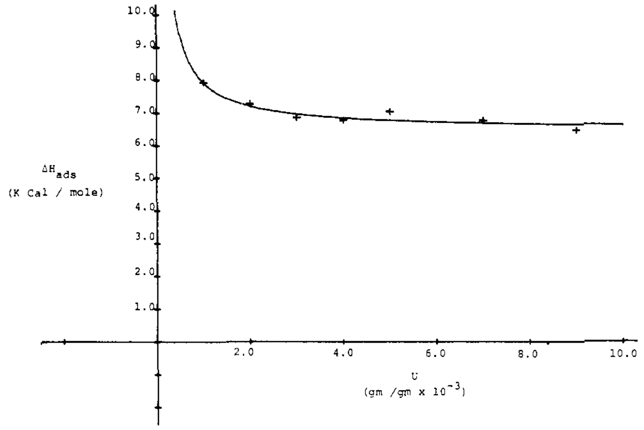

Figure 5. Dependence of isosteric heat of adsorption on moisture content.

Figure 4. The negative values of the heat of adsorption indicate an exothermic sorption process. Over the range of moisture contents studied, the isosteric heat of adsorption is highest at low moisture content and shows a slight decrease with an increase in the moisture content. Since the first molecules of water are taken up at the most active sites (highest activation energy), the evolution of heat corresponds to that of strong hydrogen bonding. The next molecules of water are adsorbed at weaker sites, as compared to the first sites occupied, and therefore lower activation energies are involved.

Since the heat of adsorption remains almost constant over the rest of the region studied, it would indicate that the rest of the active sites have an almost constant bonding energy, primarily that of hydrogen bonding in the peptide group. The absence of a dramatic change in the heat of adsorption confirms the previous interpretation of the data, in that most of the range of concentrations studied lie below the monomolecular layer. It should be noted that these data contradict one of the basic assumptions of the BET equation, according to which the heat of sorption for the first layer is constant and equal to the total heat of vaporization plus a constant heat due to site interaction. Evidently, the heat due to site interaction is higher for the first few sites occupied, while the balance of the sites do have an almost constant heat due to site interaction.

References and Notes

(1) A. V. Kiselev and Y. I. Yashin, "Gas Adsorption Chromatography", Plenum Press, New York, 1969.
(2) S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
(3) A. W. Adamson, "Physical Chemistry of Surfaces", Interscience, New York, 1963.
(4) B. H. Zimm and J. L. Lundberg, *J. Phys. Chem.*, **60**, 425 (1956).
(5) B. H. Zimm, *J. Chem. Phys.*, **21**, 934 (1953).
(6) D. G. Gray and J. E. Guillet, *Macromolecules*, **3**, 316 (1972).
(7) M. G. Neumann, *J. Chem. Educ.*, **53**, 708 (1976).
(8) E. R. Lieberman, S. G. Gilbert, and V. Srinivasa, *Trans. N.Y. Acad. Sci.*, **34**, 694 (1972).
(9) H. W. Starkweather, *J. Polym. Sci. Part B*, 1 (3), 133 (1963).
(10) U. Merten, "Desalination by Reverse Osmosis", Massachusetts Institute of Technology Press, Cambridge, Mass., 1966, Chapter 2.
(11) H. W. Starkweather, *Macromolecules*, **8**, 476 (1975).

Kinetic Study on the Inter- and Intramolecular Acetalization Reactions of Polymeric Reactants

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ABSTRACT: Inter- and intramolecular acetalizations of poly(vinyl alcohol) (PVA) carrying one or two terminal aldehyde groups were carried out in aqueous solutions as well as in dimethyl sulfoxide (Me_2SO) solutions over a wide range of the polymer concentration. The observed rate constant for intermolecular acetalization was in both the solutions independent of the polymer concentration and not significantly different from that for the acetalization of a conventional PVA with aldol, a homologous low molecular weight aldehyde. The results strongly suggest that the polymer coils interpenetrate rather freely with each other in concentrated solutions even of Me_2SO which is a good solvent of PVA (water is almost a Θ solvent of PVA). This finding is in agreement with the theory predicting that the excluded volume effect may not be large enough to be detectable under the experimental conditions of this study. In addition, the observed OH concentration effective for the intramolecular acetalization was compatible with that predicted by the statistics of polymer chains.

Intermolecular reactions of polymeric reactants have been frequently encountered, for instance, in the termination reaction of radical polymerization,[1] the gelation of polymers,[2] and syntheses of block and graft copolymers by coupling reaction.[3] Hydrolysis of a polymeric substrate with a polymer having catalytic sites such as enzymes or anionic or cationic synthetic polymers[4,5] also belongs to the polymer–polymer reactions. Kinetic studies of such polymer–polymer reactions are therefore of great significance. Although kinetics of diffusion-controlled intermolecular reactions have been studied in detail[1,6,7] especially on the termination reaction of propagating polymeric radicals in the radical polymerization, there are only a few experimental[5,8] and theoretical[9,10] studies on the chemically controlled intermolecular reactions, where the rate-determining step is not diffusion processes but chemical reactions. It is interesting to point out that Cho and Morawetz[5] found no excluded volume effect in such a polymer–polymer reaction, while Wetmur[10] found this effect to be very large.

It should be further emphasized that the kinetic studies of polymer–polymer reactions might provide valuable information with respect to the state of polymer chains in solution, since the reaction rate must be intimately related

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to the stationary state of polymer chains in solution, in which the transition rate of chain conformation is exceedingly high compared with the rate of reactions controlled by a chemical process. In dilute solution with a good solvent the mutual interpenetration of the randomly coiled chains is restricted, as suggested by the large second virial coefficient A_2. This reduction in the mutual interpenetration would be more pronounced between the chains of different chemical structures because of their poor compatibility. If this reduced mutual interpenetration leads to a decrease in intermolecular reaction rate of polymeric reactants, the kinetic approach may offer an alternative method to explore the mutual interpenetration of polymer coils in dilute solution. In addition, studies of polymer reactions may also give some suggestions on the important problem concerning the molecular state of polymer coils in concentrated solution,[11,12] similar to the recent neutron scattering studies, which show that polymer chains at high concentrations tend to their unperturbed dimensions.[13]

Intramolecular reactions of a polymeric reactant involve interesting features and have been studied in some detail.[14,15] In this reaction the chief factor influencing the reaction rate constant is the short-range interaction of segments in a polymer chain, while long-range interactions play an important role in intermolecular reactions.

Our previous paper[16] has revealed that terminal aldehyde groups of poly(vinyl alcohol) (PVA) formed upon its oxidation with ceric ion can readily react with hydroxyl groups in the same or different PVA molecules to give acetal linkages. Since this acetalization reaction seems to provide an adequate model for studying inter- and intramolecular reactions in which the chemically controlled step is rate-determining, we have kinetically studied the acetalization reaction of PVA with terminal aldehyde groups. In the present work PVA having one or two terminal aldehyde groups was synthesized and the acetalization reaction was followed in water and in dimethyl sulfoxide ($Me_2(SO)$) over a wide range of the polymer concentration. Me_2SO is known to be a good solvent[17] and water nearly a Θ solvent for PVA.[18] The rate constants observed for the intermolecular reaction will be compared with those predicted from dilute solution theories on an excluded volume effect and further with those observed for the acetalization of PVA with low molecular weight aldehyde analogues. We will also present results on the intramolecular acetalization.

Experimental Section

Materials. PVA having only one terminal aldehyde group was synthesized as in the previous paper[19] except that 2,2′-azobis(isobutyronitrile) (AIBN) was used as initiator. The procedure is reproduced here briefly. Vinyl acetate was polymerized at 60 °C in the presence of CCl_4 as chain transfer agent, the concentration of CCl_4 being 0.103 mol·L^{-1} and that of AIBN 5×10^{-5} mol·L^{-1}. Hydrolysis of this poly(vinyl acetate) (PVAc) yielded PVA having one terminal aldehyde group, hereafter designated as PVA-1, because the end group of the PVAc, $-CH_2CH(OCOCH_3)Cl$, was converted to $-CH_2CHO$ on hydrolysis, liberating CH_3COOH and HCl. The viscosity-average degree of polymerization of this PVA is 119 and the end-group determination described below shows that it has 0.81 aldehyde groups per molecule. The other PVA carrying two aldehyde groups on both of the chain ends, designated as PVA-2, was obtained by oxidizing a conventional PVA with sodium periodate which cleaves selectively and quantitatively the 1,2 glycol bonds present in PVA under formation of two aldehyde end groups. The viscosity-average degree of polymerization of PVA-2 is 114 and it contains 1.83 aldehyde groups per molecule, based on the amount of sodium periodate consumed for the oxidation. Both PVA-1 and PVA-2 were subjected to the acetalization without fractionation. Aldol selected as a low molecular weight model compound for the PVA with the terminal aldehyde group was distilled twice under reduced pressure. Acetaldehyde was purified by distilling paraldehyde over sulfuric acid. Other low molecular weight aldehydes were distilled once at atmospheric pressure. These aldehydes were stored in water and in Me_2SO as 2% solution. Me_2SO was dried over calcium hydride and then distilled under reduced pressure.

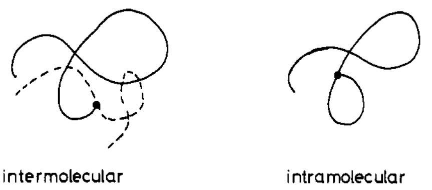


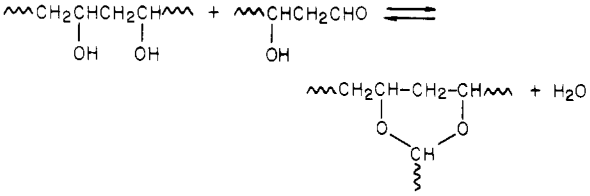
Figure 1. Schematic representation of inter- and intramolecular reactions.

Acetalization. The acetalization reaction was carried out in water or in Me_2SO throughout in the presence of 0.05 N HCl as a catalyst. In the acetalization in Me_2SO, 2.78 mol·L^{-1} water was always added, so that we need not consider the water molecules liberated (or consumed) as a result of acetalization (or deacetalization) in the kinetic analysis. The amount of added water is much larger than the water to be liberated (or consumed), but small enough not to influence the solvation of PVA by Me_2SO. The polymer concentration ranged from about 0.5 to 25 g·dL^{-1}. Erlenmeyer flasks containing the reaction mixtures were stoppered and kept in a water bath at the given temperatures. In the acetalization of PVA with low molecular weight aldehydes, the aldehyde concentration was kept at 5.45×10^{-3} mol·L^{-1} and that of PVA-0 1.88 g·dL^{-1}. PVA-0 refers to a polymer without terminal aldehyde groups; we used for this purpose a conventional PVA with the degree of polymerization of 1340.

The rate of acetalization, i.e., the rate of aldehyde consumption, was determined by neutralizing at regular time intervals an aliquot of the reaction mixture with NaOH to stop the reaction. The aldehyde remaining unreacted was determined with 3-methyl-2-benzothiazolone hydrazone hydrochloride.[20] The calibration curve required for determining the aldehyde end group attached to PVA was constructed with the use of the conventional PVA oxidized to various extents with known amounts of sodium periodate.

Results

The acetalization is a reversible reaction and proceeds as expressed by eq 1 in the case of PVA with a terminal



$$\sim CH_2CH(OH)CH_2CH(OH)\sim + \sim CH(OH)CH_2CHO \rightleftharpoons \sim CH_2CH(O)-CH_2-CH(O)\sim\,(>CH\sim) + H_2O \quad (1)$$

aldehyde group. The aldehyde group of PVA may undergo either intermolecular or intramolecular acetalization coupling reactions. This is illustrated schematically in Figure 1. Then the rate of acetalization is given by

$$-\frac{d[CHO]}{dt} = k_1[CHO] + k_2[OH][CHO] - k_{-2}[acetal][H_2O] \quad (2)$$

where k_1 is the first-order rate constant of intramolecular acetalization, k_2 is the second-order rate constant of intermolecular acetalization, and k_{-2} is the second-order rate constant of deacetalization. In our experiment the concentrations [OH] and [H_2O] are far higher than [CHO] and [acetal]. Thus eq 2 may be written as

$$-\frac{d[CHO]}{dt} = (k_1 + k_2[OH]_0)[CHO] - k_{-2}[H_2O]_0[acetal] \quad (3)$$

Table I
Kinetic Parameters for Acetalization and Deacetalization in Me_2SO Solution at 50 °C

aldehyde	k_2, L·mol⁻¹·s⁻¹	$\Delta H_2^{\ddagger}$, kcal·mol⁻¹	$\Delta S_2^{\ddagger}$, eu	k_{-2}, L·mol⁻¹·s⁻¹	$\Delta H_{-2}^{\ddagger}$, kcal·mol⁻¹	$\Delta S_{-2}^{\ddagger}$, eu
PVA-1	2.00×10^{-4}	14.3	−31.5	1.75×10^{-5}	14.7	−34.9
aldol	5.37×10^{-4}	14.1	−30.0	1.86×10^{-5}	22.1	−12.1
acetaldehyde	3.30×10^{-3}	11.1	−35.7			
propionaldehyde	1.98×10^{-3}	11.4	−35.8			
n-butyraldehyde	1.20×10^{-3}	10.9	−38.3			
isobutyraldehyde	7.35×10^{-4}	11.5	−37.5			
PVA-2 (in water)	3.04×10^{-4}	14.7	−29.4	5.56×10^{-6}	21.8	−15.4
aldol (in water)	8.91×10^{-4}	12.9	−32.7	1.26×10^{-6}	20.8	−21.3

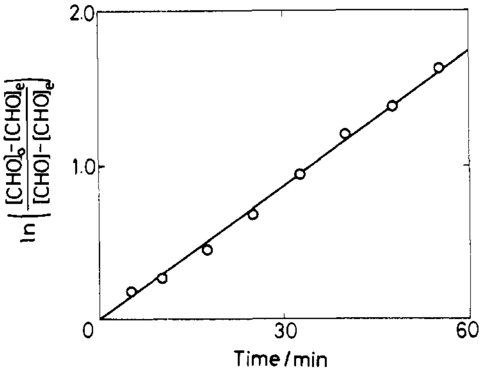


Figure 2. A reversible pseudo-first-order plot for acetalization of PVA-1 in Me_2SO solution at 50 °C. $[OH]_0 = 1.39$ mol. L⁻¹, $[H^+] = 0.05$ N, $[H_2O]_0 = 2.78$ mol·L⁻¹.

where $[OH]_0$ and $[H_2O]_0$ are the initial concentrations of the hydroxyl group and H_2O, respectively. At equilibrium, denoted by a subscript e,

$$-\frac{d[CHO]}{dt} = 0 = (k_1 + k_2[OH]_0)[CHO]_e - k_{-2}[H_2O]_0[acetal]_e \quad (4)$$

Equation 3 can be integrated to give

$$\ln\left(\frac{[CHO]_0 - [CHO]_e}{[CHO] - [CHO]_e}\right) = (k_1 + k_2[OH]_0 + k_{-2}[H_2O]_0)t \quad (5)$$

An example of the plot of $\ln(\{[CHO]_0 - [CHO]_e\}/\{[CHO] - [CHO]_e\})$ vs. the reaction time t is given in Figure 2. It is seen that eq 5 holds satisfactorily over the whole time range, though the reactant molecules become highly branched at increasing degrees of polymerization as the reaction proceeds. The good linearity seen in Figure 2 was also observed for the acetalization in H_2O. This finding suggests that the degree of polymerization of polymeric reactants might not have a marked effect on the reaction. Since the slope gives $(k_1 + k_2[OH]_0 + k_{-2}[H_2O]_0)$ and the ratio $(k_1 + k_2[OH]_0)/k_{-2}[H_2O]_0$ is obtained from eq 4, $k_2[OH]_0 + k_1$ and $k_{-2}[OH]_0$ can be calculated. The dependence of the determined $(k_1 + k_2[OH]_0)$ values on the PVA concentration expressed by $[OH]_0$ is plotted in Figures 3 and 4 for the reactions carried out at various temperatures in H_2O and in Me_2SO, respectively. The PVA samples used are PVA-2 for the acetalization in H_2O and PVA-1 for the acetalization in Me_2SO. For comparison the acetalization of PVA-1 was conducted also in H_2O and the result is given in Figure 3. Clearly, there is no noticeable difference between PVA-1 and PVA-2, indicating that the branching formed during the acetalization has virtually no influence on the reaction rate. The branching must be much more pronounced in the acetalization of PVA-2 than PVA-1, because the former has about two functional aldehyde groups in one starting molecule. Indeed, the acetalization of PVA-2 gave rise to gelation, when conducted at polymer concentrations higher than those in the present experiment. Further we have studied the effect of an addition of PVA-0 which has no aldehyde group but a high degree of polymerization. As is seen in Figure 4, PVA-0 does not exhibit any effect even when added to the reaction mixture in an amount twice that of PVA-1, again supporting the finding that the degree of polymerization does not practically influence the reaction.

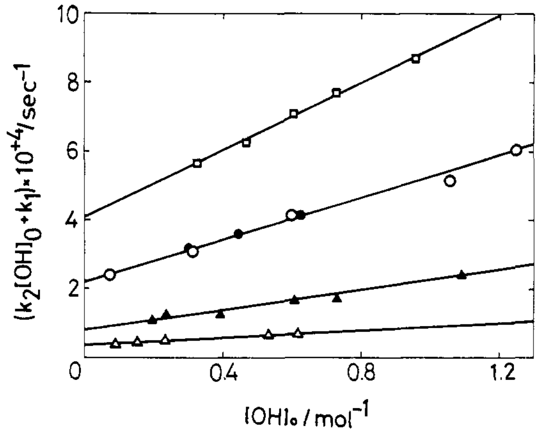


Figure 3. Dependence of $(k_2[OH]_0 + k_1)$ on the initial polymer concentration for acetalization of PVA-2 in aqueous solution, $[H^+] = 0.05$ N: (△) 30 °C; (▲) 40 °C; (○) 50 °C; (□) 60 °C; (●) 50 °C (PVA-1).

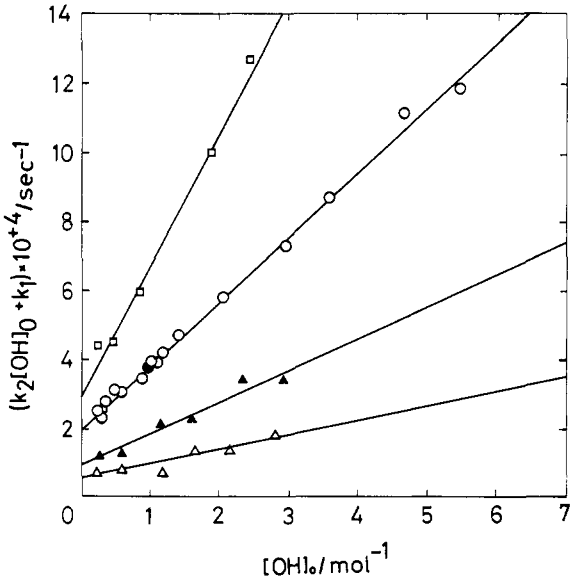


Figure 4. Dependence of $(k_2[OH]_0 + k_1)$ on the initial polymer concentration for acetalization of PVA-1 in Me_2SO solution ($[H^+] = 0.05$ N, $[H_2O]_0 = 2.78$ mol·L⁻¹): (△) 30 °C; (▲) 40 °C; (○) 50 °C; (□) 60 °C; (●) 50 °C (PVA-1 + PVA-0).

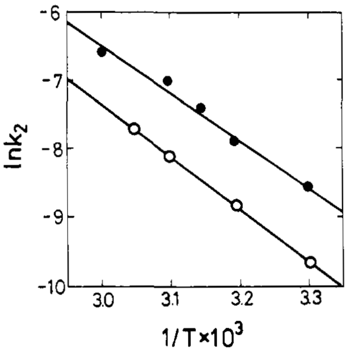


Figure 5. Arrhenius plots of second-order rate constants k_2 of acetalization in aqueous solution, $[H^+]$ = 0.05 N: (○) PVA-2; (●) aldol.

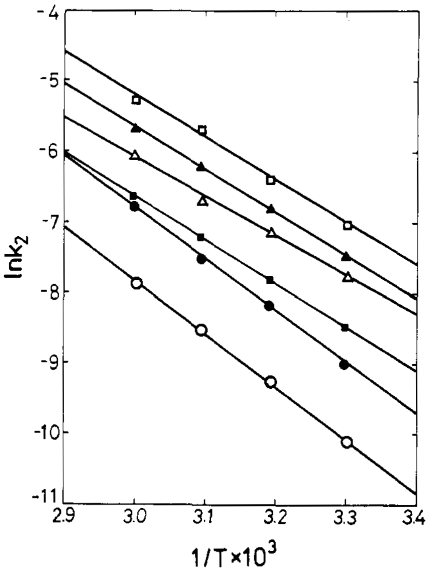


Figure 6. Arrhenius plots of second-order rate constant k_2 of acetalization in Me_2SO solution ($[H^+]$ = 0.05 N; $[H_2O]_0$ = 2.78 mol.L^{-1}): (○) PVA-1; (●) aldol; (□) acetaldehyde; (■) propionaldehyde; (△) *n*-butyraldehyde; (▲) isobutyraldehyde.

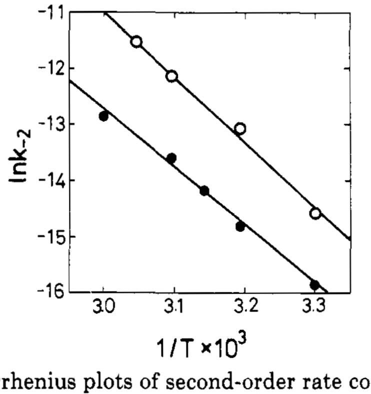


Figure 7. Arrhenius plots of second-order rate constant k_{-2} of deacetalization in aqueous solution, $[H^+]$ = 0.05 N: (○) PVA-2; (●) aldol.

The rate constants k_2 and k_1 can be calculated from the slope and the intercept of the plots in Figures 3 and 4. Arrhenius plots of k_2 are shown in Figure 5 for the reactions in H_2O and Figure 6 for those in Me_2SO together with the Arrhenius plots for the acetalization of PVA-0 with low molecular weight aldehydes. Figures 7 and 8 give similar Arrhenius plots for k_{-2}. The activation enthalpy $\Delta H^{\ddagger}$ and the activation entropy $\Delta S^{\ddagger}$ were calculated from these figures and tabulated in Table I, together with the rate constants k_2 and k_{-2} found at 50 °C.

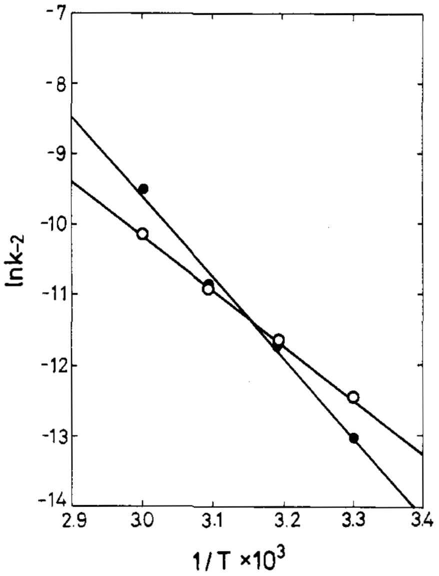


Figure 8. Arrhenius plots of second-order rate constant k_{-2} of deacetalization in Me_2SO solution ($[H^+]$ = 0.05 N; $[H_2O]_0$ = 2.78 mol·L^{-1}): (○) PVA-1; (●) aldol.

Table II
Rate Constants k_1 of Intramolecular Acetalization and Intramolecular OH Concentrations $[OH]_{intra}$

	water			Me_2SO		
T, °C	$k_1 \times 10^{-4}$, s^{-1}	$[OH]_{intra}$ mol·L^{-1}	$[OH]_{intra}$ g·dL^{-1}	$k_1 \times 10^{-4}$, s^{-1}	$[OH]_{intra}$ mol·L^{-1}	$[OH]_{intra}$ g·dL^{-1}
30	0.310	0.484	2.13	0.513	1.28	5.63
40	0.741	0.508	2.24	0.823	0.864	3.80
50	2.24	0.736	3.46	1.74	0.869	3.82
55	4.04	0.890	3.92			
60				2.92	0.763	3.36

If the intramolecular reaction is treated as a bimolecular process with a rate constant identical to that of the intermolecular reaction k_2, the rate of intramolecular acetalization $k_1[CHO]$ can be written as

$$k_1[CHO] = k_2[OH]_{intra}[CHO] \qquad (6)$$

Here $[OH]_{intra}$ is the apparent concentration of the hydroxyl group which is effective in the intramolecular reaction and hence belongs to the same polymer chain as the aldehyde group. The concentrations $[OH]_{intra}$ estimated from eq 6 are tabulated in Table II together with the rate constants k_1. For the low molecular weight aldehyde analogues such as aldol and acetaldehyde, the intramolecular reaction is not possible, so that the constant k_1 in the above equations should be omitted.

Discussion

Dependence of the Intermolecular Reaction Rate Constant k_2 on the Polymer Concentration $[OH]_0$. It is expected that the degree of interpenetration of random coils in a polymer solution may affect the rate of intermolecular polymer–polymer reaction. In order to discuss the interpenetration effect it is convenient to classify the polymer solution into two groups based on the concentration range, that is, the concentrated solution and the dilute solution, since the degree of mutual interpenetration of polymer coils must depend on the polymer concentration.

Two extremely different models on the structure of polymer coils are schematically shown for the case of concentrated solution in Figure 9. According to thermodynamic consideration the polymer molecules seem to

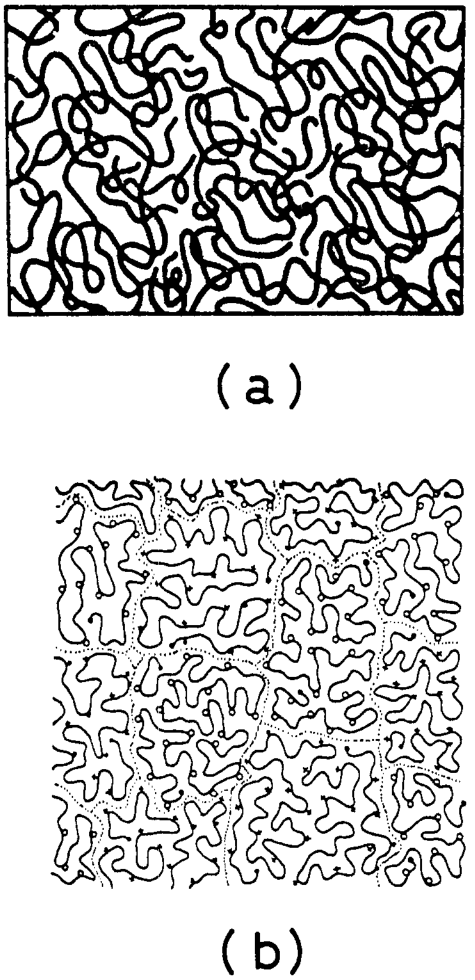


Figure 9. (a) Schematic representation of the freely interpenetrating random coil model. (b) Schematic representation of the individual cell structure model.

interpenetrate each other in sufficiently concentrated solutions, regardless of the solvency as shown in Figure 9a.[21] Vollmert and his co-workers have, however, concluded from their experiments on the polymer reactions that there is resistance to chain interpenetration even in concentrated systems where the excluded volume effect should disappear and presented the individual cell structure model as shown in Figure 9b.[22] If the polymer coils would behave as in the individual cell structure model, the rate of intermolecular reaction would be greatly reduced in comparison with that of the analogous small molecule reactions and in addition depend on the polymer concentration. In this connection the plot of $(k_2[\mathrm{OH}]_0 + k_1)$ vs. the PVA concentration $[\mathrm{OH}]_0$ in Figures 3 and 4 can give helpful information. Evidently, all the data fall on a linear plot even though $[\mathrm{OH}]_0$ is raised up to 5.5 mol·L^{-1}, i.e., 24 g·dL^{-1} in the acetalization in Me$_2$SO at 50 °C. This fact strongly indicates that the rate constant k_2 as well as k_1 remain unchanged in this polymer concentration range. Thus it follows that there is no strong restriction for the polymer coils to interpenetrate each other, as illustrated in Figure 9a. If this is true, the rate constants k_2 for the PVA with the aldehyde group should be comparable with those found for the low molecular weight model compound, aldol. Indeed, the result of Table I seems to confirm this expectation. The small difference in k_2 may not be attributed to resistance to mutual free interpenetration. It may be explained rather in terms of other causes such as the induced effect of substituent groups which often appears in the usual organic reactions, because such difference in k_2 is also observed among low molecular weight aldehydes (see Table I). In addition, the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for PVA-1 and PVA-2 do not exhibit any significant departure from those of low molecular weight analogues. Therefore it may be concluded that the polymer coils are present in the concentrated solution in a homogeneous state, interpenetrating freely, at least under our experimental condition.

For the case of dilute solutions, it has been recognized that the polymer coils can freely interpenetrate each other in Θ solvents, whereas there is some difficulty for mutual interpenetration in good solvents. All the theories concerned with the excluded volume effect on the rate of reaction involving two randomly coiled polymers predict that the reaction rate is low in good solvent media compared with the case where the excluded volume effect is not operative as in Θ solvents. In practice we do not find any deviation from the straight line in Figure 3, where the result of acetalization in water is given, which is approximately a Θ solvent for PVA. This implies that k_2 is really held constant, irrespective of the polymer concentration. On the other hand, it is expected that k_2 in Me$_2$SO, a good solvent for PVA, must be smaller in dilute solution than in concentrated solution, resulting in a smaller slope of the plots at the lower concentration. Contrary to the expectation, no deviation from the straight line can be observed in Figure 4. However, this is understandable, if the excluded volume effect is not large enough to be detectable under the experimental conditions of this study. Indeed, the rate constant estimated on the basis of the excluded volume effect[23] is in agreement with the observed rate constant, as will be shown below.

In the theory we have demonstrated that the ratio of the rate constant in a good solvent, k_2, to that for the ideal low molecular weight analogues, k_2^0, is given by

$$\frac{k_2}{k_2^0} = (3.903\bar{Z} + 1)^{-4(2-2^{1/2})/3.903} \tag{7}$$

$$\bar{Z} = \left(\frac{3}{2\pi b^2}\right)^{3/2} \beta_2 n^{3/2} \frac{1}{\alpha_s^3} = \frac{Z}{\alpha_s^3} \tag{8}$$

where b is the effective bond length, $n + 1$ is the number of segments in a polymer chain, β_2 is the binary cluster integral for a pair of segments, and α_s is the expansion factor. To obtain k_2/k_2^0 we have to estimate the $\bar{Z}$ value. To this end we have applied intrinsic viscosity data of PVA in Me$_2$SO solutions[17] to the familiar Stockmayer–Fixman relation[24,25] and found Z to be 0.34 when the degree of polymerization is 119. $\bar{Z}$ is then calculated to be 0.29 from this Z value and the equation for α_s.[26] Thus inserting this $\bar{Z}$ value into eq 7 we obtain $k_2/k_2^0 = 0.56$. This ratio, which is not much smaller than unity, implies that the excluded volume effect on k_2 is not large enough to be detectable in such dilute solutions. It may be also taken into consideration that the polymer concentrations studied might not be sufficiently low, allowing the mutual interpenetration to occur to some extent.

OH Concentration $[\mathrm{OH}]_{\mathrm{intra}}$ Effective for Intramolecular Acetalization. In analogy with the derivation of k_2 for the intermolecular reaction,[23] the rate constant $k_{1,i}$ for the intramolecular reaction of OH groups belonging to the ith segments with the terminal aldehyde attached to the 0th segment can be written

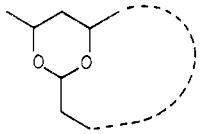
$$k_{1,i} = k_2^0 \frac{g\Omega_i^*}{\Omega_0} \tag{9}$$

Here k_2^0 is the rate constant which would be obtained if the aldehyde end group was separated from the parent polymer chain. Ω_0 and Ω_i^* are the configurational partition functions of the PVA reactant and the transition state complex, respectively. The weight factor g represents the number of reaction groups per segment.

Since the segments other than the ith one can also participate in the intramolecular reaction, we must sum up the $k_{1,i}$ to obtain the overall rate constant.

$$k_1 = \sum_{i=j}^{n} k_{1,i} \tag{10}$$

The lower limit j for summation comes from the fact that the OH groups neighboring too closely to the terminal aldehyde cannot take part in the intramolecular reaction because of bulkiness of the resulting acetal linkage:



With the use of the probability distribution function of the end-to-end distance of freely jointed chains, Morawetz and his co-workers[14] have shown k_1 to be given by

$$k_1 = k_2^0\left(\frac{3}{2\pi}\right)^{3/2}\frac{\Phi_0}{K}\sum_{i=j}^{n} g(iM_s)^{-3/2} \tag{11}$$

where M_s is the molar mass of the segment, K is the parameter in the empirical formula for the intrinsic viscosity in Θ solvent ($[\eta] = KM^{0.5}$), and Φ_0 is the universal constant ($=2.5 \times 10^{23}$). Comparison of eq 6 with 11 yields

$$[\mathrm{OH}]_{\mathrm{intra}} = \frac{1000}{N_A}\left(\frac{3}{2\pi}\right)^{3/2}\frac{\Phi_0}{K}\sum_{i=j}^{n} g(\mathrm{i}M_s)^{-3/2} \tag{12}$$

$$[\mathrm{OH}]_{\mathrm{intra}} = \frac{1000}{N_A}\left(\frac{3}{2\pi}\right)^{3/2}\frac{\Phi_0}{K}\sum_{i'=gj}^{p} (i'M_0)^{-3/2} \tag{13}$$

where N_A is Avogadro's number, M_0 is the molar mass of the repeating unit, and p is the degree of polymerization of the polymer chain. In this derivation $1000/N_A$ was introduced to express the concentration as a molarity and k_2^0 was assumed to be identical to k_2, since this calculation was confined to the solution in the Θ state. $[\mathrm{OH}]_{\mathrm{intra}}$ is identical to C_{eff} defined by Morawetz and his co-workers.[14]

We can compare the $[\mathrm{OH}]_{\mathrm{intra}}$ estimated from eq 13 with that observed for the acetalization in aqueous solutions, because H_2O is almost a Θ solvent, at least in a range of high temperatures. The observed concentrations $[\mathrm{OH}]_{\mathrm{intra}}$ given in Table II agree with the theoretical estimation, if the $gj \approx 15$. This result suggests that the intramolecular acetalization does not lead to appreciable formation of small rings consisting of less than j segments. It is interesting to point out that with increasing temperature $[\mathrm{OH}]_{\mathrm{intra}}$ decreases in water, but increases in Me_2SO. This is in accordance with the well-known fact that solution of PVA is endothermic in water and exothermic in Me_2SO.

Finally, it should be stressed that the intramolecular reaction contributes rather markedly to the whole polymer reaction even in concentrated solutions, although the intramolecular reaction is often regarded to be negligible compared with the intermolecular reaction.

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References and Notes

(1) A. M. North, "Progress in High Polymers", Vol. 2, J. C. Robb and F. W. Peaker, Ed., Iliffe, London, 1968, p 95, and references therein.
(2) I. Sakurada and Y. Ikada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 25 (1962); **41**, 103 (1963); **42**, 22 (1964).
(3) Y. Ikada, K. Maejima, and H. Iwata, *Makromol. Chem.*, **179**, 865 (1978).
(4) I. Sakurada, Y. Sakaguchi, and Y. Omura, *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 135 (1966).
(5) J.-R. Cho and H. Morawetz, *Macromolecules*, **6**, 628 (1973).
(6) G. Wilemski and M. Fixman, *J. Chem. Phys.*, **58**, 4009 (1973).
(7) K. Ito, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1991 (1974).
(8) K. Ishizu, T. Kito, T. Fukutomi, and T. Kakurai, *Polym. J.*, **7**, 228 (1975).
(9) H. Morawetz, J.-R. Cho, and P. J. Gans, *Macromolecules*, **6**, 624 (1973).
(10) J. G. Wetmur, *Biopolymer*, **10**, 601 (1971).
(11) B. Vollmert, "Polymer Chemistry", Springer Verlag, New York, 1973.
(12) D. J. Worsford, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 337 (1974).
(13) M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoit, R. Duplessix, C. Picot, and P. G. de Gennes, *Macromolecules*, **8**, 804 (1975), and references therein.
(14) N. Goodman and H. Morawetz, *J. Polym. Sci., Part* A-2, **9**, 1657 (1971); *J. Polym. Sci., Part C*, **31**, 177 (1970), and references therein.
(15) M. Sisido, T. Mitamura, Y. Imanishi, and T. Higashimura, *Macromolecules*, **9**, 316 (1976); M. Sisido, Y. Imanishi, and T. Higashimura, *ibid.*, **9**, 320 (1976), and references therein.
(16) Y. Ikada, Y. Nishizaki, H. Iwata, and I. Sakurada, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 451 (1977).
(17) R. Naito, *Kobunshi Kagaku*, **15**, 597 (1958).
(18) A. Nakajima and K. Furutachi, *Kobunshi Kagaku*, **6**, 460 (1949).
(19) Y. Ikada, T. Mita, H. Iwata, S. Nagaoka, and I. Sakurada, *Makromol. Chem.*, to be submitted.
(20) E. Sawichi, T. R. Hauser, T. W. Stanley, and W. Elbert, *Anal. Chem.*, **33**, 93 (1961).
(21) G. S. Y. Yeh, *J. Macromol. Sci., Phys.*, **6**, 451, 463 (1972).
(22) B. Vollmert and H. Stutz, *Angew. Makromol. Chem.*, **3**, 182 (1968); **20**, 71 (1971); B. Vollmert, H. Stutz, and J. Stemper *ibid.*, **25**, 187 (1972).
(23) H. Iwata and Y. Ikada, to be published.
(24) W. H. Stochmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).
(25) H. Yamakawa in "Harper's Chemistry Series", S. H. Rice, *Ed.*, Harper and Row, New York (1971).
(26) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **47**, 3991 (1967).