doi:10.1246/cl.2010.422

Published on the web April 5, 2010

Preparation of High-molecular-weight Phenolic Resins by means of a Phase-separation Reaction System

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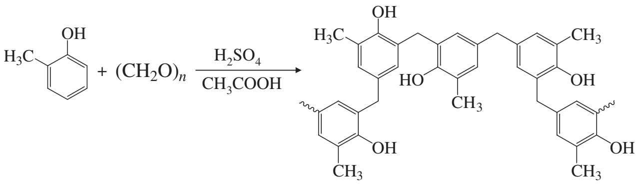
High-molecular-weight *o*-cresol resins with narrow-molecular-weight distribution were prepared using a phase-separation reaction system. The prepared *o*-cresol resins included a trace of monomer, so that the molecular-weight distribution was narrow. In high molecular weight *o*-cresol resin, the fractions of *ortho–ortho′*, *ortho–para′*, and *para–para′* methylene linkages were close to 25%, 50%, and 25%, respectively. This indicated that the reactivity of the *ortho* position was equal to that of the *para* position. It was found that the *o*-cresol ring was highly activated in phase separation reaction system using H_2SO_4/acetic acid.

Phenol resin is a typical thermosetting resin and widely used in engineering fields because of its heat-stability, electric insulation, and cost effectiveness. The resin, however, has serious shortcomings like brittleness and weak thermo-oxidative stability, which have limited the application in other fields. In order to improve these properties, some modifications are needed and a copolymerization with long chain alkyl phenols and a blend of phenolic resins with elastomers have been attempted.[1] High-molecular-weight phenolic resins have been prepared in good yield.[2,3] The advantages of high-molecular-weight polymers are 1) the increase of intermolecular interaction, 2) the increase of entanglement, and 3) the expansion of chains by excluded-volume effects. These effects will make the heat-stability and flexibility of resin higher.

On the other hand, molecular-weight distribution of phenol resins strongly affects the properties. In particular, phenolic monomer and low-molecular-weight oligomers have lower mechanical strength and show less desirable thermal properties. Consequently, it is necessary to prepare high-average-molecular-weight phenol resin with narrow-molecular-weight distribution free of low-molecular-weight species.

In this report, we attempt to prepare high-average-molecular-weight and also soluble phenolic resins from *o*-cresol as monomer. These high-molecular-weight linear phenolic resins will be more flexible and heat-stable than networked phenolic resins. In order to prepare higher-average-molecular-weight *o*-cresol resin with narrow-molecular-weight distribution, a phase separation reaction system in organic solutions was applied. The reaction conditions are optimized, and the molecular structure of high-average-molecular-weight *o*-cresol resin is investigated.

We have now found that a phase-separation reaction is carried out in acetic acid by using *o*-cresol, paraformaldehyde and H_2SO_4 as a catalyst, as shown in Scheme 1. A typical procedure follows. *o*-Cresol (1 mol) and paraformaldehyde (1 mol as formaldehyde component) were dissolved in 250 mL of acetic acid. H_2SO_4 (0.05 mol) was added dropwise and the reaction mixture was stirred at 80 °C for 1 h.



Scheme 1. Synthesis of *o*-cresol resin.

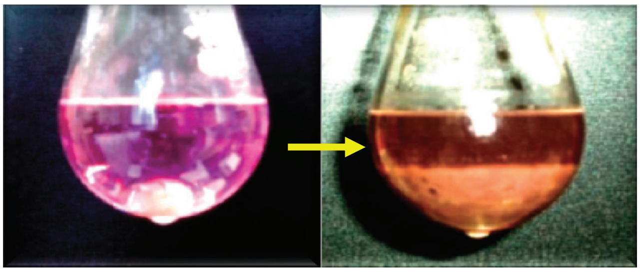


Figure 1. Photographs of reaction mixtures before and after phase separation.

The reaction mixture was separated to upper and lower phase solution. The high-molecular-weight *o*-cresol resins were included in the lower phase. The lower-phase solution was poured into a large amount of water to obtain resin. The *o*-cresol resin was dried overnight in vacuo to give an 80% yield of *o*-cresol.

Figure 1 shows typical phase-separation behavior of the reaction mixture. The molar ratio of *o*-cresol to formaldehyde (*o*-CR/F) affected the molecular weight of prepared resins. In order to prepare high-average-molecular-weight *o*-cresol resin the value of *o*-CR/F has to be unity. If the value of *o*-CR/F is larger than unity, unreacted *o*-cresol monomers were left and high-molecular-weight *o*-cresol resin was not prepared. In contrary, if the value of *o*-CR/F is smaller than unity, insoluble and gel-like swollen *o*-cresol resin was sometime formed. GPC profiles of prepared crude *o*-cresol resins (without purification by precipitation) in the lower-phase solution are shown in Figure 2. In each GPC profile a trace of *o*-cresol monomer (ca. 1 wt %) was observed, and the peak top of prepared *o*-cresol resin was shifted to higher molecular weight with increasing reaction time: the number average molecular weight M_n of each *o*-cresol resin was 2300 ($M_w/M_n = 1.8$) in 1 h, 3500 ($M_w/M_n = 2.6$) in 2 h, 5700 ($M_w/M_n = 5.9$) in 3 h, and 7500 ($M_w/M_n = 4.7$) in 4 h, analyzed by GPC using polystyrene standards. These results indicated that the reactivity of *o*-cresol and formaldehyde was so high that the phase-separation reaction system was preferred to prepare high-molecular-weight *o*-cresol resins.

The molecular structure of resins was determined by ^{1}H and ^{13}C NMR measurements. The typical ^{13}C NMR spectra of *o*-

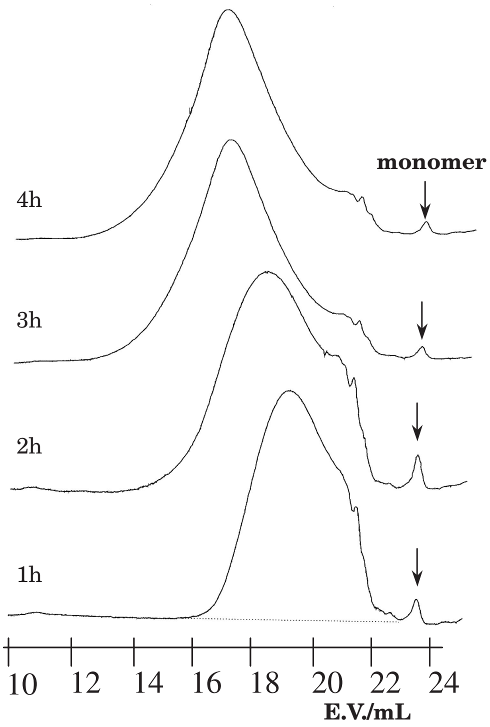


Figure 2. GPC profiles of *o*-cresol resins obtained from the lower phase solution at 70 °C (*o*-CR/F = 1.0).

cresol resins with $M_n = 1.3 \times 10^3$ ($M_w/M_n = 1.9$) and 1.0×10^5 ($M_w/M_n = 7.6$) are shown in Figure 3. These samples were obtained from the upper and lower phases under the typical reaction condition, respectively. The methylene carbon of *ortho–ortho′*, *ortho–para′*, and *para–para′* linkages give peaks in the range from 30.8 to 41.0 ppm.[4] In this work, the structure of the high-molecular-weight resin was estimated by the fractions of three kinds of methylene linkages. In high-molecular-weight *o*-cresol resin, the fractions of *ortho–ortho′*, *ortho–para′*, and *para–para′* methylene linkages were close to 25%, 50%, and 25%, respectively, as the molecular weight became higher. This indicated that the reactivity of the *ortho* position was equal to that of the *para* position in *o*-cresol ring. In a previous report, the reactivity of the *ortho* position was lower than that of the *para* position under acidic conditions for the preparation of phenolic resins.[5,6] The difference in reactivity between *ortho* and *para* positions decreases under the phase-separation reaction conditions. In the spectrum of *o*-cresol resin with $M_n = 1.0 \times 10^5$ new signals were observed at 35.0 and 30.8 ppm. The assignment was not clear, but the signals would be expected to correspond to new methylene linkages on the *meta* position. In addition, the IR spectrum of higher-molecular-weight *o*-cresol resin ($M_n = 1.0 \times 10^5$) showed a new ether stretching band at 1050 cm^{-1} (Supporting Information[7]). From these observations and the formation of insoluble *o*-cresol resins, an unexpected network is formed in this reaction system. New cross-linkages will be formed by *o*-cresol rings and phenolic hydroxy groups with formaldehyde. These results indicated that the *o*-cresol ring was highly activated in the phase-separation reaction system using H_2SO_4/acetic acid. Therefore, if *o*-CR/F < 1 gel-like *o*-cresol resins will be formed.

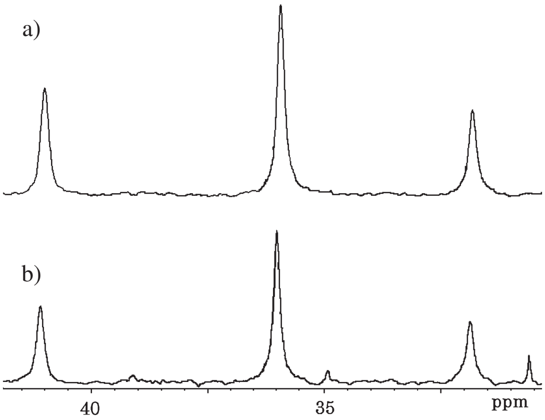


Figure 3. ^{13}C NMR spectra of *o*-cresol resins in THF-d_8: a) $M_n = 1.3 \times 10^3$ ($M_w/M_n = 1.9$) and b) $M_n = 1.0 \times 10^5$ ($M_w/M_n = 7.6$).

From the obtained results we have concluded that the phase-separation reaction system for the polymerization of *o*-cresol and formaldehyde gave high-average-molecular-weight phenolic resins in good yield. This will be due to the concentration effect of the reactive species in the polymer-rich phase.

This work was partly supported by the Grant-in-Aid for Scientific Research(C) (No. 14550844 and No. 20550185) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, for which we are grateful. P. W. also thanks Honors Scholarship for Privately Financed International Students by Japan Student Services Organization (JASSO) for financial support.

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7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.