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Preparation of a Chelating Poly(β-Diketone) Resin from Poly(Vinyl Alcohol) and Its Use in the Reversible Complexing of Metal Ions

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Summary

A water-insoluble poly (β-diketone) chelating resin has been prepared by the controlled oxidation of poly(vinyl alcohol) with chromic acid. The polymer forms stable complexes with divalent and trivalent cations, such as Co^{+2}, Cu^{+2}, Mn^{+2}, Ni^{+2}, Fe^{+3}, Au^{+3}, and UO_2^{+2}, and removes them completely from dilute aqueous solution. The ions may be recovered quantitatively from the resin complex by elution with dilute aqueous acid and the resin is reusable.

Introduction

Chelate-forming resins of several types are known and include condensation polymers derived from formaldehyde, 1,3-dihydroxybenzene, and 2,4,6-trihydroxbenzoic acid and related compounds (PARRISH 1955), or from 3-hydroxyphenylthiourea (HOJO 1959). Of perhaps greater significance are the chelating resins containing iminodiacetate, iminotriacetate and related structures substituted on polystyrene matrices (MOCK et al. 1961; HERING 1961, 1965a,b), which have found application in analytical chemistry (HERING 1965c; RILEY, TAYLOR 1968a,b). It was of interest to produce a strictly aliphatic water-insoluble chelating polymer containing a repeating β-diketone unit, which would then be expected to function in a manner analogous to 2,4-pentanedione. Two obvious approaches to the formation of the desired polymer include the controlled oxidation of poly(vinyl alcohol), containing the repeating 1,3-diol unit, and the base-catalyzed hydrolysis of a poly(vinylidene halide). Both procedures were investigated, but the oxidation method, which is described in this communcation, has thus far proved to be the more effective.

Oxidations of poly(vinyl alcohol) with a variety of oxidizing agents have been reported and include chromic acid (TRUDELLE, NEEL 1964), benzophenone with photocatalysis (TRUDELLE, NEEL 1965), copper and silver oxides (HARTEL, NEBEL 1966), hydrogen peroxide (SUCH, DAVISON 1967), N-bromosuccinimide (SAIGUSA, ODA 1954), and sodium hypochlorite and hydrogen peroxide (BAYLESS, et al. 1971). However, the principal purposes cited were to alter the properties of solutions of the original polymer, (e.g., viscosity), to modify the characteristics of films obtained from poly(vinyl alcohol) solutions, or to investigate the extent of degradation of the polymer or the degree of conversion of alcohol to carbonyl functions. One reported oxidation (OKAMURA, MOTOYAMA 1959) using uranyl acetate

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while the mixture was irradiated with ultraviolet light, led to the formation of a water-soluble product which formed a complex with Cu(II). We wish to report the preparation of a water-insoluble poly (β-diketone) resin by the partial oxidation of poly(vinyl alcohol) with chromic acid. Experiments were undertaken to determine the ability of the resin to quantitatively remove Co^{+2}, Cu^{+2}, Mn^{+2}, Ni^{+2}, Fe^{+3}, Au^{+3}, and UO_2^{+2} from dilute aqueous solutions, and subsequent quantitative recovery of each cation from the resin-ion complex.

Experimental

Oxidation. A solution prepared from 28.5 g CrO_3, 500 ml H_2O, and 175 ml conc. H_2SO_4 was added slowly to a stirred suspension of 25 g poly(vinyl alcohol) (99% hydrolyzed) in 375 ml H_2O. The oxidizing agent was added at such a rate that the temperature did not exceed 60°C. The stirred mixture was then heated to 95°C, where it was maintained for 24 hours. The dark brown solid product was filtered and washed thoroughly with water, and finally dried over anhydrous $CaCl_2$ in a vacuum desiccator at 20 Torr (yield 15.3 g). The infrared spectrum (KBr) included the following bands: 3400 cm^{-1}, s; 1700 cm^{-1}, s (absent in the starting material); 1615 cm^{-1}, s, enol C=C; 1200 cm^{-1}, s, =C-O; 1050 cm^{-1}, m, -C-O-.

Chelation of cations. The "acid" form of the resin, as obtained from the oxidation reaction, was found to be only partially effective in removing cations from their solutions at the existing pH. However, conversion of the resin to the base form, by treatment with 1 M NaOH (30 ml/g polymer), produced a material which effected total removal of each of the test ions from individual solutions. The following general procedure was used in each case:

To 3 g of resin was added 20.0 ml of an approximately 0.01 M solution of the cation, and the mixture was stirred for 15 minutes. The mixture was filtered with gentle suction and an aliquot of the filtrate was reserved for analysis. After thorough washing with water, the resin-metal complex was stirred with 20 ml of 3 M HCl or HNO_3. The mixture was then filtered and the filter cake was washed with water. The filtrate was transferred to a 100 ml volumetric flask and made up to volume. An appropriate portion of the latter solution, the original solution, and the first filtrate were then analyzed by standard photometric (Co, Fe, Mn, Ni) or volumetric (Cu) procedures. In each case the concentration of cation in the first filtrate was reduced to zero, while total recovery of the cation by acid washing of the resin-metal complex was ascertained.

Tests for complex formation with Au^{+3} and UO_2^{+2} were carried out, but only qualitative analyses were employed to detect the removal of each ion by the resin and subsequent displacement from the resin. Gold appeared to be easily complexed and eluted, but while all of the uranyl ion was taken up by the polymer, elution was somewhat slower. Stirring for 30 minutes with 5 M HNO_3 was necessary for total recovery.

One test was performed to determine the utility of the resin when packed in a column. A 15 mm. i.d. chromatography tube was packed to a height of 15 cm with the polymer (added as a slurry in water). To the column was added 20.0 ml of a 0.01 M Cu^{+2} solution, followed by 500 ml of water. No copper could be detected in the eluate. Following elution with 100 ml of 3 M HCl, analysis of the eluate verified recovery of the total amount of Cu added.

Discussion of Results

The product obtained from the oxidation of poly(vinyl alcohol) with chromic acid under the conditions described appears to be the expected poly (β-diketone) resin. While the OH band was still very much in evidence in the infrared spectrum, no attempt was made to determine the relative proportions due to unoxidized secondary alcohol groups and to enol, respectively. The band at 1050 cm^{-1}, however, appeared at a considerably reduced relative intensity as compared to the same band in the spectrum of the starting material. Attempts to completely oxidize all the alcohol groups to carbonyl resulted in severe degradation of the polymer, but partial oxidations (66-75%) produced the resins with the desirable characteristics. Oxidations of solutions of poly(vinyl alcohol) in water resulted in the precipitation of a product very similar to that obtained from the suspension, but the yield was greatly reduced (7 g. from 25 g starting material).

The utility of the chelating resin for the removal of specific ions from solution has been clearly established. The resin was also found to retain its effectiveness after multiple usage (chelation, acid wash, reconversion to base form). Preliminary tests for the selective separation of the ions from a mixture appear promising and experiments in this area are continuing. Further studies on the use of other oxidizing agents and improvement of the yield of poly(β-diketone) are in progress, as are investigations of alternate methods of producing the resin.

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