

# Hydrolysis of Polymeric Esters with Polymeric Sulfonic Acids

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Water soluble samples of partially acetylated polyvinyl alcohols (Ac-PVA) were hydrolyzed in water with various polymeric sulfonic acids, such as polystyrene sulfonic acid (PSS) or partially sulfonated polystyrene (PS-S), and the rate constants of the hydrolysis with these sulfonic acid catalysts ( $k_s$ ) were compared with those found with hydrochloric acid as a catalyst under the same condition ( $k_{HCl}$ ).

The values of  $r$ , ( $=k_s/k_{HCl}$ ), obtained in the hydrolysis of Ac-PVA's with PS-S's, were generally much larger than unity, the largest being 38.3. These large rates in the hydrolysis may be attributed to high local concentration of sulfonic acids in the neighbourhood of molecules of the polymeric ester as a result of hydrophobic attraction between the polymeric ester and the sulfonic acid in the neighbourhood of which effective hydrogen ions for the hydrolysis are localized. We have studied the influences of degree of acetylation, distribution of acetyl groups and steric configuration of Ac-PVA's, degree of sulfonation and preparation condition of PS-S, degree of polymerization of Ac-PVA or polymeric sulfonic acid, concentration of Ac-PVA and catalyst, reaction temperature and reaction medium on the  $r$ -value. Furthermore, the catalyst effects of polymeric sulfonic acids other than polystyrene sulfonic acids were investigated.

## 1. INTRODUCTION

In previous papers, we reported the studies on hydrolysis of low molecular esters with polymeric sulfonic acid catalysts,<sup>1)</sup> and on hydrolysis of partially acetylated polyvinyl alcohols (Ac-PVA's) with long chain alkyl- and alkylbenzene sulfonic acids<sup>2)</sup>.

In these papers, it was pointed out that the rate constants of the hydrolysis of more hydrophobic ester with more hydrophobic sulfonic acid were much larger than those of the hydrolysis carried out by using hydrochloric acid as a catalyst at the same equivalent acid concentrations, and these high rates were attributed to local concentration of both ester groups and sulfonic acid groups into an effective volume adjacent to the catalyst polymer or the polymeric ester, which is due to mainly hydrophobic attraction between ester and catalyst molecules in water.

In the present paper, we describe investigations of hydrolysis of polymeric esters with polymeric sulfonic acids. In this case, two following possibilities can be considered; (i) there exists attraction between substrate polymer and catalyst polymer, and (ii) such an attraction does not exist. In the case of (i), the rates of the hydrolysis should be larger than those of hydrolysis with hydrochloric acid as a result of concentration of ester groups and sulfonic acid groups, as

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shown in the previous paper<sup>1)</sup>. Moreover, the rates should be larger than those obtained in the hydrolysis of low molecular esters with polymeric sulfonic acids, because polymeric sulfonic acids have greater number of interaction sites with polymeric esters than with monomeric esters to result in stronger attraction between them. On the other hand, in the case of (ii), polymer molecules exist in a coiled form, independently to each other in the dilute solution. Ester groups in the substrate polymer coil are thus rather inaccessible to sulfonic acid units in the catalyst polymer coil, so that the hydrolysis cannot easily be carried out. Consequently the rate of hydrolysis should be smaller than that of hydrolysis with hydrochloric acid distributed homogeneously throughout the reaction system.

## 2. HYDROLYSIS OF PARTIALLY ACETYLATED PVA WITH POLYSTYRENE SULFONIC ACIDS

Two types of polystyrene sulfonic acids were employed, the one being partially sulfonated polystyrene (PS-S) prepared following the method of Roth<sup>2)</sup>. The degree of polymerization ( $p$ ) of the parent polystyrene was 370 and the degree of sulfonation was between 30 and 40 mole%. The other was polystyrene sulfonic acid (PSS) which had been obtained by the radical polymerization of commercial sodium *p*-styrene sulfonate; the limiting viscosity number,  $[\eta]$  of the polymer was about 0.2 dl./g. in 2 N-NaOH at 30°C.

Hydrolysis of partially acetylated PVA (Ac-PVA) was carried out in aqueous solutions unless otherwise specified; control experiments were always performed under the same experimental conditions, by using hydrochloric acid as a catalyst. The hydrolysis was followed by titration with N/10 NaOH.

The reaction rate constant was evaluated with the following pseudomonomolecular equations:

$$\frac{dx}{dt} = kb(a-x) \quad (1)$$

or

$$k = \frac{2.303}{t \cdot b} \log \frac{a}{a-x} \quad (2)$$

where  $a$  is the initial concentration of ester,  $b$  the equivalent concentration of catalyst,  $x$  the concentration of carboxylic acid at a time  $t$ , and  $k$  the rate constant.

The catalyst effect was quantitatively expressed by  $r$ , denoting the ratio of the constant for polymeric sulfonic acid ( $k_s$ ) to that for hydrochloric acid ( $k_{HCl}$ ), i.e.  $r = k_s/k_{HCl}$ . The  $r$ -value was evaluated with the rate constants determined by Eq. (2) at the initial conversion of hydrolysis.

### 2.1. Influences of the Degree of Acetylation and the Distribution of Acetyl Groups in Ac-PVA on $r$

Two types of Ac-PVA samples with different degrees of acetylation were hydrolyzed with PSS and PS-S (the degree of sulfonation = 31 mole%) under reaction conditions shown in Table 1. The first type of Ac-PVA with degrees of acetylation of 9.2, 15.4, 21.5, 27.0 and 33.6 mole% had a random distribution of acetyl groups along the polymer chain, which was prepared by partial acetylation

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of a conventional PVA in a mixture of acetic acid and water. On the other hand, the second type of the samples having degrees of acetylation of 9.8 and 28.2 mole% had relatively continuous sequences of acetyl groups, which was prepared from partial saponification of a conventional polyvinyl acetate by using NaOH in methanol containing a small amount of water<sup>4</sup>. Results on the  $r$ -value are shown in Table 1.

Table 1. The effect of degree of acetylation or distribution of acetyl groups of Ac-PVA's on  $r$   
Substrate : 3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C

Degree of Acetylation (mole%)	9.2	9.8*	15.4	21.5	27.0	28.2*	33.6	
$r$	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

\* Ac-PVA having somewhat continuous sequence of acetyl group.

\*\* Figures in parentheses denote the degree of sulfonation in mole%.

It is seen that for all Ac-PVA's, PSS and PS-S (31) give very large  $r$ -values ; the largest  $r$ -values is 38.3. This implies that the catalyst effect of the PS-S is 38.3 times larger than that of hydrochloric acid under the same reaction condition. The catalyst effects of PSS and PS-S increase with the degree of acetylation of Ac-PVA, and when these  $r$ -values are compared at a fixed degree of acetylation, PS-S gives larger  $r$  than PSS, particularly for samples having lower degrees of acetylation. Further, Ac-PVA having relatively continuous sequences of acetyl groups gives larger  $r$  than randomly acetylated Ac-PVA.

These phenomena suggest that interaction between acetyl groups in Ac-PVA and benzene ring in polystyrene sulfonic acid plays an important role, as was shown in the case of the hydrolysis of low molecular esters with polystyrene sulfonic acid<sup>11</sup>, and the local concentration of ester groups and sulfonic groups in the neighbourhood of polymer molecule increases to give higher catalyst effects.

### 2.2. Influence of Degree of Polymerization of Ac-PVA on $r$

Degree of polymerization ( $p$ ) of Ac-PVA employed in the foregoing experiments was 1310. To investigate the effect of  $p$  of Ac-PVA, Ac-PVA's with  $p$ 's of 80, 120, 1310 and 5000 were hydrolyzed with PSS or PS-S (degree of sulfonation : 40 mole%). As the degrees of acetylation of these samples are nearly equal, the results in Table 2 show that the influence of  $p$  of Ac-PVA on  $r$  is negligible within the range covered.

### 2.3. Influence of Ac-PVA Concentration on $r$

All substrate concentrations used in the foregoing experiments were 3.0 g./l.. In order to examine the effect of Ac-PVA concentration on  $r$ , Ac-PVA's with various degrees of acetylation of 10.6, 21.5, and 33.6 mole% were hydrolyzed by using PSS or PS-S (degree of sulfonation : 39 mole%) as catalysts at substrate concentrations shown in Table 3.

Table 2. The effect of degree of polymerization ( $p$ ) of Ac-PVA's on  $r$   
Substrate : 3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C

Substrate	$p$	80	120	1310	5000
	D. Ac.*		25.3	25.0	24.6
$r$	PSS	15.8	14.9	15.1	14.6
	PS-S(42)	—	25.7	28.9	30.4

\* Degree of acetylation in mole%

Table 3. The effect of concentration of Ac-PVA's on  $r$   
Catalyst : 0.0050 N ; temp. : 50°C

Catalyst	D. Ac. of Ac-PVA (mole%)	$r$ for the following conc. (g./l.) of Ac-PVA						
		2	3	6	10	20	35	80
PSS	10.6	—	4.9	3.9	2.9	—	—	—
	21.5	—	13.0	7.2	5.0	2.6	1.4	—
	33.6	25.4	17.7	9.7	—	—	—	—
PS-S (39)	10.6	—	17.2	9.2	5.7	—	—	—
	21.5	—	29.9	16.0	10.6	4.8	3.1	1.3
	33.6	45.6	35.2	18.8	—	—	—	—

Table 3 shows that the  $r$ -values for all Ac-PVA samples with these two sulfonic acids sharply decrease with increasing concentration of Ac-PVA. Comparing these  $r$ -values for Ac-PVA with the same degree of acetylation, the  $r$ -values for PS-S are found to decrease more rapidly than those for PSS.

#### 2.4. Influence of Catalyst Concentration on $r$

All experiments in the foregoing sections were carried out under a catalyst concentration of 0.0050 N. We made similar experiments for Ac-PVA (degree of acetylation : 21.5 mole%) under a catalyst concentration of 0.020 N and found out that  $r$ -values for each sulfonic acid became smaller with increasing catalyst concentration (Table 4).

#### 2.5. Influence of Reaction Temperature on $r$

We carried out such hydrolysis as mentioned above at various temperatures

Table 4 The effect of concentration of catalyst on  $r$   
Degree of acetylation of substrate : 21.5 mole% ; substrate : 3.0 g./l. ; temp. : 50°C

Conc. of catalyst (N)		0.0050	0.020
$r$	PSS	13.0	7.4
	PS-S (42)	27.7	22.7

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(30 and 80°C) other than 50°C, and examined the influence of reaction temperature on  $r$ . As shown in Table 5,  $r$ -value decreases with rising reaction temperature, but when  $r$ -values are compared with those of the hydrolysis of low molecular ester-polymeric acid systems and polymeric ester-*n*-dodecylbenzene sulfonic acid systems<sup>1,2</sup>, the degree of decreasing of  $r$ -values for polymeric ester-polymeric sulfonic acid systems with reaction temperature is smaller.

Table 5 The effect of reaction temperature on  $r$   
Substrate : 3.0 g./l. ; catalyst : PS-S (31), 0.0050 N

D. Ac. of Ac-PVA (mole%)	$r$ for the following reaction temp. (°C)		
	30	50	80
23.3	31.6	29.7	27.7
27.0	36.4	34.2	29.6

### 2.6. Influence of Organic Solvent Added to the Reaction System on $r$

All experiments mentioned above were carried out in water. If a large  $r$ -value is due to the local concentration of the ester in the neighbourhood of polymeric sulfonic acid molecule caused by hydrophobic interaction, however,  $r$  is expected to decrease when organic liquid is added to the reaction mixture. We have carried out the hydrolysis in aqueous acetone or in aqueous dioxane. The results are given in Table 6, together with the experimental conditions. As was expected,  $r$  decreases rapidly by addition of organic liquid to the reaction mixture. Moreover, unlike the hydrolysis of low molecular weight esters, particularly in the case of PSS as a catalyst,<sup>1</sup>  $r$  is smaller than unity.

Table 6. The effect of added dioxane or acetone on  $r$   
Substrate : 3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C ; organic solvent : 30 vol%

Catalyst	D. Ac. of Ac-PVA (mole%)	Organic solvent	$r$
PSS	9.2	Dioxane	0.94
"	33.6	"	0.74
PS-S (31)	9.2	"	1.3
"	33.6	"	1.8
PSS	9.2	Acetone	0.72
"	33.6	"	0.79
PS-S (31)	9.2	"	0.69
"	33.6	"	0.88

### 2.7. Influence of Steric Configuration of Ac-PVA on $r$

Recently, PVA's with various steric configurations were derived from polyvinyl trifluoroacetate, isotactic polyvinyl ether and polydivinyl-*n*-butyral, and the acetalization reactions with these PVA's, hydrolysis reactions with completely acetylated products of these samples, etc. were investigated<sup>5</sup>. We hydrolyzed partially

randomly acetylated samples of these PVA's with PSS as a catalyst, and compared the  $r$ -values with those for the conventional Ac-PVA. Together with starting polymer of Ac-PVA employed in these experiments, the degree of acetylation and its  $p$ , the  $r$ -values obtained are summarized in Table 7.

Table 7. The effect of steric configuration of Ac-PVA's on  $r$   
Substrate : 3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C

Ac-PVA				
No.	Parent PVA derived from	D. Ac. (mole%)	$p$	$r$
A	Polyvinyl acetate	21.1	57	11.7
		21.5	1310	13.0
		24.4	"	15.1
		27.0	"	17.5
B	Polyvinyl trifluoroacetate	24.0	1000	15.1
		27.2	"	18.5
C	<i>isot.</i> -Polvinyl ether	23.2	1000	13.0
		27.2	"	16.4
D	Polydivinyl- <i>n</i> -butyral	21.0	55	19.1
		26.8	55	22.2

Comparing with  $r$ -values for Ac-PVA's having similar  $p$  and degree of acetylation,  $r$  decreases in the order of D>B>A>C. This order is consistent with that found in other reactions with these samples, so the results above obtained may be attributed to the difference of steric configuration of Ac-PVA's.

#### 2.8. Influence of Allyl Alcohol Unit or *iso*-Propenyl Alcohol Unit in Ac-PVA on $r$

Vinyl alcohol copolymers containing a small fraction of allyl alcohol or *iso*-propenyl alcohol were prepared by the radical copolymerization of vinyl acetate with allyl acetate or *iso*-propenyl acetate followed by complete saponification. Partially acetylated products of these copolymers were hydrolyzed with PSS or PS-S (degree of sulfonation : 41 mole%) and  $r$ -values of these products were compared with that for Ac-PVA. Properties of the copolymers, reaction conditions and results are listed in Table 8.

Comparing with  $r$ -values for Ac-PVA having the same degree of acetylation,  $r$ -values for allyl alcohol copolymers are nearly independent of their composition, whereas  $r$ -values for *iso*-propenyl alcohol copolymers slightly increase with *iso*-propenyl alcohol content.

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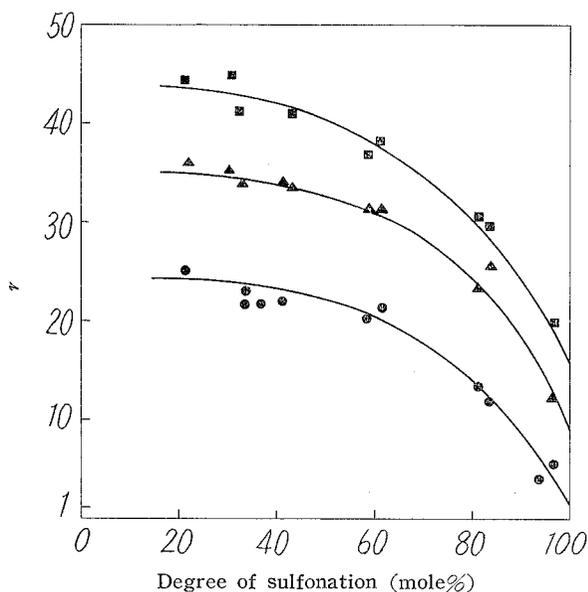
Table 8. Hydrolysis of partially acetylated vinyl alcohol copolymers  
Substrate : 3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C

Substrate			$r$	
Comonomer	Mole% of comonomer	D. Ac. (mole%)	PSS	PS-S (41)
None	0	14.2	9.0	25.6
"	"	23.3	13.0	34.8
"	"	27.0	17.5	39.1
Allyl alcohol	5.6	23.4	12.3	32.0
"	21.3	27.3	16.7	43.1
<i>iso</i> -Propenyl alcohol	4.1	20.4	12.3	23.5
"	17.8	17.8	17.6	35.1

### 3. HYDROLYSIS OF Ac-PVA WITH VARIOUS POLYMERIC SULFONIC ACIDS.

#### 3.1. Hydrolysis with PS-S with Various Degrees of Sulfonation

In the foregoing section, it was pointed out that PS-S with lower degrees of sulfonation gave larger  $r$ -value than PSS. We have carried out hydrolysis of various Ac-PVA's of degrees of acetylation of 9.2, 23.3 and 33.6 mole% using PS-S's with various degrees of sulfonation which were prepared by sulfonation of PS with chlorosulfonic acid in ethylene dichloride, and have investigated in detail the effect of degree of sulfonation of PS-S on  $r$ . Results are given in Fig. 1.



Substrate : 3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C  
Degree of acetylation of Ac-PVA (mole%) : ● 9.2 ; ▲ 23.3 ; ■ 33.6

Fig. 1 Hydrolysis of Ac-PVA's with polystyrene sulfonated in ethylene dichloride.

Within a range of the degree of sulfonation of 20 mole% to 50 mole%,  $r$ -value for each Ac-PVA is nearly constant. On the other hand, above 50 mole%,  $r$ -value decreases rapidly with increasing degree of sulfonation.

### 3.2. Hydrolysis with PS-S Prepared under Other Sulfonation Conditions.

As sulfonated product of polystyrene (PS) was precipitated during sulfonation, the structure of resultant PS-S was expected to be different in the distribution of sulfonic acid groups among the polymer molecules and within the polymer molecule, depending on the solvent used for the sulfonation. We have sulfonated PS mentioned in the foregoing section in carbon tetrachloride, instead of ethylene dichloride as a solvent, and hydrolyzed Ac-PVA by using this PS-S as a catalyst. As shown in Fig. 2,  $r$ -value for each Ac-PVA almost linearly increases with decreasing degree of sulfonation. Comparing with Fig. 1 it is shown that  $r$ -values for Ac-PVA with the same degree of acetylation have different tendency in its dependency on degree of sulfonation.

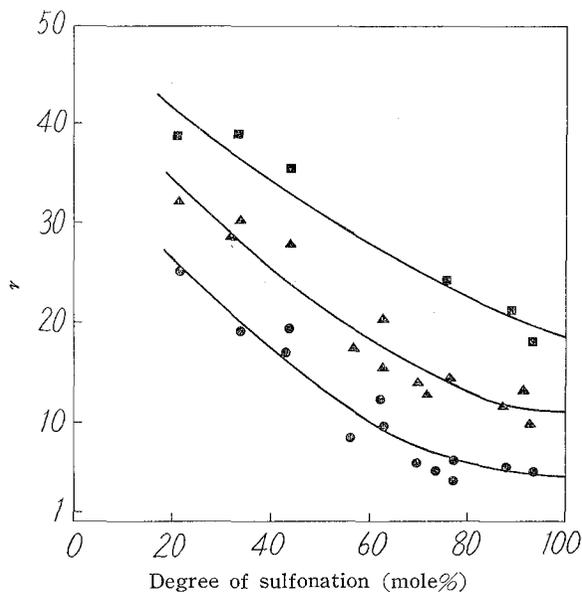


Fig. 2 Hydrolysis of Ac-PVA's with polystyrene sulfonated in carbon tetrachloride (The reaction condition is the same as Fig. 1)

### 3.3. Hydrolysis with PSS Prepared under Various Polymerization Conditions

In order to investigate the effect of  $p$  on the catalytic effect, PSS's with various  $p$ 's were prepared by the polymerization of sodium  $p$ -styrene sulfonate at a monomer concentration of 27 g./dl. using ethylmercaptan as a chain-transfer-agent. Further, as described in the previous paper<sup>13</sup>, it was found that PSS polymerized at lower monomer concentrations was less effective in the hydrolysis of  $n$ -butyl acetate than PSS obtained at higher monomer concentrations, and it was inferred that this sample was rather syndiotactic. We have carried out similar experiments on the hydrolysis of Ac-PVA, and studied the effect of steric configuration of PSS on  $r$ . At the same time, we also studied the hydrolysis with partially sulfonated isotactic

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polystyrene (*iso*-PS-S) having a degree of sulfonation of 92 mole%. Preparation condition of PSS, reaction condition and results are summarized in Table 9.

Table 9. Hydrolysis of Ac-PVA with PSS prepared under various conditions  
Substrate : 3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C

Catalyst	Polymerization		$[\eta]_{2N-NaOH}^{30^\circ C}$ (dl./g.)	$r$ for Ac-PVA of the following D. Ac. (mole%)		
	Monomer (g./dl.)	Temp. (°C)		9.2	23.3	33.6
PSS	27	50	1.2	4.3	12.9	19.5
/*	''	''	0.20	3.8	11.2	16.8
/*	''	''	0.06	3.4	9.7	16.0
''	1.0	80	0.14	3.5	8.2	11.8
''	0.5	80	0.03	2.9	6.4	9.4
isotactic PS-S (92)			0.82	4.7	12.7	17.8
atactic PS-S (92)			0.04	4.7	12.2	20.7
'' (100)**			0.20	4.5	12	18

\* Ethylmercaptan was added in the polymerization mixture.

\*\* The  $r$ -value for this catalyst was determined by extrapolation of the data in Fig. 1.

Table 9 shows that  $r$ -values for all Ac-PVA's are rather dependent on steric configuration of PSS, than on its  $p$ , as previously shown in the hydrolysis of low molecular esters<sup>1)</sup>. However,  $r$  for *iso*-PS-S is nearly equal to that of sulfonated atactic PS. It is true that more detailed experiments are necessary to draw a conclusion, but by taking into consideration that  $r$ -value for PSS polymerized at higher monomer concentrations is nearly equal to that of completely sulfonated atactic PS (100), we may say that there does not exist so large difference between steric configuration of isotactic PS and that of atactic PS.

### 3.4. Hydrolysis with Partially Neutralized PS-S (degree of sulfonation: 77 mole%) with Strong Bases

Experiments were carried out with PS-S (77) partially neutralized with various strong bases utilizing residual free sulfonic acid groups for the hydrolysis, and the results as listed in Table 10 were obtained under the experimental condition shown therein. As a result of the introduction of bulky hydrophobic groups by the neutralization,  $r$ -values drastically decrease.

### 3.5. Hydrolysis with Various Polymeric Sulfonic Acids other than Polystyrene Sulfonic Acids

All experiments in the foregoing sections were carried out with polystyrene sulfonic acids. The following polymer catalysts were used for further experiments: the methods of preparation were described in detail elsewhere<sup>6)</sup>.

BS : Benzene sulfonic acid.

TPMS : Triphenylmethane mono-sulfonic acid.

Table 10. Hydrolysis of Ac-PVA with partially neutralized PS-S (77.4)  
 Catalyst : 0.0050 N ; Ac-PVA : 3.0 g./l. ; temp. 50°C

Neutralization		$r$ for Ac-PVA of the following D. Ac. (mole%)		
Base	Degree (%)	9.2	23.3	33.6
None	0	4.8	13.8	23.6
NaOH	33	4.0	11.2	14.1
"	66	2.1	4.3	7.1
(CH <sub>3</sub> ) <sub>4</sub> NOH	33	2.1	2.2	5.1
(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NOH	33	1.9	1.7	2.3

- BS-PVA : Partially butyracetalized sulfonic acid PVA obtained by partial acetalization of PVA with crotonaldehyde in the presence of sulfuric acid.
- BzS-PVA : Partially benzacetalized sulfonic acid PVA obtained by partial acetalization of PVA with *o*-benzaldehyde sulfonic acid.
- BzDS-PVA: Partially benzacetalized disulfonic acid PVA obtained by partial acetalization of PVA with 2,4-benzaldehyde disulfonic acid.
- PVS : Polyvinyl sulfonic acid obtained by polymerization of sodium vinyl sulfonate.
- S-PANa : Partially sulfonated polyacenaphthylene obtained by partial sulfonation of polyacenaphthylene prepared by radical polymerization.
- S-PS-ANa : Partially sulfonated styrene-acenaphthylene copolymer obtained by partial sulfonation of styrene-acenaphthylene copolymer (content of styrene : 16 mole%).
- S-PMS : Partially sulfonated poly- $\alpha$ -methyl styrene obtained by partial sulfonation of poly- $\alpha$ -methyl styrene prepared by an ionic polymerization.
- S-PS-Sti : Partially sulfonated styrene-stilbene copolymers obtained by partial sulfonation of styrene-stilbene copolymer (content of stilbene : 20 and 30 mole%).
- PS-VS : Styrene-vinyl sulfonic acid copolymer obtained by hydrolysis of a copolymer from butyl ester of vinyl sulfonic acid and styrene.

Chemical structures of the above sulfonic acids are illustrated together with those of polystyrene sulfonic acids in Fig. 3. The degrees of sulfonation of these samples were calculated on the assumption that one monomer unit in these samples would contain only one sulfonic acid.

Hydrolysis of Ac-PVA (degree of acetylation : 21.5 mole%) was carried out with BS-PVA (degree of sulfonation : 8.6 and 44.6 mole%), BzS-PVA (42.6 mole%), BzDS-PVA (30.0 mole%) and PVS. The  $r$ -values obtained are shown in Table 11, together with those for the hydrolysis with BS and TPMS.

The  $r$ -values in Table 11 are in all cases near unity, i.e., no remarkable accelerating effect has been observed compared with hydrochloric acid at the same equivalent concentration. This is similar to the case of the hydrolysis of low mo-

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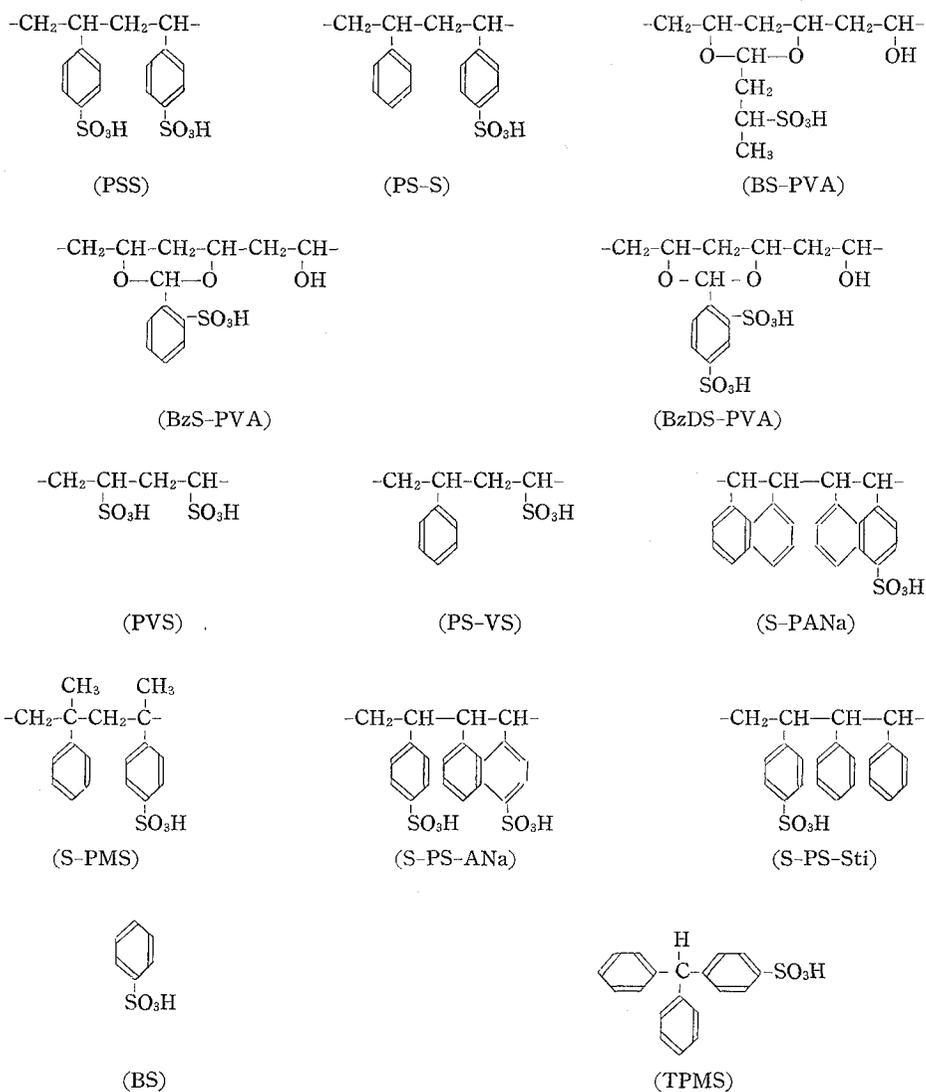


Fig 3. Sulfonic acids used as catalysts.

Table 11 Hydrolysis of Ac-PVA with some polymeric and low molecular sulfonic acids.

Degree of acetylation of Ac-PVA : 21.5 mole% ; substrate :  
3.0 g./l. ; catalyst : 0.0050 N ; temp. : 50°C

Catalyst	$r$
BS	0.94
TPMS	1.1
BS-PVA (8.6)	0.92
" (44.2)	1.3
BzS-PVA (42.6)	1.1
BzDS-PVA (30.0)	1.3
PVS	0.72

lecular esters with these sulfonic acids<sup>17</sup>. Therefore, we may say that hydrophobic character of partially acetalized sulfonic acid PVA's is not strong enough to make the local concentration of Ac-PVA sufficiently high in the neighbourhood of this catalyst molecule.

Comparison of the catalytic effects of S-PANa, S-PS-ANa, S-PMS, S-PS-Sti and PS-VS with those of polystyrene sulfonic acid was carried out and the results obtained are listed in Table 12, together with degree of sulfonation of these sulfonic acids, their  $[\eta]$ 's determined in 2N-NaOH at 30°C and the results for PS-S's with similar degree of sulfonation to that of sulfonation of the sulfonic acids mentioned above.

Table 12. Hydrolysis of Ac-PVA's with various sulfonated aromatic polymers.  
 Catalyst : solvent for sulfonation,  $(\text{CH}_2\text{Cl})_2$ ; conc., 0.0050 N ;  
 Ac-PVA : 3.0 g./l. ; temp. : 50°C

Name	Catalyst		$r$ for Ac-PVA of the following D. Ac (mole%)		
	Degree of sulfonation (mole%)	$[\eta]_{2\text{N-NaOH}}^{30^\circ\text{C}}$ (dl./g.)	10.6	24.6	33.6
PS-S	30	0.2	24	35	43
"	70	0.2	18	29	34
"	80	0.2	16	25	30
S-PANa	74	0.4	20.8	30.8	44.5
S-PS-ANa (16:84)*	69	0.4	22.3	29.1	38.2
S-PMS	76	0.2	8.3	17.2	27.7
S-PS-Sti (8:2)*	69	0.2	3.5	9.1	—
" (7:3)*	81	0.2	1.1	2.2	—
PS-VS (71:29)*	29	—	4.1	20.7	34.9

\* Molar ratio of two monomer units in copolymer.

Although  $pH$  values of these sulfonic acids were nearly the same as those of polystyrene sulfonic acids at the same equivalent concentration and all sulfonic acids employed in this experiment other than PS-VS were more hydrophobic than PS-S of the same degree of sulfonation, all  $r$ -values for the hydrolysis of Ac-PVA's with these sulfonic acids were not larger than those of PS-S. By considering the experimental fact that  $r$  varies with its steric configuration of PSS, these phenomena suggest that the catalytic effect of polymeric sulfonic acids is dependent not only on their hydrophobicity but also on their steric configuration. Smaller  $r$ -values for PS-VS would be due to PS-VS being less hydrophobic than PS-S.

#### 4. DISCUSSION

In the foregoing sections, it was shown that hydrophobic sulfonic acids were more effective as catalysts for the hydrolysis of Ac-PVA than hydrochloric acid. This fact was explained in terms of local concentration of esters and sulfonic acids in the neighbourhood of the polymer molecule due to hydrophobic attraction between Ac-PVA and polymer catalyst.

As shown in the hydrolysis of low molecular ester with polymeric sulfonic

acids<sup>1)</sup>, the hydrolysis of polymeric esters with polymeric sulfonic acids will be quantitatively discussed in this section.

It is assumed that the hydrolysis of polymeric esters takes place in the effective volume ( $V_P$ ) adjacent to this polymer. Furthermore, hydrochloric acid catalyst (total mole number =  $M_{HCl}$ ) is assumed to be distributed homogeneously throughout the reaction system, the total volume of which being  $V$ , whereas hydrogen ion, that is the counter ion of sulfonic acid group in polymeric sulfonic acid is assumed to be highly concentrated in the neighbourhood of this polymer at experimental concentration. Therefore, if, in the hydrolysis of polymeric esters with polymeric sulfonic acids,  $M_{S.P}$  mole, *i.e.* a part of sulfonic acid groups of polymeric sulfonic acid, the total mole number of which is  $M_S$ , is bound within the volume  $V_P$ , adjacent to the polymeric ester and the real rate constant of hydrolysis with bound sulfonic acid,  $\kappa$ , is the same as that of hydrolysis with hydrochloric acid, we can express the rate of this hydrolysis  $R_S$  as

$$R_S = \kappa \cdot \frac{M_{S.P}}{V_P} \cdot \frac{M_E}{V_P} \cdot V_P \quad (3)$$

where  $M_E$  is the total mole number of ester. On the contrary, if the same reaction as mentioned above takes place only in the effective volume ( $V_S$ ) adjacent to the polymeric sulfonic acid and  $M_{E.S}$  mole, *i.e.* a part of ester groups, is bound within this  $V_S$ , we can also express the rate of hydrolysis  $R'_S$  as

$$R'_S = \kappa \cdot \frac{M_{E.S}}{V_S} \cdot \frac{M_S}{V_S} \cdot V_S \quad (4)$$

As  $R_S$  should be equal to  $R'_S$ , the following equation can be derived from Eq. (3) and Eq. (4);

$$M_{S.P} \left( \frac{V_S}{M_S} \right) = M_{E.S} \left( \frac{V_P}{M_E} \right) \quad (5)$$

$V_S/M_S$  and  $V_P/M_E$  in this equation denote effective volumes per mole of sulfonic acid and per mole of ester, respectively. The left-hand side of Eq. (5) denotes the region which sulfonic acids occupy in the  $V_P$  and the right-hand side that which esters occupy in the  $V_S$ . In these regions, the hydrolysis reaction can actually proceed. Therefore these regions should be equal to each other. This equality is substantiated by Eq. (5).

As the rate of hydrolysis of polymeric ester with hydrochloric acid,  $R_{HCl}$  can be expressed by

$$R_{HCl} = \kappa \cdot \frac{M_E}{V_P} \cdot \frac{M_{HCl}}{V} \cdot V_P, \quad (6)$$

the following equation for  $r$  can be obtained from Eqs. (1), (3), (4) and (6), using  $M_S = M_{HCl}$ ;

$$r = \frac{k_S}{k_{HCl}} = \frac{M_{S.P}}{V_P} \cdot \frac{V}{M_S} = \frac{M_{E.S}}{V_S} \cdot \frac{V}{M_E} \quad (7)$$

Therefore, according to Eq. (7),  $r$  is nothing other than the ratio of concentration of sulfonic acid in the region around the polymeric ester, where the hydrolysis actually takes place, to the bulk concentration of sulfonic acid; on the other hand,  $r$  is equal to the ratio of concentration of ester in the region around the polymeric sulfonic acid to the bulk concentration of the ester. In the combination of ester and sulfonic acid which should give large  $M_{S.P}$  or  $M_{E.S}$ , large  $r$ -value would be obtained.

As was shown in the previous sections,  $r$ -value obtained at constant concentrations of catalyst and substrate did not depend on  $p$  of Ac-PVA or that of polystyrene sulfonic acids. This means that  $M_{S,P}/V_P$  or  $M_{E,S}/V_S$  in Eq. (7) is independent of  $p$ . One of the simplest interpretation for these values being independent of  $p$  is that  $M_{S,P}$  and  $V_P$ , or  $M_{E,S}$  and  $V_S$  are independent of  $p$  of Ac-PVA or that of polystyrene sulfonic acid, respectively. If  $V_P$  or  $V_S$  is, for example, equal to a volume occupied by flexible polymer coils, this volume should change with  $p$  of the polymer, and so the fact that  $V_P$  or  $V_S$  is independent of its  $p$  shows that  $V_P$  or  $V_S$  is a volume along flexible polymer chains.

Next,  $r$ -value at a constant concentration of catalyst decreased with increasing concentration of substrate. Using an assumption that the bonding of polymeric ester with polymeric sulfonic acid is of a Langmuir type, this experimental fact is understood by considering that  $M_{E,S}/V_S$  in Eq. (7) does not increase in proportion to increase of bulk concentration of ester,  $M_E/V$ , to result in lower  $(M_{E,S}/V_S)/(M_E/V)$ , *i.e.* lower  $r$ . Further, the experimental fact, that  $r$ -value at a constant concentration of substrate decreased with increasing concentration of catalyst, is also explained by considering that the increase of  $M_{S,P}/V_P$  in Eq. (7) is not proportional to that of bulk concentration of catalyst,  $M_S/V$ .

The fact, that  $r$ -value increased with increasing degree of acetylation of Ac-PVA, shows that  $M_{S,P}/V_P$  in Eq. (7) increases. As  $V_P$  is nearly independent of the degree of acetylation of substrate at a constant concentration of substrate,  $M_{S,P}$  is considered to increase with increasing degree of acetylation of Ac-PVA. The  $r$ -value for Ac-PVA having relatively continuous sequence of acetyl groups was larger than that for randomly acetylated PVA with a similar degree of acetylation. It was already pointed out, in the hydrolysis of low molecular esters with polymeric sulfonic acids, that the amount of bound ester with a certain sulfonated structural unit along the PS-S molecule depended on whether the structural unit adjacent to the sulfonated unit was sulfonated or not<sup>13</sup>. Therefore, the effectiveness of the continuous sequence also shows that the amount of bound sulfonic acid with a certain ester group ( $E$ ) along the polymeric ester molecule, *i.e.*  $M_{S,P}$ , depends on whether the structural unit adjacent to this ester group is an ester group ( $E$ ) or vinyl alcohol unit ( $V$ ); namely,  $M_{S,P}$  for  $-E-(E)-E-$  is larger than that for  $-V-(E)-V-$ . Next, as an adsorption of ester is considered to take place mainly in the neighborhood of unsulfonated benzene ring in a PS-S molecule,  $M_{E,S}$  in Eq. (7) increases with decreasing degree of sulfonation at constant concentrations of sulfonic acid and substrate, and as  $V_S$  is nearly constant under our experimental conditions,  $M_{E,S}/V_S$  is considered to increase with decreasing degree of sulfonation. As was already shown in previous sections, the dependency of  $r$  for the PS-S sulfonated in ethylene dichloride on its degree of sulfonation was different from that of  $r$  for the PS-S sulfonated in carbon tetrachloride. This was attributed not to the distinction between distributions of composition of resultant PS-S, but to the difference between the sequences of sulfonic acid group along the PS-S molecule, as was shown in detail elsewhere<sup>13</sup>.

By considering that Ac-PVA's having various steric configurations gave various  $r$ -values and more hydrophobic polymeric sulfonic acids did not always give larger  $r$ -value than PS-S, we can say that  $M_{S,P}$  or  $M_{E,S}$  in Eq. (7) varied not only with

the hydrophobicity of these sulfonic acids, but also with their steric configuration.

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