

# SOME FUNDAMENTAL ASPECTS OF POLYMER REACTIONS

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## 1. INTRODUCTION

In discussing the reactivity of macromolecules, it is generally assumed that a functional group attached to a high polymer has a chemical reactivity similar to that which would be observed for such a group in small molecules<sup>1</sup>. This generalization may essentially be true, but we often find reactions in which a functional group attached to a high polymer exhibits widely different reactivity to that in small molecules.

The size of a molecule is generally unimportant, but the fact that a functional group of a high polymer always has neighbouring groups is the most fundamental feature of polymer reactions.

In this lecture, based chiefly on our own experiments, I will discuss simple polymer reactions in which neighbouring groups exert great effects on the reactivity of a functional group attached to a polymer.

## 2. REACTIVITY OF FUNCTIONAL GROUPS OF POLYMER MOLECULES

### (a) Hydrolysis of polyvinyl acetate

First let us consider an example in which the reactivity of functional groups of polymer molecules is similar to that of the corresponding low molecular weight compounds. In 1944 we carried out alkaline hydrolysis of polyvinyl acetate in acetone-water (75:25 by volume)<sup>2</sup>. This mixture is used because both polyvinyl acetate and alcohol are soluble in it. When methanol or ethanol is used as a solvent the reaction mechanism becomes more complicated because alcoholysis takes place simultaneously.

The rate constant  $k$  was evaluated graphically at various degrees of conversion with the following equation:

$$(dx/dt) = k(a - x)(b - x) \quad (1)$$

where  $a$  is the initial concentration of ester,  $b$  that of alkali and  $x$  the concentration of carboxylic acid at time  $t$ . The initial rate constant  $k_0$  was extrapolated from the  $k$  conversion curve. A comparison of the initial rate constants for the hydrolyses of polyvinyl acetate and some low-molecular-weight acetates is given in *Table 1*.

Although  $k_0$  for polyvinyl acetate is only one tenth of that for ethyl acetate it does not differ so markedly from that for isopropyl acetate, which is an ester of a secondary alcohol as polyvinyl acetate. This is a good example, demonstrating that the reactivity of functional groups of polymer molecules is similar to that of low-molecular compounds.

Table 1. Comparison of the rate of alkaline hydrolysis of polyvinyl acetate with those of some low-molecular-weight esters. Solvent, acetone-water (75:25); alkali, NaOH; temperature 30°C

Acetate	$\begin{array}{c} \text{—CH—CH}_2\text{—} \\   \\ \text{O} \\   \\ \text{COCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{—CH}_3 \\   \\ \text{O} \\   \\ \text{COCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\   \\ \text{O} \\   \\ \text{COCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{—CH}_2\text{—CH—CH}_3 \\   \qquad \qquad   \\ \text{O} \qquad \qquad \text{O} \\   \qquad \qquad \qquad   \\ \text{COCH}_3 \qquad \text{COCH}_3 \end{array}$
$k_0$ (l.mole <sup>-1</sup> . min <sup>-1</sup> )	0.37	3.5	0.57	4.4

Smets and his coworkers<sup>3</sup> carried out alkaline hydrolyses of polyvinylpyrrolidone derivatives and homologues to show similarity in apparent activation energy and collision frequency for the polymeric molecules and their low molecular homologous substances.

### (b) Hydrolysis of polymethyl acrylate

Alkaline or acid hydrolysis of polymethyl acrylate is a good example showing the very considerable difference between the reactivity of functional groups attached to a polymer and those attached to a low-molecular-weight compound. Table 2 gives a comparison of the initial rate constants for the hydrolysis of polymethyl acrylate and some low-molecular methyl esters of similar structure<sup>4</sup>.

Table 2. Comparison of the rates of alkaline and acid hydrolyses of polymethyl acrylate with those of some low-molecular-weight ester (at 25°C)

Ester	$\begin{array}{c} \text{—CH—CH}_2\text{—} \\   \\ \text{CO} \\   \\ \text{OCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{—CH}_3 \\   \\ \text{CO} \\   \\ \text{OCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3\text{—CH—CH}_3 \\   \\ \text{CO} \\   \\ \text{OCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{—CH}_2\text{—CH}_2 \\   \qquad \qquad   \\ \text{CO} \qquad \qquad \text{CO} \\   \qquad \qquad \qquad   \\ \text{OCH}_3 \qquad \text{OCH}_3 \end{array}$
Acetone-water $k_0$ { (5:2)* (2:5)* (6:1)†	0.1 0.1 5.2‡	3.8 8.8 —	1.2 2.8 210	4.8 7.2 —

\* Alkaline hydrolysis with NaOH,  $k_0$  is given in l.mole<sup>-1</sup> min<sup>-1</sup>.

† Acidic hydrolysis with HCl,  $k_0$  is given in 10<sup>-3</sup>l.mole min<sup>-1</sup>.

‡ Measured at 50°C.

Not only in alkaline, but also in acid hydrolyses,  $k_0$  for polymethyl acrylate is much smaller than that for low-molecular-weight esters. The apparent activation energy of the hydrolysis was 12 kcal/mole for polymethyl acrylate and 11–11.5 kcal/mole for methyl isobutyrate and dimethyl glutarate. The small  $k_0$  for polymethyl acrylate seems to be attributed to the steric hindrance of neighbouring groups. We will return to this problem when we consider the effect of tacticity on the reaction rate.

### 3. CHANGE OF THE APPARENT RATE CONSTANT IN THE COURSE OF THE REACTION

#### (a) Esterification of polyvinyl alcohol with monochloroacetic acid and its reverse reaction

Esterification of polyvinyl alcohol ( $P = 1200$ ) with monochloroacetic acid and its reverse reaction were carried out in monochloroacetic acid-water mixtures<sup>5</sup>. The rate constants were calculated using the following equation for the reversible reaction:

$$dx/dt = k(a - x)b - k'xc \quad (2)$$

where  $a$ ,  $b$ ,  $c$ , and  $x$  are the initial concentrations of hydroxyl group, monochloroacetic acid, water, and ester group, respectively, and  $k$  and  $k'$  are the rate constants for the esterification and the hydrolysis, respectively.

The rate constant for the esterification may be calculated from

$$-\log(1 - p/p_e)/t = kb/2.303 p_e \quad (3)$$

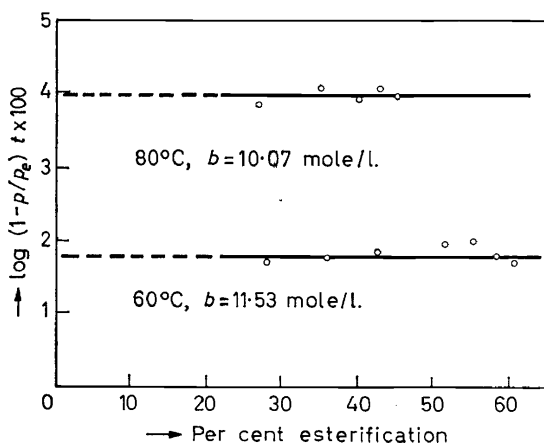
where  $p$  and  $p_e$  are the degrees of esterification at time  $t$  and at equilibrium, respectively.

Experiments were carried out at two different temperatures. As may be seen from *Figure 1*, in the range covered by the experiments,  $k$  remains constant.

The equation for hydrolysis is

$$\frac{\log[(p_i - p_e)/(p - p_e)]}{t} = \frac{k'b}{2.303 p_e} \quad (4)$$

where  $p_i$  is the initial degree of esterification. From *Figure 2* it may be seen that  $k'$  also remains unchanged.



*Figure 1.* Esterification of polyvinyl alcohol in monochloroacetic acid-water

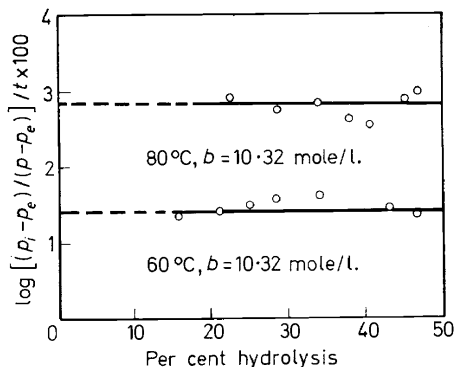


Figure 2. Hydrolysis of polyvinyl monochloroacetate in water-monochloroacetic acid

**(b) Hydrolysis of polyvinyl acetate**

Polymer reactions are not always as simple as in the case of polyvinyl monochloroacetate. Alkaline and acid hydrolyses of polyvinyl acetate are good examples<sup>2</sup>. Figures 3 and 4 show the courses of methanolysis in pure methanol and hydrolysis in acetone-water, respectively. Both curves are sigmoidal and the course of the reaction seems to be autocatalytic. If we calculate the apparent rate constant  $k$  with equation (2),  $k$  increases linearly with increasing degree of conversion (see Figure 5).

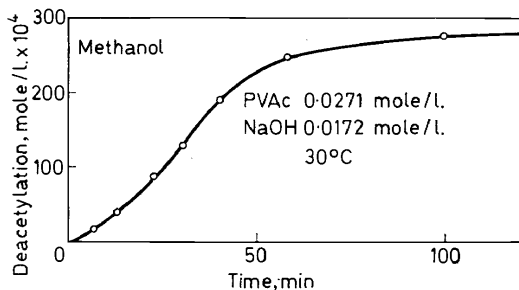


Figure 3. Methanolysis of polyvinyl acetate in pure methanol

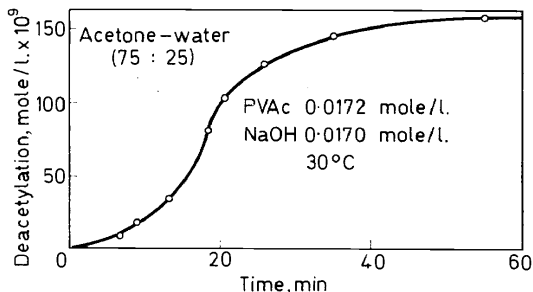


Figure 4. Hydrolysis of polyvinyl acetate in acetone-water (75:25)



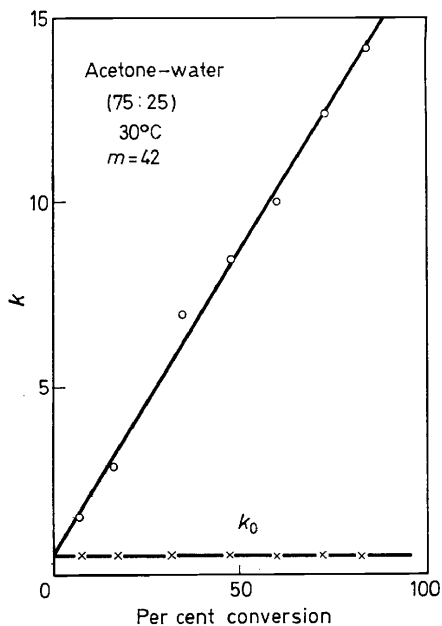


Figure 5. Hydrolysis of polyvinyl acetate in acetone-water (75:25)

Table 3. Relation between  $m$  and  $k_2/k_1$

$\alpha = k_2/k_1$	2	10	20	30	60	100
$m$	1.8	10	17	22	33	45

diacetate was carried out at first in water. The results are shown in *Figure 6*. The rate constant remains almost unchanged in the course of the reaction. When we use acetone-water (75:25) as a solvent,  $k$  increases with conversion (see *Figure 7*). Although the effect of a neighbouring group is much smaller than in the case of polyvinyl acetate, it is true that the effect exists.

It is very important to understand the mechanism of the accelerating effect of the neighbouring group. The property at first seems to be due to a steric effect, but it is not true because the effect disappears when pure water is used as a solvent. The behaviour is to be attributed to local concentration of alkali due to attraction by free hydroxyl groups. It was shown that alkali is really adsorbed by polyvinyl alcohol. It is highly probable that alkali is more easily adsorbed from acetone-water than from pure water. We are now carrying out adsorption experiments with radio-chemically crosslinked polyvinyl alcohol. We would call such an effect a hydrophilic effect because it is found when hydrophilic groups are contained in a polymer molecule.

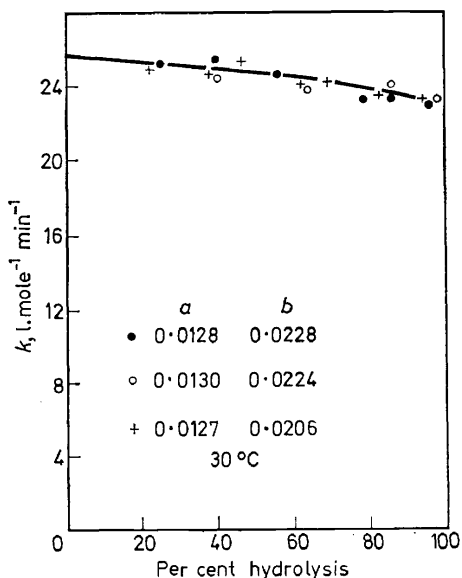


Figure 6. Hydrolysis of ethylene glycol diacetate in water with NaOH

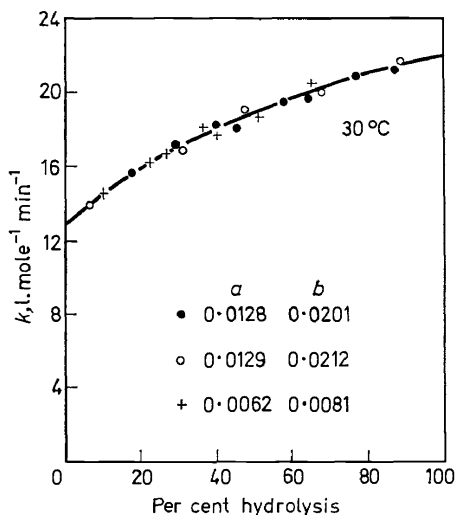


Figure 7. Hydrolysis of ethylene glycol diacetate in acetone-water (75:25)

**(c) Hydrolysis of polymethyl acrylate**

The course of hydrolysis of polymethyl acrylate was studied in acetone-water mixtures of different compositions<sup>4</sup>. The concentration of polymethyl acrylate was 0.07 mole/l., the concentration of NaOH in most cases 0.08 mole/l. and the reaction temperature 40°C. Figure 8 shows the relations between logarithm of apparent rate constant calculated by equation (2)

and percent hydrolysis. Although there is no great difference in the initial rate constant, the value of the change of  $k$  with percent conversion varies widely from one composition to another. In acetone-rich systems,  $k$  increases rapidly with percent hydrolysis, at acetone: water = 4:3 by volume,  $k$  is almost independent of the conversion, and in water-rich systems  $k$  decreases rapidly with increasing percent hydrolysis.

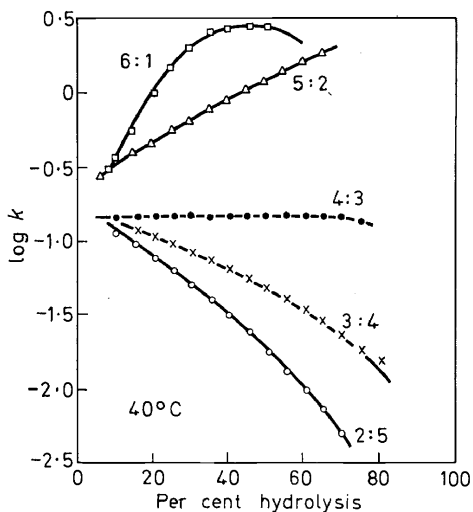


Figure 8. Hydrolysis of polymethyl acrylate in acetone-water mixtures with NaOH (Figures by the curves show the acetone-to-water ratio)

Similar experiments were carried out also at 25° and 50°C; there was no great change in the shapes of the curves. The apparent activation energy was found to be *c.* 12 kcal/mole throughout the reaction.

The rapid drop of  $k$  with increasing percent hydrolysis in water-rich systems may be attributed to the formation of carboxylate groups, which dissociate into ions in water-rich systems; polymer molecules become negatively charged and repel hydroxyl ions so that the hydrolysis reaction is depressed. This is the same electrostatic effect as Katchalsky<sup>9</sup> has reported for the hydrolysis of pectin.

With increasing concentration of acetone, the dissociation of carboxylate groups become less extensive and the effect of the electrostatic repulsion becomes suppressed. Undissociated carboxylate groups show a similar hydrophilic effect to hydroxyl groups in the case of hydrolysis of polyvinyl acetate, and attract NaOH, so that the catalyst concentration in the neighbourhood of polymer molecules becomes higher to increase  $k$ . On the other hand, even in acetone-rich systems it is true that the dissociation takes place and the charge number of polymer molecule increase with increasing percent hydrolysis to exert a negative effect. Therefore a maximum will

appear in the log  $k$ -percent hydrolysis curves. We do not intend to neglect the steric effect, but the attraction and repulsion effects of the catalyst seem to be much more important.

#### 4. THE EFFECT OF THE DEGREE OF POLYMERIZATION ON THE REACTION RATE

##### (a) Hydrolysis of polyvinyl acetate

The effect of the degree of polymerization on the rate of alkaline hydrolysis was studied for polyvinyl acetates with various degrees of polymerization; the viscometrically determined degree of polymerization ( $\bar{P}_v$ ) varied from 50 to 20,000<sup>2</sup>. The degree of polymerization had practically no effect on the rate of hydrolysis, but a polyvinyl acetate of  $\bar{P}_v = 50$  seemed to have a slightly higher rate. Therefore experiment was undertaken again with polyvinyl acetate of a very low degree of polymerization, which had been prepared by polymerization of vinyl acetate in butyraldehyde<sup>10</sup>; the degree of polymerization was found to be  $\bar{P}_v = 11.6$  and  $\bar{P}_n = 9.8$ . The rate of alkaline hydrolysis of this polyvinyl acetate was compared in dioxane-water (3:1 by volume) at 40°C with that of a conventional polyvinyl acetate ( $\bar{P}_v = 2300$ ). As may be seen from *Figure 9*, there is no essential difference between two samples except that the  $k$ -percent hydrolysis curve for the polyvinyl acetate of the very low degree of polymerization lies somewhat higher than the other.

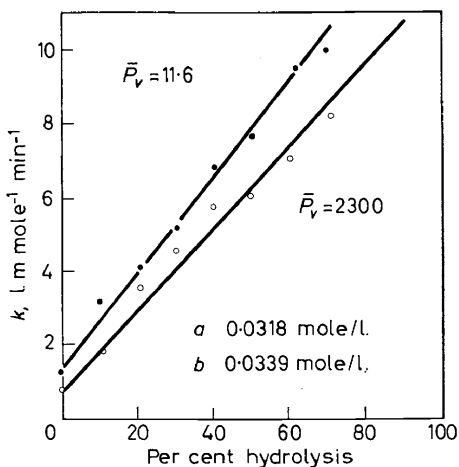


Figure 9. Hydrolysis of polyvinyl acetates of low and high degrees of polymerization

##### (b) Hydrolysis of polyallyl acetate

The effect of degree of polymerization on the rate of polymer reaction is not always so simple as that demonstrated in the foregoing section. According to our unpublished work<sup>11</sup>, the behaviour of polyallyl acetate in alkaline hydrolysis is different from that of polyvinyl acetate.

Polyallyl acetates of higher degrees of polymerization were prepared by

reduction of polymethyl methacrylate to polyallyl alcohol, based upon a process proposed by Schulz<sup>12</sup>, followed by acetylation. Polyallyl acetates of lower degrees of polymerization were prepared from polyallyl alcohol or esters which had been obtained by direct polymerization of the corresponding monomer.

Polyallyl acetate of the lowest degree of polymerization used in the experiment had a molecular weight of 580. Figure 10 shows relations between apparent rate constants at percent hydrolyses 0% ( $k_0$ ) and 50% ( $k_{50}$ ) and degree of polymerization. As a qualitative measure of the degree of polymerization,  $[\eta]$  measured in acetone at 30°C was used as the abscissa.

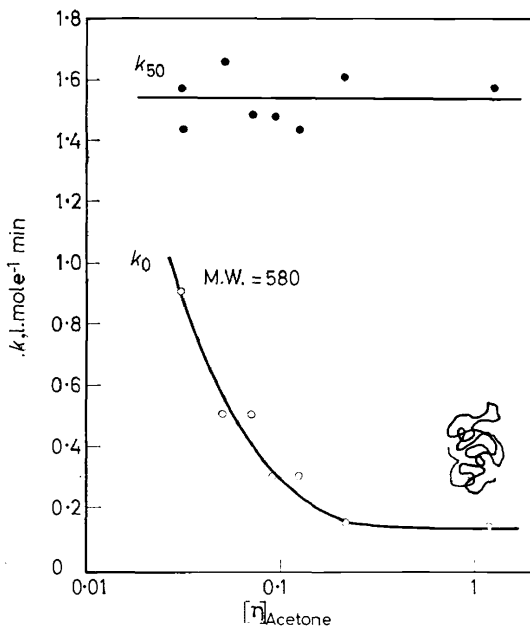


Figure 10. Rate constants of hydrolysis (at per cent hydrolysis of 0 and 50) for polyallyl acetates of various degrees of polymerization

As may be seen from the figure,  $k_0$  decreases rapidly with increasing degree of polymerization, while  $k_{50}$  is almost independent of it. An acetone-water (8:2 by volume) mixture was used in the experiment as the solvent, because both the initial and final polymers are soluble in this mixture, but the mixture is a poor solvent for polyallyl acetate. The polymer molecule is therefore, at the initial stage of the reaction, in a state of tighter coiling, which hinders chemical reaction. With increasing degree of hydrolysis, the mixture becomes a better solvent and the coiling is loosened. This is the reason why the apparent rate constant increases with percent hydrolysis especially by polymers of higher degrees of polymerization and becomes independent of the degree of polymerization when hydrolysis has taken place to some extent.

## 5. NEIGHBOURING GROUP EFFECT ON THE REACTIVITY

It was recognized by Morawetz and Zimmering<sup>13</sup>, and Zimmering *et al.*<sup>14</sup> in a study of the hydrolysis of acrylic and methacrylic copolymers containing a small portion of *p*-nitrophenyl methacrylate that the hydrolysis of the ester groups was much more rapid than the hydrolysis of *p*-nitrophenyl esters of monofunctional group. They demonstrated that the reaction does not involve hydroxyl ions but that the velocity of the process is governed by the attack of an ionized carboxyl on the ester function.

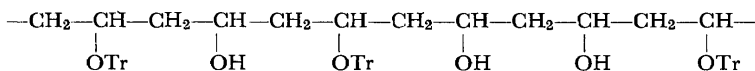
Smets and his co-workers<sup>15</sup> also carried out interesting experiments on the hydrolysis of methacrylic acid-methacrylate copolymer and obtained similar results.

These reactions are rather specific while the effects are observed only when an ionized carboxyl can react with an ester group.

The neighbouring-group effect which was pointed out in the course of the alkaline hydrolysis of polyvinyl acetate and polyacrylate is not specific but more general and fundamental.

We shall now consider some examples of steric and electrostatic effects not pertaining to the rate of reaction but concerning the final conversion of polymer:

The first example is the triphenylmethylation of polyvinyl alcohol<sup>16</sup>. It was shown experimentally that the highest degree of substitution was 42.4%. If we assume that the two direct neighbours of a trityl group are not able to undergo the reaction, the theoretical value for the maximum conversion is 43.2%; the agreement is satisfactory. The residual hydroxyl groups could be acetylated.



The second example is the electrostatic effect on polymer reaction. By acetalization of polyvinyl alcohol with aldehydes which do not contain an ionizable group it is not difficult to obtain a percentage acetalization which is near to the theoretically expected value of 86.5%<sup>17</sup>.

Aldehyde	Acetalization %
Palmitinaldehyde	85.0
Chloroacetaldehyde	85.8
<i>o</i> -Chlorobenzaldehyde	84.6
Benzaldehyde	83.0

When acetalization is carried out with aldehydes which contain a sulphonic acid group, it is impossible to reach such a high degree of acetalization<sup>18</sup>. The maximum degrees of acetalization for aldehyde sulphonic acids were as follows:

Aldehyde	Acetalization %
$\beta$ -Butyraldehyde sulphonic acid	57.6
<i>o</i> -Benzaldehyde sulphonic acid	44.0
2,4-Benzaldehyde disulphonic acid	36.0

The results seem to show that not only isolated but some other hydroxyl groups are unable to undergo the acetalization reaction due to the repulsive effect of sulphonic acid groups.

## 6. EFFECT OF THE TACTICITY ON THE REACTION RATE

Glavis<sup>19</sup> reported in 1959 that conventional and syndiotactic polymethyl methacrylates are hydrolysed in an alkaline medium relatively slowly, while the hydrolysis of isotactic polymer proceeds very rapidly and to a higher conversion.

Smets and De Loecker<sup>20</sup> prepared methacrylic-ester-acid copolymers from syndiotactic polymethyl methacrylate (*A*) and from polymethyl methacrylate which is considered as a mixture of conventional and isotactic polymers (*B*), and carried out hydrolysis in a buffered aqueous solution at different degrees of neutralization. Polymer *A* hydrolysed about four to five times faster than the conventional polymethyl methacrylate while polymer *B* hydrolysed very slowly.

Similar experiments were carried out by Smets and Van Humbeeck<sup>21</sup> on acrylic acid copolymers. In the case of acrylic-acid-methacrylate copolymers the isotactic system hydrolysed 3 to 5 times more rapidly than the conventional ones.

### (a) Hydrolysis of polyvinyl acetates

We shall explain in some detail the effect of the tacticity of polyvinyl acetates on the rate of alkaline hydrolysis.

Isotactic polyvinyl acetate derived from isotactic polyvinyl ether, conventional (atactic) polyvinyl acetates, polyvinyl acetate derived from poly(vinyl trifluoroacetate) and that derived from poly(vinyl butyral) were hydrolysed in a mixture of acetone-water (7:3 by volume) using NaOH as the catalyst<sup>22</sup>. Conventional ones include eight different polymers obtained by polymerization of various vinyl esters at different temperatures. The percentage hydrolysis *versus* reaction time curves are shown in *Figure 11*.

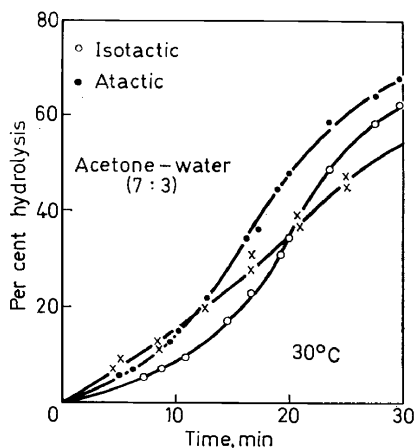


Figure 11. Alkaline hydrolysis of polyvinyl acetates of various tacticities

## SOME FUNDAMENTAL ASPECTS OF POLYMER REACTIONS

The courses of hydrolyses of all conventional polyvinyl acetates and that of polyvinyl acetate derived from poly(vinyl trifluoroacetate) may be represented by a single curve, whereas those of isotactic polyvinyl acetate and polyvinyl acetate derived from poly(vinyl butyral) differ remarkably from the first curve. The initial apparent rate constant  $k_0$  and a measure of the autocatalytic effect  $m$  are shown in *Table 4*. Experimental data for syndiotactic polymer are not available.

*Table 4.* Rate of the hydrolysis of polyvinyl acetates of various tacticities

<i>Tacticity</i>	$k_0$	$m$
isotactic	0.14	49
atactic	0.23, 0.21	39, 38
rich in head-to-head structure	0.50	5.6

The structure of polyvinyl acetate and polyvinyl alcohol derived from poly(vinyl butyral) is not yet clear; the infrared spectrum of these polyvinyl alcohols differs slightly from that of a conventional one. It was once considered to be rich in syndiotactic structure, but according to our recent research it is more plausible that it is rich in head to head structure.

The initial rate of hydrolysis of the atactic polymer is larger than that of the isotactic one, while  $m$  of the former is smaller than that of the latter. In the case of the atactic structure, steric hindrance is smaller because the distance of acetyl groups is longer than it is in the isotactic structure, therefore an atactic polymer exhibits larger  $k_0$ . When the hydrolysis of ester groups occurs to some extent, hydroxyl groups, and hence adsorbed hydroxyl ions, are located closer to an unreacted acetyl group in the case of isotactic than in the case of syndiotactic polymer; therefore  $m$  is greater for the isotactic polymer.

Acetalization reactions of the above three kinds of polyvinyl alcohol were also compared. *Table 5* shows the equilibrium constants for the acetalization; we can see here again that there are large differences in chemical activity among these three kinds of polymer.

*Table 5.* Equilibrium constant for the acetalization of polyvinyl alcohols with various tacticities

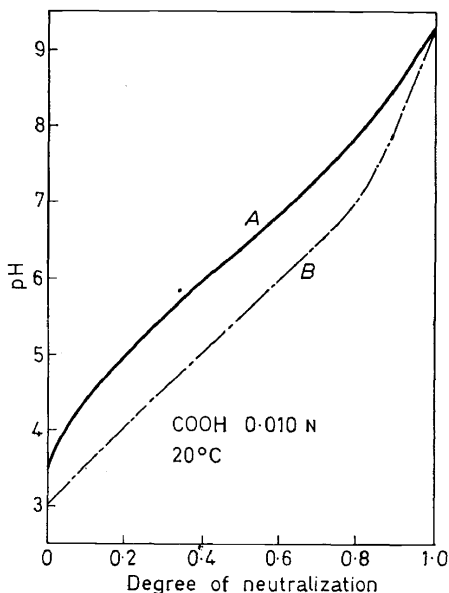
<i>Tacticity</i>	<i>Equilibrium const.</i>
isotactic	3100
atactic	1200, 1400
rich in head-to-head structure	17

### (b) Hydrolysis of polymethyl acrylates

In a study of the titration curve of neutralization of polyacrylic acids derived from polyacrylic esters obtained by a radical polymerization of the corresponding monomer, and polyacrylic acids obtained by polymerization

of acrylic acid it was found that with one exception all polyacrylic acids give a practically identical titration curve (see *Figure 12*)<sup>23</sup>.

The exceptional polyacrylic acid was obtained by polymerization of acrylic acid under such a condition that the electrostatic repulsive forces between growing chain and monomer were very large. The polymerization condition was: solvent, water-ethanol (94.9:3.8); monomer conc., 1%; initiator, azobisisobutyronitril, pH was adjusted to 7 and the temperature was 60°C. The titration curve for this polyacrylic acid lies under that for the conventional polymers. From the polymerization condition and the comparison of titration curves, it was considered that this exceptional polymer is rich in syndiotactic structure.



*Figure 12.* Potentiometric titration curves of polyacrylic acids (*A* conventional, *B* special)

The conventional polyacrylic acids and the syndiotactic one were converted to methyl ester, and the rate of alkaline hydrolysis of these esters was measured in acetone-water (7:3 by volume)<sup>24</sup>. The rate of hydrolysis is shown in *Figure 13*. Corresponding to titration curves, the hydrolysis rates of all conventional polymethyl methacrylates fall on a curve, whereas that of the syndiotactic polymer is widely separated from the others,  $k_0$  for the conventional and syndiotactic polymers was 0.09 and 1.7 l. mole<sup>-1</sup> min<sup>-1</sup>, respectively. It is noteworthy that the latter value nearly agrees with that of methylisobutyrate which has already been given in *Table 2*. It seems that an ester group of polymethyl acrylate is more or less isolated when the polymer has a syndiotactic structure, so that steric hindrance of neighbouring groups is not very large and shows nearly the same activity as a simple monofunctional low-molecular-weight ester.

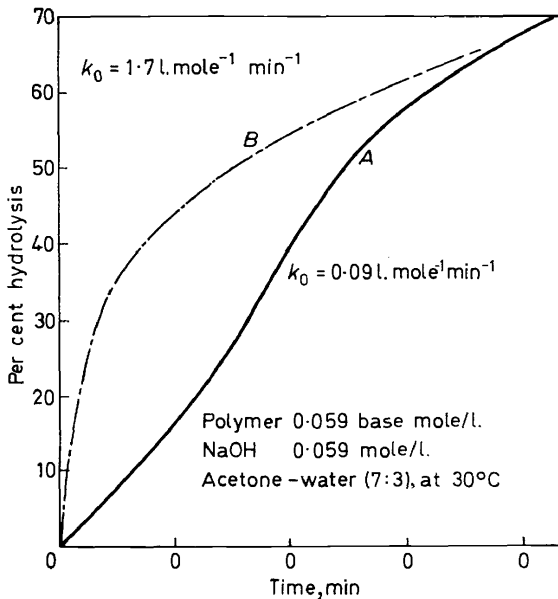


Figure 13. Hydrolysis of polymethyl acrylates (*A* conventional, *B* special)

## 7. HYDROPHOBIC INTERACTION IN THE POLYMER REACTIONS<sup>25</sup>

### (a) Hydrolysis of esters with polymeric sulphonic acids

It was recently recognized that hydrophobic interaction plays an important role in the polymer reactions. The first typical example is the hydrolysis of low-molecular-weight esters with polymeric sulphonic acids such as polystyrenesulphonic acid.

In the case of the hydrolysis of ester with hydrochloric acid, it may be assumed that acid and ester molecules are distributed homogeneously throughout the reaction system and that hydrolysis takes place at any point in the system. On the other hand, in the case of hydrolysis with polymeric sulphonic acid, we may assume that hydrogen ions, counter ions of the sulphonic groups, are located exclusively in the neighbourhood of polymer molecules (*Figure 14a*). Hydrolysis can occur only in this region of the solution, because outside the region hydrogen ions capable of causing hydrolysis do not exist. If the ester molecules are distributed homogeneously in the solution, there is no apparent change in the rate of reaction, because the decrease of the volume of reaction is cancelled with the increase of the local hydrogen ion concentration. If the ester molecules are adsorbed by the polymer catalyst, the situation is somewhat different (*Figure 14b*). The concentration of the ester becomes higher just at the place where hydrogen ions are concentrated; in such a case it is expected that the polymer sulphonic acid shows a higher apparent rate constant than hydrochloric acid.

A comparison was carried out of the hydrolysis rate of ester with polystyrenesulphonic acid and hydrochloric acid.

Two types of polystyrenesulphonic acids were employed for the experiments; one is a polystyrenesulphonic acid obtained by the polymerization of monomeric styrenesulphonic acid (PSS) and the other a partially sulphonated polystyrene (PS-S), the degree of sulphonation of PS-S varying between 23 and 77 mole %.

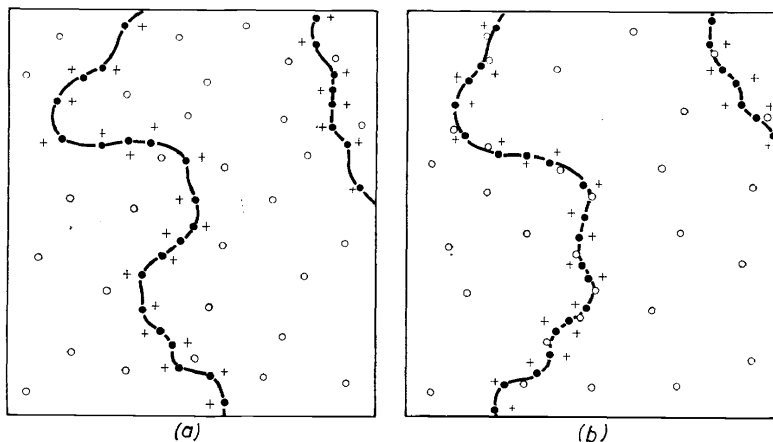


Figure 14. Hydrolysis of ester with polymeric sulphonic acids. ○ Ester, ● Acid, + Hydrogen ion. (a) No local concentration of ester. (b) Local concentration of ester

Hydrolyses of methyl- and *n*-butyl acetates were carried out with polystyrenesulphonic acids and hydrochloric acid. The experimental conditions and results are given in Table 6;  $r$  of the last column of the table being a ratio of the apparent rate constant for the polymer catalyst to that for hydrochloric acid:  $r = k/k_{\text{HCl}}$ .

Table 6 shows that methyl acetate is hydrolysed with polystyrenesulphonic acids with a greater rate constant than hydrochloric acid. It is

Table 6. Hydrolyses of methyl acetate and *n*-butyl acetate with polystyrenesulphonic acids in water

Catalyst	Methyl acetate Ester conc. : $2.50 \times 10^{-2}$ M catalyst conc. : $5.00 \times 10^{-3}$ N temp. : 40°C		<i>n</i> -Butyl acetate Ester conc. : $2.85 \times 10^{-2}$ M catalyst conc. : $5.00 \times 10^{-3}$ N temp. : 40°C	
	$k. 10^2$ l.mole <sup>-1</sup> min <sup>-1</sup>	$r$	$k. 10^2$ l.mole <sup>-1</sup> min <sup>-1</sup>	$r$
HCl	2.31	1.00	2.30	1.00
PSS	2.39	1.03	4.42	1.92
PS-S(77)	2.79	1.21	5.91	2.57
PS-S(65)	3.25	1.41	6.94	3.02
PS-S(52)	3.53	1.53	10.35	4.50
PS-S(40)	3.63	1.57	14.5	6.31
PS-S(33)	4.86	2.10	18.3	7.96
PS-S(23)	5.06	2.19	23.5	10.22

remarkable that the lower the degree of sulphonation the greater the catalytic effect of the polystyrenesulphonic acid. It shows clearly that benzene rings, especially nonsulphonated benzene rings, exhibit a cooperative effect for the catalysis.

In the case of *n*-butyl acetate which has a longer alkyl group than methyl acetate, general aspects are similar but polystyrenesulphonic acids have a greater catalytic effect than in the case of methyl acetate.

Similar experiments had been carried out with various esters at various temperatures and we came to the conclusion that a large *r* value is due to the local concentration of ester in the neighbourhood of polymer molecule caused by hydrophobic interaction. If this conclusion is true, *r* is expected to decrease when some organic liquid is added to the reaction mixture. The hydrolysis was thus carried out in aqueous acetone instead of in pure water. As was expected, *r* decreased rapidly by addition of acetone to the reaction mixture (see *Table 7*).

*Table 7.* Effect of added acetone on the rate of hydrolysis of *n*-butyl acetate with polystyrenesulphonic acids (Ester conc.  $2.85 \cdot 10^{-2}$  M; catalyst conc.  $5.00 \cdot 10^{-3}$  N; temperature 40°C)

Vol. % acetone in reaction mixture	<i>r</i> for following catalyst	
	PS-S (40)	PSS
0	6.31	1.92
15	2.61	1.48
30	1.55	1.12

Such a hydrophobic interaction is not always observed for polymeric sulphonic acids independent of its nature, but only those polymeric sulphonic acids with strongly hydrophobic groups exhibit the effect. *Table 8* gives examples of polymeric sulphonic acids with  $r \doteq 1$  and  $r > 1$ .

Experiments were also undertaken with cross-linked sulphonated polystyrenes such as Dowex 50 W<sup>26</sup>, because it is possible in this case to measure the adsorbed amount of the ester on the resin, and to compare the local concentration of ester with the effectiveness of the catalyst. As it is impossible to measure the adsorbed amount with H-type resins because of the simultaneous hydrolysis of ester, the adsorption measurements were carried out with Na-type resins. When  $c_0$  is the initial concentration of ester of the system and  $c_i$  the concentration of ester in the resin phase, then  $c_i/c_0$  is a measure of the local concentration of ester in the neighbourhood of polymer molecules. The value of  $c_i/c_0$  was compared with *r* measured with the use of H-type resins. Several examples are shown in *Table 9*. As may be seen from the table, there is a close parallelism between *r* and  $c_i/c_0$ , so that it may be said that our argument that larger *r* values are mainly due to local concentration of ester in the neighbourhood of polymer molecules is definitely proved.

Mention will now be made of the electrostatic interaction in the hydrolysis of esters with polymeric sulphonic acids.

Table 8. Catalytic effect of polymeric sulphonic acids

<i>A. r</i> is nearly equal to 1	
PVS:	Polyvinyl sulphonic acid;
PVS-VA:	Copolymer of vinyl sulphonic acid and alcohol;
PVBS:	Polyvinyl butyral sulphonic acid;
PVBes:	Polyvinyl benzal sulphonic acid;
<i>B. r</i> is larger than 1	
PSS:	Polystyrenesulphonic acid;
PS-S:	Partially sulphonated polystyrene;
PVS-St:	Copolymer of vinyl sulphonic acid and styrene;
PAN-S:	Partially sulphonated polyacenaphthylene;
PMS-S:	Partially sulphonated poly $\alpha$ -methylstyrene;
PS-Sti-S:	Partially sulphonated copolymer of styrene and stilbene

Table 9. Comparison of ester adsorption ( $c_i/c_0$ ) and catalyst effectiveness  $r$  (at 40°C)

	<i>Ester</i>	<i>Methyl acetate</i>	<i>n-Butyl acetate</i>	<i>tert-Butyl acetate</i>	<i>Phenyl acetate</i>	<i>Hexyl acetate</i>
Dowex W × 2	$c_0^*$		0.0305	0.0295		
	$c_i^*$		0.0863	0.0758		
	$c_i/c_0$		2.83	2.57		
	$r$		2.70	1.74		
Dowex W × 4	$c_0^*$	0.0504	0.0305	0.0295	0.0157	0.0136
	$c_i^*$	0.0814	0.0956	0.0804	0.0789	0.0721
	$c_i/c_0$	1.62	3.13	2.73	5.02	5.30
	$r$	1.52	2.90	1.84	6.30	4.70

\*  $c_0$  and  $c_i$  are given in mole/l.

When esters of an amino acid are employed, it may be expected that the local concentration of the ester in the neighbourhood of a polymer molecule occurs due to the electrostatic attraction between sulphonic acid groups of the catalyst and amino groups of the substrate to result in a higher rate of hydrolysis.

Experiments were carried out employing *o*- and *p*-aminobenzoates in 50 vol. % aqueous acetone keeping catalyst and substrate concentration constant. The initial rate constant  $k_0$  was determined graphically by extrapolation. The results are shown in Figure 15; as expected  $r$  has large values. It is noteworthy that  $r$  increases with increasing degree of sulphonation. This is a remarkable contrast to the case of hydrophobic interaction, where  $r$  decreases with increasing degree of sulphonation (see Figure 16). If isolated sulphonic acid groups contribute to increase  $r$ , the above result is difficult to explain, as the effect of PS-S of a lower degree of sulphonation is practically the same as that of hydrochloric acid; a certain sequence of sulphonic acid groups seem to be essential to show large  $r$ -values.

### (b) Hydrolysis of polymeric esters with long-chain alkyl and alkylbenzene sulphonic acids<sup>27</sup>

Now we wish to treat the reverse case of the above-mentioned hydrolysis of low-molecular-weight esters with polymeric sulphonic acids, i.e., the

SOME FUNDAMENTAL ASPECTS OF POLYMER REACTIONS

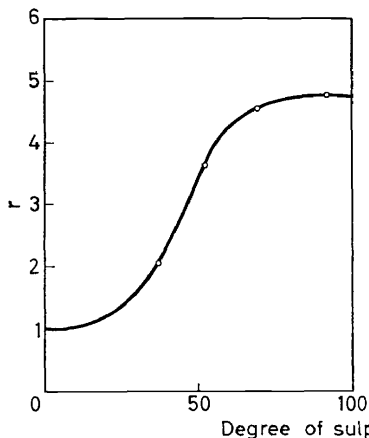


Figure 15

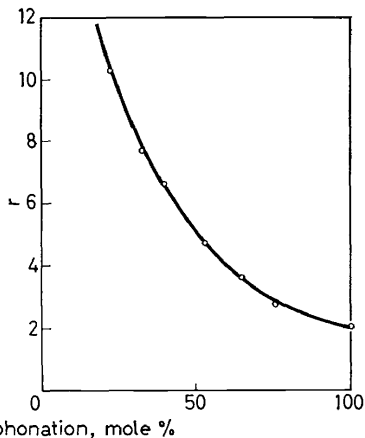


Figure 16

Figure 15. Hydrolysis of *p*-aminobenzoate with polystyrenesulphonic acids in 50% aqueous acetone (catalyst conc., 0.05N; ester conc., 0.08M; temp. 80°C)

Figure 16. Hydrolysis of butyl acetate with polystyrenesulphonic acids in water (catalyst conc., 0.05N; ester conc., 0.00285M; temp. 40°C)

hydrolysis of polymeric esters with low-molecular-weight sulphonic acids (Figure 17). As a polymeric ester, water-soluble partially-acetylated polyvinyl alcohol and as the catalysts, alkyl- and alkylbenzene sulphonic acids were employed. Experimental details and results are shown in Table 10.

As may be seen from the table, octyl sulphonic acid is found to show nearly the same rate of hydrolysis as that with hydrochloric acid, whereas, in the case of hydrolysis with alkyl and alkylbenzene sulphonic acids such as dodecyl, hexadecyl, octadecyl and dodecylbenzene sulphonic acids, much higher rates are observed. These higher rates may be attributed to

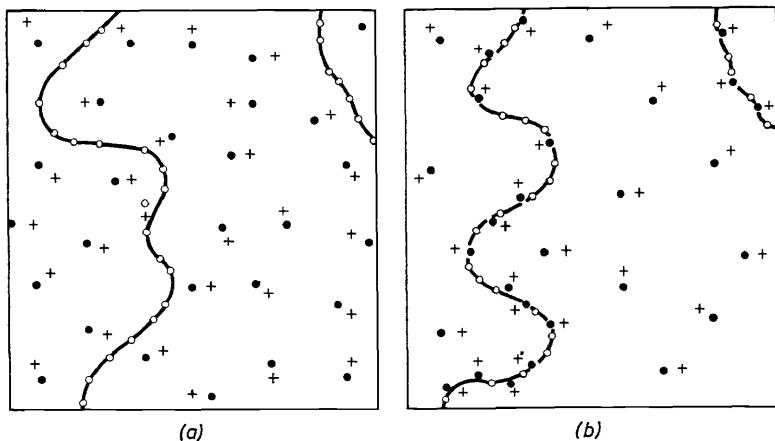


Figure 17. Hydrolysis of polymeric esters with low-molecular-weight sulphonic acid. O Ester, ● Acid, + Hydrogen ion. (a) No local concentration of sulphonic acid. (b) Local concentration of sulphonic acid

## ICHIRO SAKURADA

Table 10. Hydrolysis of acetylated polyvinyl alcohols with low-molecular-weight sulphonic acids

(Conc. of acetylated polyvinyl alcohol 0.30 g/l.)

Catalyst	Catalyst conc. N	Temp. °C	<i>r</i> for polyvinyl alcohol with following degree of acetylation		
			9.21	23.3	33.6
Octyl s.a.	0.010	40	1.1	1.1	1.3
Dodecyl s.a.	"	"	12.5	13.5	12.4
Hexadecyl s.a.	"	"	—	19.1	22.1
Dodecylbenzene s.a.	"	"	20.7	20.6	20.7
Dodecyl s.a.	0.0050	50	10.4	9.3	10.8
Hexadecyl s.a.	"	"	19.3	20.0	—
Octadecyl s.a.	"	"	—	19.1	22.1
Dodecylbenzene s.a.	"	"	19.3	16.7	19.9

higher local concentration of the long-chain sulphonic acid in the neighbourhood of polymer molecules as a result of the hydrophobic attraction between the substrate and catalyst molecules.

**(c) Hydrolysis of polymeric esters with polymeric sulphonic acids<sup>28</sup>**

Finally, mention will be made of the hydrolysis of polymeric esters with polymeric sulphonic acids; in this case both substrate and catalyst are polymers. If hydrophobic interaction exists, it is expected that the effect is here is more pronounced. Experiments were carried out using partially-acetylated polyvinyl alcohols as substrates and polystyrenesulphonic acids as catalysts. Experimental details and results are shown in Table 11. It is seen that for all partially-acetylated polyvinyl alcohols the polystyrene sulphonic acid gives large *r*-values; the largest *r* value is about 40. This implies that the catalyst effect of the polystyrenesulphonic acid is 40 times greater than that of hydrochloric acid under the same reaction conditions. With increasing degree of acetylation *r* increases, and partially-sulphonated polystyrene PS-S (31) exhibits much larger *r* values than pure polystyrenesulphonic acid. Further, acetylated polyvinyl alcohols having a relatively long sequence of acetyl groups give larger *r* than randomly-acetylated polyvinyl alcohol. All these phenomena suggest that the hydrophobic interaction between acetyl groups of acetylated polyvinyl alcohol and benzene rings of polystyrene sulphonic acid plays an important role in the hydrolysis.

Table 11. Hydrolysis of acetylated polyvinyl alcohol with polystyrenesulphonic acids (Substrate conc., 3.0g/l.; catalyst conc., 0.0050 N; temperature 50°C)

Degree of acetylation (mole %)	9.2	9.8*	15.4	21.5	27.0	28.2*	33.6
<i>r</i> { PSS	4.8	10.8	8.8	13.0	17.5	20.2	19.5
{ PS-S (31)	18.5	36.1	22.2	29.9	34.2	36.7	38.3

\* These polyvinyl alcohols have a somewhat longer sequence of acetyl groups.

In conclusion I would say that the most important aspect of polymer reactions is not the size of molecule but the fact that a functional group of polymer molecule always has neighbours. In some cases a neighbour exhibits specific interaction with functional groups as was pointed out by Morawetz, Smets and others; but hydrophilic, electrostatic and especially hydrophobic interaction between neighbouring groups and molecules of the reaction's partner is more general and therefore fundamental.

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