

As the secondary direction for research on these possibilities, the effects of polym.-temperature on the changes of values of r are examined. The results are abulated as follows ;

Polym. Temp.	r_1	r_2
25°C	2.5 ± 0.21	0.14 ± 0.02
65°C	7.0 ± 2	0

Then the conditions of $r_1 > 1$ and $r_2 > 1$, could not be attained at ordinary temperature range.

34. Studies on Chemical Reactions of Polyvinyl Compounds

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Kinetics of deacetylation of polyvinyl acetate was discussed. The theory was in good agreement with experimental results, and based on this theory velocity constants of elementary reactions were calculated. Assuming that acetyl groups which have hydroxyl groups as their neighbour can be more easily deacetylated than other, it was concluded that at the initial stage of the reaction apparent velocity constant must increase nearly proportionally to the reaction degree. This is in good accordance with experimental results.

In connection with this reaction, saponification velocity of di-ester was also studied. In this case, apparent velocity constant can never be greater than twice of that at initial reaction.

Reaction velocity of acetalization and simultaneous acetalization-acetylation of polyvinyl alcohol was also discussed. The conclusion may be expressed as follows.

$$K_1 = K_0 \left\{ 1 - \frac{2X^2}{(2-X)^3} \right\} \quad (1)$$

$$K_2 = K_0 \left\{ 1 - \frac{2(X+2Y)^2}{(2-X)^3} \right\} \quad (2)$$

where K_1 and K_2 are apparent velocity constants, K_0 that of initial reaction, and X , Y are degree of acetalization and acetylation in mole fraction. K_1 becomes 0 when X reaches a value of 0.8603. This value is in good accordance with 0.8647 obtained by P. J. Flory.

Mixed acetalization of polyvinyl alcohol was also studied, and it was suggested that exchange of acetal A and aldehyde B, and of acetal B and aldehyde A should be considered.