NOTES 3503

Preparation of a Permselective Membrane Based on Cellulose

In the course of study of the graft polymerization of N-carboxyanhydrides (NCA's) of amino acids on the alkoxide derivatives of polyhydroxy polymers such as cellulose acetate, polyvinyl alcohol, etc., and on viscose solutions, we have studied the possibility of attachment of cysteic acid units to cellulose by reaction of NCA of cystine with viscose solutions as follows:

$$\begin{array}{c} \text{Cellulose-Xanthate} + \begin{bmatrix} -\text{SCH}_2\text{CHCO} \\ \text{NHCO} \end{bmatrix}_2^2 \\ \text{Cellulose-Xanthate-[cystine]}_n \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{Cellulose-[cystine]}_n \xrightarrow{\text{Br}_2/\text{H}_2\text{O}} \\ \text{Cellulose-O-CO-CH-CH}_2\text{SO}_3\text{H} \\ \text{NH}_2 \\ \text{I} \\ \text{Cellulose-O-CO-NH-CH-CH}_2\text{SO}_3\text{H} \\ \text{COOH} \\ \end{array}$$

The reaction of the NCA with cellulose xanthate may lead to the attachment of single amino acid units to the cellulose backbone or of polypeptide fragments. However, cleavage of the disulfide bond of the cystine by oxidation with bromine² will lead to the formation in both cases of a cysteic acid derivative of cellulose in which single cysteic acid units are attached to the cellulose.

The mode of attachment of the amino acid to the cellulose was not investigated but it may be either through the carboxyl group as ester (I) or through the amino group as carbamate (II).

Films cast from the viscose solution after the above treatment were found to have permselective properties.

EXPERIMENTAL

Preparation of Cysteic Acid Derivative of Cellulose

Cellulose xanthate was prepared by the usual procedure³ from 6 g. alkali cellulose dissolved in 4% sodium hydroxide solution; L-cystine NCA (0.33 g.) was added with stirring. The homogeneous reaction mixture was left for two hours at room temperature and cast as a thin film on a glass plate. The film was held in aqueous sulfuric acid for regeneration of the cellulose,³ and the amino acid derivative of cellulose was thus obtained in film form. It was oxidized with a saturated aqueous bromine solution for about 1.5 hr. to oxidize the cystine bonds to cysteic acid. The film was washed with water and ethanol and dried. It contained 0.5% nitrogen corresponding to 6% cysteic acid.

The use of the film as a permselective membrane was determined. The permselectivity of the film was measured by placing it between 0.1 and 0.05N KCl solutions and measuring the EMF across it. The value found was 8.4 mV.

In a similar experiment a film of cellulose-cysteic acid was prepared. It contained 0.3% nitrogen and the EMF measured was 7.3 mV.

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Yair Avny Albert Zilkha

Department of Organic Chemistry The Hebrew University Jerusalem, Israel

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