

pure water, whereas the equilibrium swelling ratio increases monotonously over the concentration range studied.

The structures of these two types of intramolecular hydrogen bonds are not known in detail, but it may be said that the "long range hydrogen bonds" are of the same kind as the intermolecular hydrogen bonds found in the concentrated solutions of PVA (presumably, the hydrogen bonds between the hydrated PVA molecules⁹), and the "short range hydrogen bonds" are so strong that the urea solutions cannot destroy them and the NaOH solution can break them only when its concentration exceeds about 6%, suggesting that neighboring OH groups would fit in each other very favorably (this must be closely related to the irregularity of the *d,l*-form of the OH groups).

The above point of view finds another support in the dependency of the behavior of $[\eta]$ upon molecular weight of the polymer. The increase of $[\eta]$ (i.e., the "long range" effect) is gradual and larger with the higher molecular weight, whereas the fall of $[\eta]$ (i.e., the "short range" effect) is rapid and the concentration at which it occurs is approximately independent upon the molecular weight.

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Studies on Copolymerization of Vinyl Benzoate

Investigations on the copolymerization of different monomers are of wide interest in as much as they may lead to suitable modification of the properties of the resulting product. The reactivities of different monomers also may be compared through studies of this nature. From a theoretical point of view, it is the reactivity ratios rather than the kinetic investigations which have received the greater attention. In the present paper studies on copolymerization of vinyl benzoate with vinyl acetate and styrene are reported.

The reactivity ratio of the monomers has been calculated by means of the well-known equation deduced by Alfrey and Goldfinger,¹ Mayo and Lewis,² and Wall³:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$

where r_1 and r_2 are the reactivity ratios of the two monomers; $[M_1]$ and $[M_2]$ represent the composition of the monomer feed mixture and $d[M_1]$ and $d[M_2]$ represent the incremental addition of the two monomers to the polymer.

Experimental Procedure

Vinyl benzoate was prepared from vinyl acetate and purified as usual. Vinyl acetate and styrene were freed from inhibitor and then distilled in vacuum. Benzoyl peroxide, used as an initiator, was purified by recrystallization.

Carefully weighed amounts of the monomers were mixed with suitable weights of benzoyl peroxide so as to give the same molar ratio of monomer to initiator in each case. Pairs of monomers in different proportions were pipetted into reaction tubes of Pyrex glass, flushed with nitrogen, chilled by liquid N₂, evacuated, and sealed. The mixture was polymerized to a less than 10% conversion at a temperature of $79.6 \pm 0.01^\circ\text{C}$. The polymer was isolated and purified by precipitation from benzene solution by methyl alcohol and was carefully dried in vacuum. Analysis of the copolymer was done by micro estimation of carbon in each case. Experimental results are given in Table I.

TABLE I
Copolymerization of Vinyl Benzoate

Second monomer	Composition of the feed mixture		Per cent conversion	Composition of the copolymer		r_1	r_2
	Moles of vinyl benzoate, $[M_1]$	Moles of 2nd monomer, $[M_2]$		Moles of vinyl benzoate $(d[M_1])$	Moles of 2nd monomer $(d[M_2])$		
Vinyl acetate	1.43	4.30	9.8	0.30	0.65	1.5	0.7
	2.15	3.23	10	0.41	0.46		
	2.87	2.15	9.5	0.53	0.26		
Styrene	1.43	4.31	10.7	0.01	0.95	0.05	38
	1.43	1.73	6	0.02	0.94		
	2.86	1.73	6	0.05	0.89		

The values from Table I were substituted in the copolymer composition equations, and r_1 and r_2 determined graphically as represented in Figures 1 and 2.

Reactivity of the Monomers towards Vinyl Benzoate Free Radical

Since r_1 is the ratio of the reaction rate K_{11}/K_{12} of the vinyl benzoate free radical with its own monomer to that of the same radical towards the second monomer, it is obvious that $1/r_1$ is the comparative reactivity rate of the second monomer towards vinyl benzoate free radicals. Thus the relative reactivity of monomers with vinyl benzoate free radicals is: (1) for styrene monomer, 20; (2) for vinyl benzoate, 1; and (3) for vinyl acetate, 0.67.

Hence, towards vinyl benzoate free radicals the reactivities are in the order styrene > vinyl benzoate > vinyl acetate.

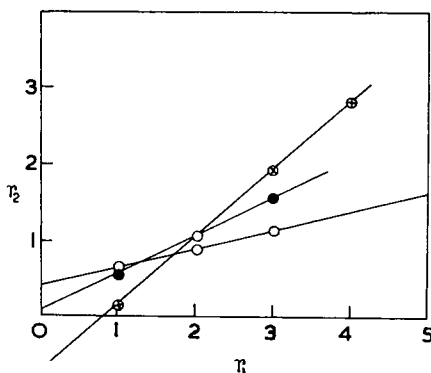


Fig. 1. Copolymerization of vinyl benzoate with vinyl acetate.

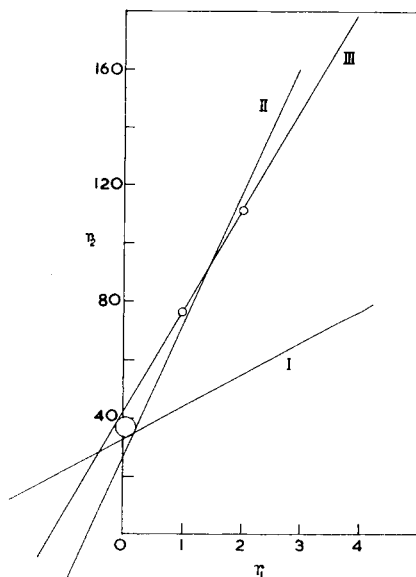


Fig. 2. Copolymerization of vinyl benzoate with styrene.

Discussion

In the copolymerization of styrene and vinyl acetate, it has been found that vinyl acetate radicals are about 100 times as reactive towards the styrene monomer as towards vinyl acetate monomer,⁴ whereas we observe that with vinyl benzoate radicals the reactivity is only 20 times as great. Copolymerization of vinyl benzoate with vinyl acetate proceeds in the usual manner.

All these observations can be explained by a consideration of the order of resonance stabilization of the free radicals: Styrene free radicals are highly stabilized by resonance, and the contribution of resonance is almost absent in the case of vinyl acetate free radicals. Vinyl benzoate occupies an intermediate position in this respect.

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

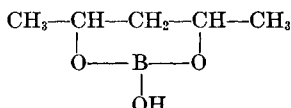
Physical and chemical properties, including infrared absorption spectra, of a high polymer can be accurately studied with the aid of a low molecular weight model substance whose chemical structure is similar to that of the polymer.

For a general (atactic) 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, $\text{CH}_3\text{—CH(OH)—CH}_2\text{—CH(OH)—CH}_3$. 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



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 $9\ \mu$ of each of the diols may correspond to the $1096\ \text{cm}^{-1}$ ($9.12\ \mu$) band of polyvinyl alcohol, which was assigned, to the $\nu(\text{CO})$ 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 $8.7\ \mu$ ($1157\ \text{cm}^{-1}$), initially small, became very intense, and at the same time a band appeared at $9.08\ \mu$ ($1108\ \text{cm}^{-1}$),