydrochloric acid to pH 7. After that, the mixture were dissolved in an appropriate amount of Acetone-d6, and then DEPT135 spectrum was conducted on the Avance 500 Bruker NMR nuclear magnetic resonance spectrometer (Bruker AG).

2.3 Synthesis of 2,6-DHMMP

108g (1mol) of $p$-cresol was added to 200g of 20% NaOHaq, and then 178.4g of 37% formaldehyde solution (2.2mol of formaldehyde) was added with stirring to reacted at 60 °C for 4 hours. After cooled to room temperature, the mixture was neutralized with hydrochloric acid, filtered, washed three times, and dried at 50°C for 8 hours to obtain a white powdery solid. m.p. 114-118 °C, yield:≥90%, 2,6-DHMMP content: ≥97%, paraformaldehyde content:≤1%, soluble in common solvents for PS plate.

2.4 Synthesis of $p$-cresol/phenol novolac resin

51.7g (0.55mol) of phenol, 1g of oxalic acid and 12g of ethylene glycol monoethyl ether(EGME) were added into the reaction flask, and heated to 70 with stirring. With stirring, a total of 75.6g (0.45mol) 2,6-DHMMP was added to the reaction flask in 1h, during which the temperature was maintained at 70-80°C. Then the mixture was reacted at 90°C and refluxed temperatures for 1h, respectively. After that, the solvent was distillation, which taked 2.5h to reach 135°C, raised to 160°C 1 in 1h, raised to 200 in 0.5h, and maintained at 200°C for 0.5h. Ten the pressure was then gradually reduced to ≤0.1MPa and maintained 20-30min. 101.2g of $p$-cresol/phenol novolac resin was obtained.

A series of $p$-cresol/phenol novolac resin can be obtained at various of molar ratio of $p$-cresol to phenol. $p$-/m-cresol resin and $p$-/m-cresol/phenol resins can be obtained also according to this method wherein some technology should be adjusted appropriately. In all processes, the amounts of oxalic acid and EGME were 1% and 10-15% of the total phenol weight, respectively.

2.5 Measurement

The softening point (°C) of resins was measured by the ring and ball method accordance to national standard GB12007.6-89. $M_W$ and $M_W/M_N$ were analyzed via gel permeation chromatography by HLC-8320GPC(TOSO Co. Ltd.). THF was selected as solvent and PHS was used as calculation standard. Resin viscosity (mm²s⁻¹) was calculated with the standard of 33w% EGME resin solution accordance to national standard GB/T265.

3. Results and discussion

3.1 Optimum synthesis conditions of 2,6-DHMMP with NaOH as catalyst

We investigated the reaction of 2,6-xylenol and formaldehyde in 20% NaOHaq(equal molar of NaOH and $p$-cresol, similarly hereinafter)
according to method in literature[10]. The results showed that most of product was 4-hydroxymethyl-2,6-xylenol while temperature was lower than 15 °C, about half was bis(3,5-dimethyl-4-hydroxybenzyl)methane(DMHBM) when temperature was higher than 25°C, and almost all was DMHBM when temperature was higher than 40°C, which indicated that in basic conditions temperature played a very important role in the stability of hydroxymethylated phenolic compound. It also might be the reason that the conventional synthesis of 2,6-DHMMP are used basically concentrated alkali, low temperature, and long reaction time. We have also studied the reaction between p-cresol and formaldehyde at 60-70 °C in the presence of 1-2w% sodium hydroxide of the mass of p-cresol, and found that only hydroxymethyl reaction is occurred, and the main product is single hydroxymethylated p-cresol. After reaction for 6-8 hours under the condition, the yield of 2,6-DHMMP was only 30%[11]. Thus, even if the reaction temperature is high, the bishydroxymethyl reaction cannot occur completely due to insufficient amount of NaOH. Therefore, we propose that, in the premise condensation reaction does not occur, higher amount of NaOH than previous 1-2w%, or an appropriate higher reaction temperature than previous room temperature or 30-40°C, it takes shorter time for completely hydroxymethylation of p-cresol. Therefore, we studied the reaction of p-cresol and formaldehyde in 20% NaOHaq at different temperature.

DEPT135 was used to monitor the reaction between p-cresol and formaldehyde. The reaction mixture may include the product P1-P5 as shown in Fig. 1, as well as p-cresol and formaldehyde that did not react. The reactive position 2,6 and unreactive position 3,5 are all carbon atoms in the benzene ring, with peaks around 115 ppm and 128 ppm respectively. The inverted peak for -CH2OH is about 61 ppm. When there is condensation product, such as P3, P4 and P5, the -CH2- inverted peak will be around 30 ppm(Fig.2.). In DEPT135, the integral value of benzene ring carbon atom is coordinated with its number. Once the reaction of p-cresol and formaldehyde happens, no matter engaged in either hydroxymethyl reaction or condensation reaction, the number of 2,6-position carbon atom will decreases, whereas the 3,5-position carbon atom does not participate in the reaction. Therefore, the ratio of integral value of 2,6-position carbon atom ($I_{26}$) to integral value of 3,5-carbon atoms ($I_{35}$), namely $R_{(o)}$, is the residual percentage of the active sites in the reaction mixture, which could be used to quantitatively describe the reactive situation. The occurrence of an inverted peak at about 30 ppm is adopted to determine whether there is a condensation product or not.

As shown in Fig. 3, the reaction activity of p-cresol was high under concentrated alkaline conditions. Even at 30-40°C, the active points
remains only about 15% after 3 hours of reaction, whereas, it took 48 hours for reaction of all active points. According to the DEPT135 results, there was no condensation product after reaction at 30-40°C for 72 hours, which might be the reason that a reaction at room temperature or a slightly higher one for 2-3 days were used in previous reports. Higher the reaction temperature is, higher the reaction rate of the active point is. Over 85% of active points participated in reaction in 15 minutes at 60°C, and it tooks only 2 hours for reaction of all active points. In the condition of 60°C, DEPT135 results showed that there was no condensation product after reaction for 2-6 hours. At 70°C, the reaction time continuous decreased, but there was a small amount of condensation product at the late stage of reaction. When the reaction temperature was further increased, such as at 90°C or reflux temperature, condensation product was generated at the initial stage of reaction and its amount was really high when all the active point was reacted. We further confirmed our experiments at 60°C, and found that it tooked 2-3 hours for reaction of all active points at 55-60°C, particularly the product was only 2,6-DHMMP.

When the temperature is below 50°C, it tooks longer time for reaction of all active points even thought there is no condensation product. Otherwise, there was a small number of single hydroxymethylated p-cresol in the product. Using 2,6-DHMMP is to avoid the end-blocked effect of p-cresol due to its low reactivity. If a small amount of single hydroxymethylated p-cresol or p-cresol was in the final product, the effect of end-blocked was still existent. If there is a very small amount of condensation product P5 as shown in Fig. 1, it brings some problems for molecule design even though there was no end-blocked effect. In summary, the optimum reaction temperature is 55-60°C, and the optimum reaction time is 4 hours to ensure that all active sites can participate in reaction. The product obtained under these conditions contains no condensation product or p-cresol that does not engage in reaction, particularly, the reaction time is greatly shortened than before.

When the ratio of p-cresol to formaldehyde and reaction temperature were constant, reducing the amount of catalyst NaOH, it tooked longer time to consume all active points. When the amount of NaOH is 25%(molar percent, similarly hereinafter) of that of p-cresol, it took 10 hours for the reaction of all active points.

3.2 Optimum synthesis conditions of 2,6-DHMMP with organic base as catalyst

When the novolac resins are used in for LCD and IC photoresist, the metal ion content is a very important indicator. If NaOH is used as catalyst in the synthesis of 2,6-DHMMP the metal ion in the resin, particular sodium ion, will be greatly exceeded. Therefore, the primary choice of catalysts are organic bases with low metal ion content, such as trimethyl amine(TMA), triethyl amine(TEA) and tetramethyl ammonium hydroxide(TMAH, obtained using the electrolytic method ).

Base on the results with NaOH as catalyst, the influence of amount of TMAH was studied at 60°C. The DEPT135 results showed that, when the amount of TMAH was less than 10%, there was a small amount of unreacted active sites after long time of reaction, whereas, condensation product would be formed when the temperature was higher than 70°C. Results showed that at 60°C, all the active sites could be reacted within 10 hours if only the amount of TMAH was not less than 25% of p-cresol amount. In addition, more the amount of TMAH was, shorter time the reaction tooked.
When TMA or TEA was less than 10%, active points cannot react completely even in a long reaction duration. Elemental analysis showed that the product contained high N amount, particularly when TMA was used as catalyst, which suggested that the TMA or its salt could hardly be removed by washing with water. And gelling reaction happened during condensation reaction of 2,6-DHMMP and m-cresol when the ratio of formaldehyde to phenol was high and temperature was over 140°C. However, it’s not clear whether it is related to TMA residue in 2,6-DHMMP. In summary, when TMA is used as catalyst, low amount of catalyst cannot have ideal catalytic effect, whereas, high amount of catalyst resulted in large amount of catalyst residue in the product and effect condensation reaction in acid catalyzed reaction. Therefore, according to the DEPT135 result, the optimal catalyst amount is 20-50% of TMA or TEA in p-cresol.

3.3 Characteristics of novolac resins synthesized from 2,6-DHMMP and phenolic compounds

Under acidic conditions and temperature over 80°C, 2,6-DHMMP easily can be enrolled in condensation reaction with m-cresol and phenol, etc. Base on that, 2,6-DHMMP can be used to syntheses novolac resins in acidic condition.

A series of p-cresol/phenol novolac resins were synthesized. As shown in Table 1, when the ratio of formaldehyde to total phenolic compounds(phenol and p-cresol) is over 0.95, it’s easy to synthesize resins whose M_W is over 20,000. In addition, though the M_W was as high as 20000-30000, the M_W/M_N was only 15-20. The resins with M_W higher than 20000 has excellent resistance to alkali and alcohol, also due to a more regular structure in the resin.

The traditional method for p-cresol/phenol resins synthesis is that phenol(reactive point: ortho and para positions), p-cresol(reactive point: ortho position) and formaldehyde react under acid catalyst. The product with this method is disordered and contains o-o, o′-o′ and o-o′methylene bridges are at about 30ppm. O′-p and o-p methylene bridges resonate at about 35ppm. Peak of p-p methylene bridge is at about 40ppm. However, in DEPT135 spectrum of resins obtained from 2,6-DHMMP and phenol(Fig.4.b), there are only two resonances in methylene regions, which occur at about 30ppm and 40ppm respectively. The result shows that there is almost no p-p methylene bridge in these resins. It is obviously that condensation of two 2,6-DHMMP is almost impossible during the whole reaction course. Furthermore, it is very difficult to get o-o and o-p methylene bridges because there is no formaldehyde. Unreacted para position aromatic carbons of phenol should resonate at about 120ppm. In fact, peak at 120ppm is very weak, which indicates that almost all of p position aromatic carbons of phenol took part in reaction. Therefore, p-cresol/phenol resins synthesized by stepwise base-acid catalyzed reaction have more ordered structural configuration in which aromatic rings are linked only by o-o′ and o′p methylene bridges(Fig.4.a). The alternating structure is beneficial to the formation of intermolecular hydrogen bond, and thus resins prepared by 2,6-DHMMP and phenol have higher alkali and alcohol resistance in else same condition.
naphthol or 2,6-xylenol, especially \( \beta \)-naphthol and 2,6-xylenol, in the synthesis of \( p \)-cresol/phenol resin. Results showed that 2-5% of \( \beta \)-naphthol or 2,6-xylenol, the resin with \( M_W \) of 15,000 was difficult to dissolve in isopropanol. Though the \( M_W \) was high, it did not affect the sensitivity of the photosensitive compositions. The \( p \)-cresol/phenol resin synthesized by conventional methods has a \( M_W \) of 4000, and low alkali resistance, which limit its use in printing plate. Therefore, the \( p \)-cresol/phenol phenolic resin synthesized by stepwise base-acid catalyzed reaction method has a good prospect in the resist and printing plates.

The tradition \( p-m \)-cresol resin synthetic method is to put \( p \)-cresol and \( m \)-cresol together and condensation reaction occurs at acid catalyzed condition, in which 15-25% of \( p \)-cresol did not participate in the reaction due to lower reactivity of \( p \)-cresol than \( m \)-cresol. The unreacted \( p \)-cresol is either removed by evacuation or remains in the resin, thus the monomer is high in the resin. Moreover, the ratio of formaldehyde to total phenol should be not too high, e.g. it should be below 0.8 when \( p \)-cresol and \( m \)-cresol (4:6) were used to synthesize the \( p-m \)-cresol resin, or there will be more insoluble product.

### Table 1: Properties of novolac resins obtained by stepwise base-acid catalyzed reaction

<table>
<thead>
<tr>
<th>Novolac resins</th>
<th>F/P</th>
<th>( M_W ) and ( M_W/M_N )</th>
<th>Viscosity ((\text{mm}^2\text{s}^{-1}))</th>
<th>soften point ((^\circ\text{C}))</th>
<th>alcohol resistance</th>
<th>alkali resistance</th>
</tr>
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<tbody>
<tr>
<td>( p )-/( m )-cresol/phenol resins</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.9</td>
<td>4000, 2.0</td>
<td>60</td>
<td>150</td>
<td>S. 13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.925</td>
<td>9000-11000, 2.8-3.0</td>
<td>110</td>
<td>146</td>
<td>S. 20</td>
<td></td>
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<tr>
<td></td>
<td>0.94</td>
<td>17000, 10-12</td>
<td>170</td>
<td>154</td>
<td>S.S. 30</td>
<td></td>
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<tr>
<td></td>
<td>0.95</td>
<td>26000, 15</td>
<td>260</td>
<td>149</td>
<td>D.S. 30</td>
<td></td>
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<tr>
<td></td>
<td>0.98</td>
<td>( &gt;30000, 18-20 )</td>
<td>300</td>
<td>/</td>
<td>D.S. /</td>
<td></td>
</tr>
<tr>
<td>( p )-/( o )-cresol/phenol resins</td>
<td>0.95</td>
<td>18000-20000, 10-12</td>
<td>171</td>
<td>154</td>
<td>D.S. 60</td>
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<tr>
<td></td>
<td>0.97</td>
<td>30000, 15-20</td>
<td>315</td>
<td>154</td>
<td>D.S. 100</td>
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<tr>
<td>( p )-cresol/phenol/( \beta )-naphthol resin</td>
<td>0.94</td>
<td>12000, 5-7</td>
<td>155</td>
<td>153</td>
<td>D.S. /</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.875</td>
<td>3000, 1.9</td>
<td>54</td>
<td>155</td>
<td>S. 17</td>
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<tr>
<td></td>
<td>0.9</td>
<td>4000, 2.2</td>
<td>77</td>
<td>160</td>
<td>S. 34</td>
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<td></td>
<td>0.74</td>
<td>8600, 7.8</td>
<td>/</td>
<td>135</td>
<td>S. 28</td>
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<tr>
<td></td>
<td>0.89</td>
<td>20000, 12</td>
<td>/</td>
<td>142</td>
<td>S. /</td>
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</tr>
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</table>

F/P: the molar ratio of formaldehyde to total phenolic compounds(phenol, \( m \)-cresol, \( p \)-cresol, etc)
S: soluble in isopropanol
D.S: difficultly soluble in isopropanol

Results in Table 1 show that \( p-m \)-cresol novolac resins synthesized by the reaction of 2,6-DHMMP and \( m \)-cresol have outstanding characters. First, almost all of the 2,6-DHMMP and \( m \)-cresol took part in condensation after reacted at 70-200\(^\circ\text{C}\) for 6-8h under catalyst of acid, and most of unreacted monomers are removed by evacuation at 200\(^\circ\text{C}\) for about 0.5h, which induce the trace contents of monomers and dimer in the final product. Second, the synthesis of \( p-m \)-cresol resin by the stepwise base-acid catalyzed method needs that the ratio of formaldehyde to total phenol is not more than 0.925. And resin with high \( M_W \) and low \( M_W/M_N \) can be synthesized by adjusting the ratio of 2,6-DHMMP and \( m \)-cresol. Resin with \( M_W \) as high as 10,000, or even higher than 20000 can be synthesized in appropriate conditions. When the \( M_W \) was no more than 25,000, the \( M_W/M_N \) was generally not more than 15. Third, when condensation occurred between 2,6-DHMMP and \( m \)-cresol, it is very inclined to get \( m \)-cresol and \( p \)-cresol alternating co-condensation product, or a structure very close to that. High content of \( p \)-cresol and regular structure of the resin make it easy to meet such requirements of resistant to alkaline and etching. \( P-m \)-cresol resins obtained by conventional acid-catalyzed method can be dissolved in 0.6% NaOHaq or 2.38% TMAHaq, whereas \( p-m \)-cresol resin (2.5/7.5)
obtained by using \textit{m}-cresol and 2,6-DHMMMP is difficult to dissolve when the molecular weight is only 4000-5000, suggesting the impact of the regular structure to the alkali resistance.

In order to obtain a \textit{p}/\textit{m}-cresol resin with moderate resistance to alkaline, the amount of 2,6-DHMMMP should be reduced appropriately and a appropriate amount of formaldehyde should be added to adjust ratio of formaldehyde to total phenolic compounds in order to control the molecular weight. Synthesized resin has excellent resistance to alkali and etching.

4. Conclusion

DEPT135 detection of the reaction of hydroxymethylation of \textit{p}-cresol was a very effective and sample method to optimize the reaction conditions of 2,6-DHMMMP as flowing: \textit{p}-cresol/formaldehyde/NaOH=1/2.2/1, reacted at 55-60 \textdegree \text{C} for 4 h. In fact \textit{p}-cresol can be bis hydroxymethylated fully while the molar ratio of NaOH and \textit{p}-cresol ranged from 1 to 0.25, however reaction time should increased as the amount of NaOH decreased.

TMA, TEA and TMAH were used as organic alkaline catalyst to produce 2,6-DHMMMP with very low metal ions content. The optimum reaction conditions with TMAH as alkaline catalyst was similar to that concluded in the presence of NaOH. The optimum molar ratio of TMA or TEA to \textit{p}-cresol was 0.2-0.5 and reaction time and temperature were the same. TMAH was preferred catalyst while organic alkaline was necessary.

Various series of novolac resins with extremely high or low M\textsubscript{W} and narrow M\textsubscript{W}/M\textsubscript{N} can be obtained by the co-condensation of 2,6-DHMMMP and phenol, \textit{m}-cresol, etc, in other words, by stepwise base-acid catalyzed reaction from \textit{p}-cresol and other phenolic compounds. Structural configuration of these novolac resins is alternating or semi alternating. The obtained phenol/\textit{p}-cresol novolac resins have excellent alcohol resistance and good alkaline resistance. \textit{P}/\textit{m}-cresol novolac resins have good etching resistance and high heat resistance.

References

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