33. X-ray Studies on the Reaction between Polyvinyl Alcohol and Congo Red

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It is known that polyvinyl alcohol is precipitated from its aqueous solution with congo red, a substantive dye, as with boric acid. According to our experiments, in 1.5% congo red solution gelatination occurs while in 3% solution syneresis takes place. Changes in X-ray diagrams also begin to be remarkable from this concentration. The most strong interference corresponds to a spacing of 4.21 Å.

By the immersion of polyvinyl alcohol films or filaments in congo red solutions of various concentrations, similar results are obtained. After the immersion, the films and the filaments are plastic and can be drawn to several times of their initial length. X-ray diagrams of such drawn filaments show three new interferences on the meridian. The spacings are 13.25, 8.80 and 6.54Å respectively. The fiber period calculated from the above spacings is 26.4 Å. While such interferences can be found neither by pure polyvinyl alcohol nor by congo red powder, it may be assumed that these interferences belong to a complex between polyvinyl alcohol and congo red. A provisional estimation of the monoclinic unit cell of the complex is as follows: $a=8.20$ Å, $b=26.4$ Å, $c=4.57$ Å, $\beta=81°30'$.

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34. The Viscosity of the Deformed Rod-like Macromolecule in Solution

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The model of a rod-like macromolecule regularly crooked zigzag on the same plane was adopted.

This model is supposed to be a medium state between the rigid molecule of spherical or ellipsoidal type assumed by Einstein, Jeffery, Eisenschitz, etc. and the flexible molecule of pearlnecklace type assumed by Debye-Bueche.

To calculate the frictional force of our model, it is assumed that this force is nearly equal to the total sum of frictional forces acting on each sphere alternately arreanged. Following results has been obtained by the hydrodynamic method, under the condition that the velocity gradient of the flow is " q " and the rotational energy per unit volume of the macromolecule has components in three directions,

$$E_R(I)=\frac{G}{16}\eta_0 q^2\left\{\sin^2\phi+\frac{1}{n^2}\cos^2\phi\right)\left(\frac{l}{d}\right)^2\Big\}$$

$$E_R(II)=\frac{G}{16}\eta_0 q^2\left\{\sin^2\phi\left(\frac{l}{d}\right)^2\right\}$$

$$E_R(III)=\frac{G}{16}\eta_0 q^2\left\{\frac{1}{n^2}\cos^2\phi\left(\frac{l}{d}\right)^2\right\}.$$

G: total volume of macromolecule n: number of elements

ϕ: angle between two elements l: total length of a molecule

Using above relations, the following equation can be obtained for the viscosity of a rod-like macromolecule in solution.

$$\eta=\eta_0\left\{1+2.5G+\frac{G}{24}\left\{\sin^2\phi+\frac{1}{n^2}\cos^2\phi\right)\left(\frac{l}{d}\right)^2\right\}.$$

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35. Studies on the Polyvinyl Octyl- and Enant-acetals

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The octyl-, enant- or its mixed acetals with butyral were made from polyvinyl alcohol in water, benzene or dioxane. The experimental results on the solubility of acetals are shown in Table I.

Table I. Solubility of acetals, acetalized in water phase.
(Polyvinyl alcohol 5 g., 17.5% HCl 50 cc., equivalent ratio of aldehyde used, 1 : 1, Temp. 30°C., Time 30 min.,) S: Soluble; I: Insoluble.

Kinds of aldehydes	Degree of acetalization (Mole %)	Solubility against					
		Methanol	Ethanol	Acetone	Butyl-acetate	Cyclo-hexanone	Dioxane
Form-	33.1	I	I	I	I	I	I
Acet-	43.2	S	S	I	S	S	S
Propion-	59.6	S	S	S	I	S	S
Butyr-	62.8	S	S	I	I	S	S
Enant-	63.6	I	I	I	I	S	S
Octyl-	64.0	I	I	I	I	S	S

Enantacetal was also soluble in ethylenechloride, nitrobenzene, mixture of benzene-ethylenechloride (1:1), benzene-carbon tetrachloride (1:1), benzene-ethanol (1:1) in hot state or partially soluble in aniline.

The mechanical properties of films obtained from both acetals were measured