Phenolic Resins. I. Condensation Polymers from 8-Hydroxyquinoline and Formaldehyde

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(Received November 15, 1966)

Although the condensation reactions between phenols and formaldehyde have been studied extensively,[1] the condensation polymers between 8-hydroxyquinoline and formaldehyde were not reported on. Since such polymers were expected to be capable of chelation, an investigation was undertaken on these polymers in our laboratories. When our work was almost finished, Degeiso, Donaruma and Tomic[2] reported on the synthesis of a condensation polymer from 8-hydroxyquinoline and formaldehyde and the use of such polymer for a separation of UO_2^{2+} from Cr^{3+}, Co^{2+} and Al^{3+} at pH 3, and of UO_2^{2+} from Zn^{2+} at pH 2.

Only a part of our findings, not covered by Degeiso's paper, will be reported on in this paper, which describes the preparation of 8-hydroxyquinoline-formaldehyde polymers with various degrees of condensation by three different methods, the preparation of chelate polymers with various metal ions, and the thermal stabilities of these polymers and chelate polymers.

Results and Discussion

8-Hydroxyquinoline and formaldehyde were condensed by three different methods. The resin A, prepared by use of oxalic acid as the catalyst, softened at 90—95°C. The resin B, prepared by use of oxalic acid and hydrochloric acid, had the softening point near 140°C. The resin C, prepared by use of barium hydroxide, did not melt but moistened at 200°C and solidified at 290°C.

When the resin A was heated with 15—37wt% of hexamethylenetetramine at 160°C for 20 min,

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[1] For instance, M. Imoto, H. Kakiuchi and K. Wo, "Formaldehyde, Its Chemistry and Applications," Asakura Shoten, Tokyo (1965).

[2] R. C. Degeiso, L. G. Donaruma and E. A. Tomic, *J. Appl. Polymer Sci.*, **9**, 411 (1965).

it became very viscous but did not solidify. Since 8-hydroxyquinoline is a bifunctional phenol, this behavior is understandable.

The metal chelates of the 8-hydroxyquinoline-formaldehyde polymers were prepared by mixing the dimethylformamide solution of the polymer and the dimethylformamide solution of a metal acetate and refluxing the mixture. The metal chelate of the polymer precipitated, which was filtered and dried. The Mn^{2+}, Cu^{2+} and Co^{2+} chelates of the polymer were prepared from their acetates. The chelate polymers were green powdery polymers which did not melt when heated up to 360°C.

The content of manganese in the Mn^{2+} chelate polymer was analyzed, and it was found that only 69.4% of the theoretical content of manganese was present in the chelate polymer. This non-stoichiometric chelation may be ascribed to the steric reasons imposed by the polymer chains. The infrared spectrum of the chelate polymer indicated the presence of small amount of OH.

The chelate polymers were powdery even at 360°C, and could not be used for molding. But these chelate polymer could be condensed with an ordinary Novolak-type phenol-formaldehyde resin by heating the mixture with hexamethylenetetramine at 160°C, and by this method some molded objects could be prepared.

The thermal stabilities of the polymers were determined by measuring the weight loss of the polymers in air at 400°C. The resin C lost 40.6% of its original weight in first one hour, 33.4% in next one hour and 7.1% in another one hour at 400°C. The Mn^{2+} chelate of the resin C lost 79.6% of its original weight in first one hour, and none in next two hours at 400°C. The thermal stability of other metal chelates was similar or worse than this. Then, the thermal stabilities of these polymers were compared with that of a phenol-formaldehyde resin. A Novolak-type phenol resin was cured by treatment with 15% hexamethylenetetramine at 160°C, and the weight loss of the cured resin at 350°C in 30 min was found to be 6.6%. The resin C, under the identical condition, lost 12.1%, whereas the Mn^{2+} chelate of the resin C lost 31.1% of the original weight. These findings indicate that the polymers with chelate structure are thermally less stable than the polymers without chelate structure. The reason may be as follows. Though the presence of ionic and coordination bondings may increase the stability of the polymer to some extent, these metal ions can change their ionic valency and thus may catalyze the degradative oxidation of the polymer. At any rate, the metal chelates of 8-hydroxyquinoline-formaldehyde polymer cannot be used as a heat-resisting polymer, although such polymer may have much use for the separation of various metal ions.

Experimental

Condensation of 8-Hydroxyquinoline with Formaldehyde. *Method A.* A 37% formaldehyde solution containing 2 g (0.024 mol) of formaldehyde was mixed with 5 g (0.03 mol) of 8-hydroxyquinoline and 0.06 g of oxalic acid dihydrate, and the mixture was refluxed for five hours. The resin formed was washed by refluxing it in water and methanol, and was dried. The resin A thus obtained weighed 4.0 g and softened at 90—95°C.

Method B. 8-Hydroxyquinoline (2.9 g, 0.02 mol), 2.0 g of 37% formaldehyde solution (0.024 mol), and 0.1 g of oxalic acid dihydrate were mixed and refluxed for 2 hr. To this, 1 m*l* of 1.2 N hydrochloric acid was added, and the mixture was heated for 11 hr. After washed and dried, the resin B weighed 2.2 g and softened near 140°C.

Method C. 8-Hydroxyquinoline (2.9 g, 0.02 mol), 2.5 g of 37% formaldehyde solution (0.03 mol), and 0.1 g of barium hydroxide octahydrate were mixed and heated at 80°C for 3.5 hr. After washed and dried, the resin C weighed 3.0 g. It did not melt but moistened at 200°C and solidified at 290°C.

Metal Chelates of 8-Hydroxyquinoline-Formaldehyde Polymer. Mn^{2+} Chelate. 0.435 g of the resin C (containing 3.0 mmol of 8-hydroxyquinoline unit) was dissolved in 10 m*l* of dimethylformamide. To this solution was added a 10 m*l* of dimethylformamide containing 0.367 g of manganese acetate tetrahydrate (1.5 mmol). The mixture was refluxed for 10 min, and the chelate polymer precipitated was filtered and dried. The green powdery polymer weighed 0.54 g. When heated, it darkened near 300°C but did not melt up to 360°C. The manganese content of the chelate polymer was analyzed by dissolving it in nitric acid. The polymer contained 10.4% manganese, whereas the theoretical value was 15.0%.

Another method of preparation was to heat the metal acetate and the polymer without any solvent. When 0.10 g of the resin C (0.690 mmol of quinoline unit) and 0.085 g of manganese acetate tetrahydrate (0.345 mmol) were heated, acetic acid evaporated at 150—200°C. After the mixture was heated up to 300°C, the appearance and the physical properties of the chelate polymer was the same as those of the chelate polymer obtained by the DMF method. The infrared spectrum was almost the same except the presence of some acetate peaks, indicating the presence of some unreacted manganese acetate in the chelate polymer prepared by this direct method.

Similar chelate polymers were prepared from resins A and B as well.

Cu^{2+} and Co^{2+} Chelates. The method used for Mn^{2+} was applied for the preparation of Cu^{2+} and Co^{2+} chelates. From cupric acetate and cobaltous acetate, green powdery chelate polymers were obtained. The appearance and the physical properties of these chelate polymers were similar to those of the Mn^{2+} chelate.