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Infrared Spectra of the Stereoisomers of Pentane-2,4-diol as a Model for Polyvinyl Alcohol

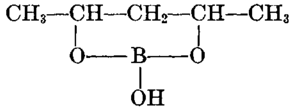
Physical and chemical properties, including infrared absorption spectra, of a high polymer can be accurately studied with the aid of a low molecular weight model substance whose chemical structure is similar to that of the polymer.

For a general (atatic) vinyl polymer, however, it is necessary to prepare two models which correspond to the short-range sequences in the polymer chain, i.e., with isotactic and syndiotactic dispositions, respectively, of its functional groups.

The simplest two models for polyvinyl alcohol are given by pentane-2,4-diol, CH_3—CH(OH)—CH_2—CH(OH)—CH_3, We first aimed at the separation of its two stereoisomers by adopting the chromatographic method employed by Khym et al.,[1] who succeeded in the separation of a sugar mixture.

To strengthen the adsorptive power of the diol to the borate form anion-exchanger, it was converted to a sodium-borate complex type and developed by dilute sodium borate solution. The elution curve indicated that it could be clearly separated into the two constituents by this procedure.

The two kinds of the boric acid complex crystal prepared were identified by analysis as the monodiol-boric acid complex of pentane-2,4-diol



$$\begin{array}{ccccccccc} CH_3 & - & CH & - & CH_2 & - & CH & - & CH_3 \\ & & | & & & & | & & \\ & & O & - & B & - & O & & \\ & & & & | & & & & \\ & & & & OH & & & & \end{array}$$

but were found to differ in melting point and crystalline form as shown in Table I, where β denotes the form which eluted faster.

Crystallization of the β-diol, derived from its complex in a super-saturated solution in CS_2, kept at room temperature (below 20°C.) for about two weeks. The liquid β-diol began to crystallize at once when a crystal was added. The α-diol could not be brought to crystallization by the same procedure. Further x-ray analysis now in progress will determine the type of stereoisomer to which each of them belongs.

Infrared spectra of the α- and β-diols and their boric acid complexes are reproduced in Figures 1 and 2. The intense band near 9 μ of each of the diols may correspond to the 1096 cm.$^{-1}$ (9.12 μ) band of polyvinyl alcohol, which was assigned, to the ν(CO) mode of the polymer by Krimm et al.[2] As shown in Figure 3, marked differences were found between the diol types when the infrared absorption measurements were conducted on their dilute CS_2 solutions. In the α-diol, the band near 8.7 μ (1157 cm.$^{-1}$), initially small, became very intense, and at the same time a band appeared at 9.08 μ (1108 cm.$^{-1}$),

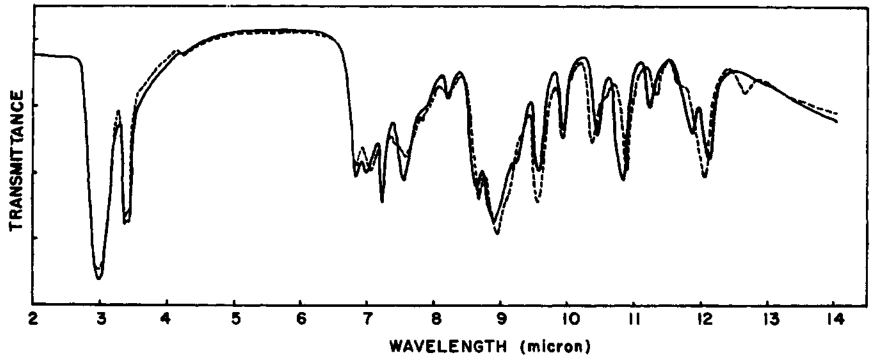


Fig. 1. Infrared spectra of α,β-diols. (—) α-Diol. (- -) β-Diol.

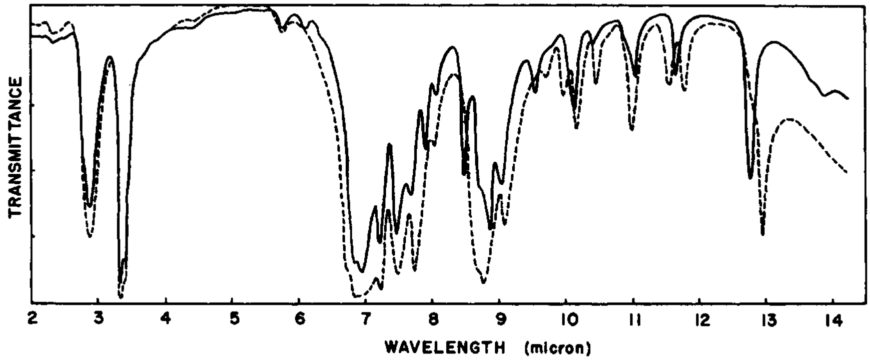


Fig. 2. Infrared spectra of the boric acid complexes of α,β-diols in Nujol. (—) α-Diol boric acid complex. (- -) β-Diol boric acid complex.

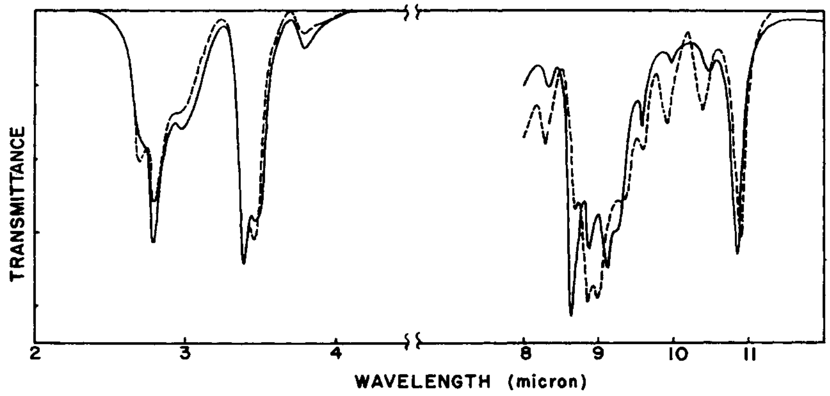


Fig. 3. Infrared spectra of the CS_2 solution of α,β-diols. (—) α-Diol. (- -) β-Diol.

TABLE I
Boric Acid Complexes

	M.p., °C.	C, %	H, %	Crystal form and axial ratios
α	85	46.67	8.65	monoclinic, $a{:}b{:}c = 0.561{:}1{:}1.141$, $\beta = 113°$
β	37	45.52	8.36	orthorhombic, $a{:}b{:}c = 0.627{:}1{:}1.090$
	theor.	46.21	8.53	

TABLE II
Diols

	B.p., °C.	M.P.,	C, %	H, %	Crystal form and axial ratios
α	96/11.5 mm., Hg	—	56.60	11.56	
β	99/12.7 mm. Hg	52–53	56.54	11.45	monoclinic, $a{:}b{:}c = 1.32{:}1{:}1.40$, $\beta = 92°$
		theor.	57.71	11.55	

seemingly in the sacrifice of the band near 9 μ. In the β-diol, however, the band near 8.7 μ did not suffer so great a change, but a small splitting was observed in the intense band near 9 μ. Two absorptions observable at 2.76 and 2.81 μ (3623 and 3559 cm.$^{-1}$) may be attributed to ν(OH) modes, respectively, of free and intramolecularly hydrogen bonded hydroxyl groups.[3] The linear band-intensity ratio at 2.81 to 2.76 μ is, however, greater in the α-diol than in the β-diol. This would suggest that the molecular structure of the former might have a stronger tendency to form intramolecular hydrogen bonding when they were dissolved in a nonpolar solvent. If so, the most probable structure of the α-diol would be "isotactic," where its two hydroxyl groups are located on one side of the carbon chain.

In Figure 4 are reproduced the spectra of the β-diol measured in crystalline and molten states. Large splitting in the intense band near 9 μ was brought about by crystallization, giving a new band at 9.17 μ (1091 cm.$^{-1}$).

Deuteration effects were examined. As shown below, deuteration of OH to OD seems to have cancelled out not only the band-splitting by crystallization seen above, but also the "dilution-splitting" as observed before.

Figure 5 shows the spectra of the partial deuterated α- and β-diols, the latter being kept in crystalline state. In Figure 6 are reproduced the spectra of their dilute CS_2 solutions, where neither splitting of the band near 9 μ for the β-diol nor a new appearance of an intense band beyond 9 μ were observed for the α-diol.

These facts would suggest that factors responsible for the special changes brought by crystallization or dilution could operate only in the system where light hydrogen atom hydrogen bondings were formed inter- or intramolecularly.

It has been shown[2] that deuteration in polyvinyl alcohol weakens the 1096 cm.$^{-1}$ (9.12 μ) band, giving two new bands at 1128 (8.87) and 1052 cm.$^{-1}$ (9.51 μ). Without giving any assignment to the 1128 cm.$^{-1}$ band, Krimm et al. assumed that the 1096 cm.$^{-1}$ band shifted to 1052 cm.$^{-1}$ on the substitution of OD for OH.

Based on the experimental results given by the model diol compounds, we propose, however, an alternative assumption that it would rather shift to 1128 cm.$^{-2}$. A "new" band at 1052 cm.$^{-1}$ may be similar to the 1040 cm.$^{-1}$ shoulder band of the undeuterated polymer and also to the 9.5 $\sim$ 9.6 μ band of the models.

As for the 1144 cm.$^{-1}$ band of polyvinyl alcohol which was regarded by Japanese investigators[4,5] and others[6] as its crystallization-sensitive band, it seems to us that it may be associated with the 1157 cm.$^{-1}$ band of the α-diol, since the latter could become intense, like the former, making the absorption in the region of 8 to 11 μ resemble that of the polymer.

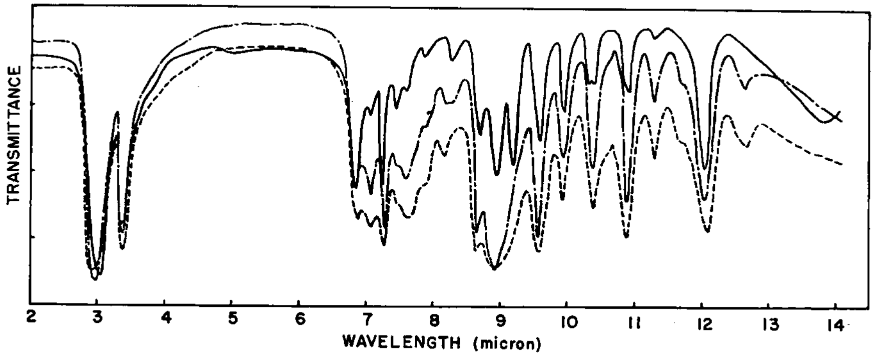


Fig. 4. Infrared spectra of β-Diol. (—) Crystal in Nujol. (— -) Liquid. (- -) Melt at 60°C.

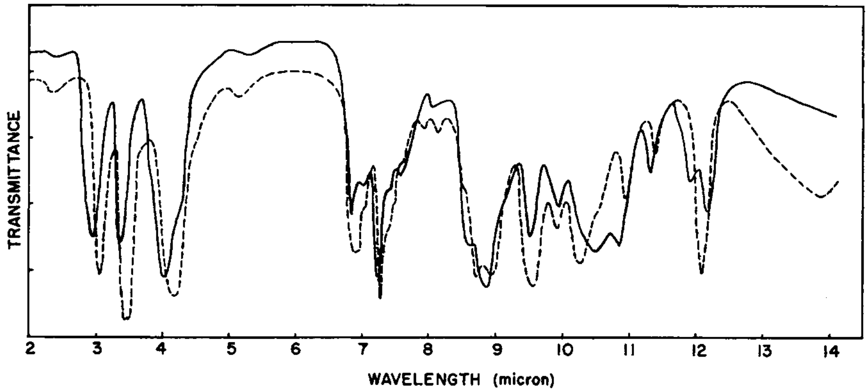


Fig. 5. Infrared spectra of partial deuterated α,β-diols. (—) α-diol (liquid). (- -) β-Diol (crystal in Nujol).

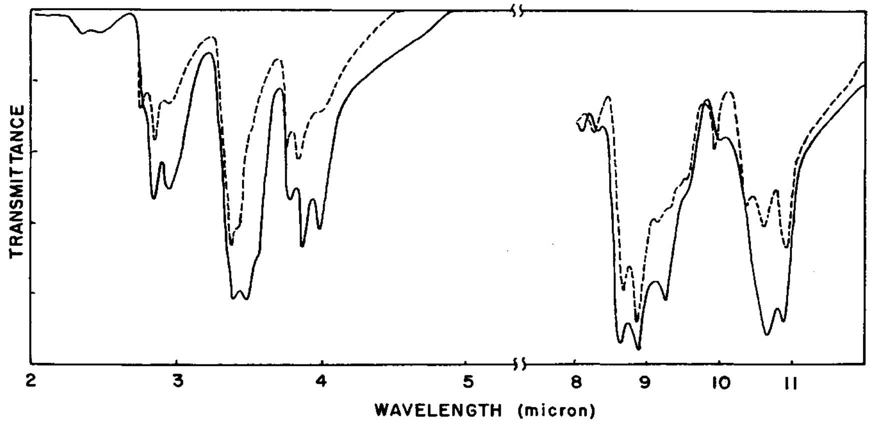


Fig. 6. Infrared spectra of partial deuterated α,β-diols in CS_2 solution. (—) Δ-Diol. (- -) β-Diol.

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The Viscosity Anomaly at Low Concentrations with Polystyrenes of Low Molecular Weight

Polymers in the most usual range of M.W. (10^5–10^6) have often been found to show upward deviations from the linear η_{sp}/c vs. c relationship at very low concentrations ($c <$ 0.01 g./dl.). Various explanations have been suggested,$^{1-3}$ e.g., *1*(a) the disentanglement of polymer chains, i.e., the achievement of complete solution at very low concentrations which is not attained at high, and (b) the hydrodynamic effect of an expansion of the polymer coils in solution at very low concentrations.

On the other hand, it has been argued^{4,5} that the anomaly is not a true effect of the viscosity but rather an artefact arising from adsorption of polymer on the surface of the viscometer resulting in: *2*(a) reduction in the true concentration in solution, and (b) reduction in the effective radius of the viscometer capillary.

To detect, and even more to measure, the effect with polymers of high molecular weight requires experiments of very great precision, since very small errors in the measurement of flow-time make for large errors in η_{sp}/c when c and η_{sp} are very small. However, with polymers in the M.W. range 1,500–30,000 we have found that the same effects are observable at much higher concentrations (0.2–1.0 g./dl.) and are easily detected, if not accurately measured, by the normal techniques of viscometry.

Figure 1 shows the viscosity behavior in benzene at 25°C. of two unfractionated samples of polystyrene, where P I is a H_2SO_4-initiated polymer of $\bar{M}_n$ 11,000 and P II is a thermal polymer (60°C. in CCl_4) of $\bar{M}_n$ 33,000. For both polymers, both η_{sp}/c and ln η_r/c show linear relations with c at high concentrations, but as can be seen from the magnified plots, a noticeable "upsweep" sets in below ~0.4 g./dl. for P I, and ~0.2 g./dl. for P II. At the lowest concentrations the errors are very great in the derived values of η_{sp}/c, and the exact course of the upsweep is uncertain.

In these experiments no especially precise methods of timing were used, but the measurements were very carefully made with a normal Ostwald viscometer of long flow time (477 sec. with benzene). The *maximum* variation in the flow time measurement was ∓ 0.5 sec., which includes the variation of the stopwatch and that arising from temperature fluctuations of the thermostat of $\sim\mp 0.01$°C. The points on the curves represent the mean of six flow-time measurements, and the maximum variation is also shown.