

Study on Ketalization Reaction of Poly(vinyl Alcohol) by Ketones. IV. Reaction between Poly(vinyl Alcohol) and Aliphatic Ketones and Behavior of Polyvinylketal in Water

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SYNOPSIS

Ketalization reaction of poly(vinyl alcohol) (PVA) by aliphatic ketones, dimethylsulfoxide (DMSO) as solvent, under the presence of acidic catalyst, in homogeneous system was carried out and the synthesis of polyvinylketals were successfully performed. The equilibrium constant at 40°C is ca. 0.07 in the case of methyl *n*-propyl ketone (nPK) and methyl *n*-butyl ketone (nBK), but is ca. 0.05 in the case of methyl *i*-propyl ketone (iPK) and ca. 0.01 in the case of methyl *i*-butyl ketone (iBK) and methyl *t*-butyl ketone (tBK), respectively. Moreover, the ketalization degree of polyvinylketal by iBK and tBK reached to only ca. 35 mol % as the maximum. It seems that these were due to steric hindrance of bulky side chain of ketones. But the heat of reaction is 7.5 kcal/mol in all aliphatic ketones, it seems to proceed the same ketalization reaction mechanism. Films prepared from the polyvinylketals were soaked in water and degree of swelling, solubility, and hydrolysis of films were measured. The reaction of film with water, in acidic side, at first the film swells, and then, as the deketalization reaction proceeds, the film dissolves in water. The dissolution time is controlled by the kind of ketones, ketalization degree, and pH of water which reveals that deketalization reaction proceeds proportional to proton concentration. It is more difficult to dissolve highly ketalized polyvinylketals obtained by propyl ketones and butyl ketones than that by acetone. The hydrolysis of polyvinylketal film proceeds in the order as follows: acetone > MEK > nPK > iPK = nBK > iBK > tBK. This phenomenon seems to be affected by hydrophobicity of the film surface which depends upon the kind of the original ketones.

INTRODUCTION

As mentioned in the previous report,^{1,2} polyvinylketal with any ketalization degree was successfully obtained from PVA and acetone and MEK, DMSO as solvent, in homogeneous system. On the other hand, in aqueous media, no ketalization reaction proceeds; the results were explained on the basis of the extreme low values of equilibrium constant (ca. 0.07 at 40°C). It becomes clear as well^{2,3} that polyvinylketal films deketalized easily and dissolved in acidic water, but the polyvinylketal obtained by MEK is more stable in water than that from acetone since MEK was hydrophobicity.

This paper is concerned with the acid-catalyzed synthesis of polyvinylketal from other aliphatic ketones, nPK, iPK, nBK, iBK, tBK, in homogeneous system, the values of equilibrium constant, and the solubilities in various solvents. Studies of degree of swelling, solubility, deketalization degree, and so on with polyvinylketal films of various ketalization degree soaked in water of several pH values were made and reported. Also, these behaviors are compared with those of polyvinylketal from acetone and MEK.

EXPERIMENTAL

Samples and Reagents

PVA of average degree of Polymerization, 1800, saponification degree above 99.4% (NH-18 from Ni-

hon Gohsei Co., Ltd.) was used. DMSO (water content 0.05%), *p*-toluene sulfonic acid (PTS), guaranteed reagent (Nacalai Tesque Inc.), were used without further purification. Propyl ketones and butyl ketones (guaranteed reagent, Nacalai Tesque Inc.) were dried over anhydrous sodium sulfate and distilled before the use.

Synthesis Method

PVA dried at 105°C for more than 2 h was dissolved in DMSO (4–5 wt %). Then the prescribed amounts of PTS and ketones were added, and the mixture was kept at the prescribed temperature under vigorous shaking. The reaction from beginning to end proceeds in homogeneous system. When a large amount of ketone was used, PVA was precipitated, so that a long time was needed to dissolve. Therefore, it was effective that the ketone dissolved in a small amount of DMSO was added to reaction mixture. In the case of a very large amount of ketone, the ketone–DMSO solution should be added dropwise and slowly. Prescribed hours later, the reaction mixture was neutralized by 1 *N* NaOH aqueous solution and then the reaction product was precipitated with tetrahydrofuran, ethyl acetate, or water and dried under vacuum. The polymer thus obtained was dissolved in methanol (refer to Table IV), precipitated by tetrahydrofuran, ethyl acetate, or water and dried. This procedure was carried out twice.

Analysis Method

The ketalization degree of polyvinylketal (PVKL) was determined by iodoform method, the quantitative analysis of ketone released by perfect deketalization of PVKL, as previously described.¹

Solubility in Organic Solvents

In 3 mL solvent, 10 mg PVKL was introduced, kept under a certain temperature for 1 day, and the state of dissolution was observed.

Film Preparation Method

To obtain transparent film, PVKL dissolved in ethanol (5 wt %) is gradually allowed to dry on a glass plate at room temperature. As solvent for PVKL, various concentrations of ethanol aqueous solution were used depending upon the ketalization degree, as described previously.³ During film preparation, hydrolysis of PVKL was not observed.

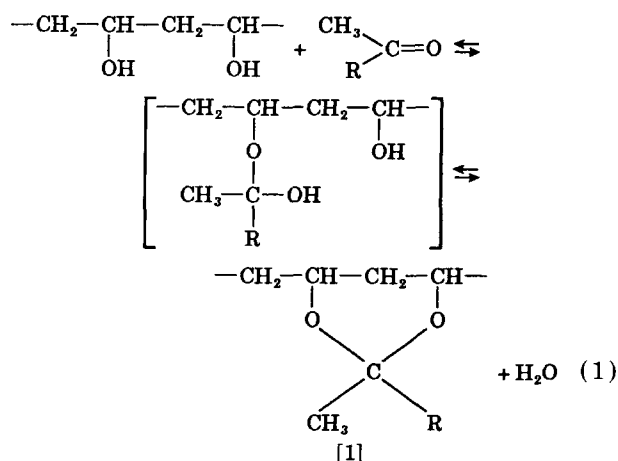
Behavior of PVKL in Water

Samples were soaked in water of various pHs kept at prescribed temperature. Prescribed hours later, film is removed from water and degree of swell, solubility, deketalization degree, and the time needed for complete dissolution of film were measured according to the method described previously.³

RESULTS AND DISCUSSION

Mechanism of Ketalization Reaction between PVA and Ketones

The reaction between PVA and ketones seems to proceed as follows:



Since in the reaction system using water as solvent, no PVKL was formed, the ketalization reaction between PVA and ketones was carried out in homogeneous system in DMSO. The ketalization reaction proceeds rather rapidly, and it was found that in 24 h equilibrium is reached. The reactions were further carried out for more than 48 h, reaction equilibrium was confirmed, and the equilibrium ketalization degrees were determined. From the values, in accordance with eq. (2), equilibrium constant *K* was calculated. Results obtained are listed in Table I.

$$k = \frac{x^2}{(a-x)(b-x)} = \frac{X^2}{(1-X)(E-X)} \quad (2)$$

where *a* (mol/L) = PVA initial concentration (value obtained against 2 basic PVA mole), *b* (mol/L) = ketone initial concentration, *x* (mol/L) = PVKL concentration, *X* = *x*/*a* = ketalization degree, and *E* = *b*/*a* = ketone equivalent (mol ratio ketone against 2 basic PVA mol).

Table I Equilibrium Constants of Ketalization Reaction by Various Aliphatic Ketones^a

Temperature (°C)	Ketone	Ketone Equivalent	Ketalization ^b (mol %)	<i>K</i>
40	nPK	6.00	46.6	0.074
	nPK	1.50	20.0	(0.038)
	iPK	6.00	42.0	0.055
	iPK	3.00	29.6	0.046
	iPK	1.50	(17.5)	(0.028)
	nBK	6.00	45.3	0.068
	nBK	1.50	28.0	0.089
	iBK	6.00	24.9	0.014
	iBK	3.00	17.7	0.013
	iBK	1.50	11.1	0.010
	tBK	6.00	20.8	0.009
	tBK	3.00	16.0	0.011
	tBK	1.50	(8.8)	(0.006)
	Acetone ¹	6.00	46.0	0.071
	MEK ²	6.52	49.2	0.079
30	nPK	6.00	52.0	0.103
	iPK	6.00	46.6	0.073
	nBK	6.00	51.0	0.097
	iBK	6.00	25.3	0.015
	tBK	3.00	18.3	0.015
50	nPK	6.00	41.6	0.053
	iPK	6.00	35.6	0.035
	nBK	6.00	41.3	0.052
	iBK	6.00	17.9	0.007
	tBK	3.00	12.9	0.007

^a PVA initial concentration = 0.15–0.6 mol/L; PTS concentration = 2.5 g/L.

^b = equilibrium ketalization degree.

The values of *K* for nPK and nBK are ca. 0.07, for iPK ca. 0.05, and for iBK and tBK ca. 0.01 at 40°C. The values for nPK and nBK are equal to those for acetone¹ and MEK,² but the values for iPK, iBK, and tBK are lower than those for acetone and MEK. Steric hindrance of bulky side chain of ketones seems to affect the equilibrium.

In order to obtain the maximum ketalization degree of PVKL, ketalization reaction was carried out at 25°C with ketone equivalent 36.00, for 100 h, and the results are listed in Table II. In the case of nPK and nBK, the ketalization degree was ca. 60 mol %, in the case of iPK, it was ca. 50 mol %, but in the case of iBK and tBK, the value of only ca. 35 mol % was obtained. These results also show the effect of steric hindrance as described above.

Polyvinylketals and their sample numbers studied in this work are listed in Table III. Figure 1 shows the temperature dependence of equilibrium constant of the reaction between PVA and ketones. The heat of reaction determined from the gradient of line is 7.5 kcal/mol, the same as that of acetone or various

aldehydes. It can be interpreted that the ketalization reaction of aliphatic ketones proceeds according to identical mechanisms with the ketalization reaction of acetone and acetalization reactions of various aldehydes.¹

Based on ¹H- and ¹³C-NMR measurement, as previously described,¹ the structure of these ketalization products were confirmed to be [1] in eq. (1).

Solubility in Various Solvents

The solubilities of various PVKL in various solvents are listed in Table IV.

In DMSO, all ketal samples and also PVA dissolved, which shows it is the best solvent for carrying out homogeneous reaction; in DMF, all samples except for PVKL(iBK) and PVKL(tBK) dissolved at high temperature (60°C). In nonpolar solvents such as acetone, ether, petroleum ether, ethyl acetate, methylene chloride, carbon tetrachloride, cyclohexane, benzene, etc., all samples are insoluble.

Table II Maximum Ketalization Degree of PVKL

No.	99	101	103	89	109
Ketone	nPK	iPK	nBK	iBK	tBK
Ketalization degree (mol %)	58.0	51.8	59.5	32.4	34.7

Interesting solubility behavior was found with water, the details of which will be described later.

As alcohol is the best solvent for purifying polymers and preparing film, the solubilities at various concentrations were determined. As is clear from Table IV, PVKL becomes soluble in alcohol as the proportion of OH groups in the polymer decreases. Both methanol and ethanol were tried, identical behavior being observed. At the same ketalization degree, according to increase of carbon atom of the ketone, PVKL appears to have lower solubilities in ethanol.

Behavior of Various PVKL of Different Degrees of Ketalization in Acidic Water

At first, films of different ketalization degrees PVKL are soaked in water of pH 3.00 at 37°C, and deketalization degree, solubility, and degree of swell are determined.

Table III Polyvinylketals and Their Sample Numbers Studied in This Work

Ketone	Sample No.	Ketalization Degree (mol %)
nPK	148	5.0
	114	11.0
	98	20.0
	91	46.6
iPK	99	58.0
	171	6.7
	100	17.5
nBK	92	34.7
	101	51.8
	177	5.8
	104	28.0
iBK	102	44.9
	103	59.5
	88	11.1
tBK	87	24.9
	89	32.4
	108	4.9
	107	12.5
	125	20.8
	109	34.7

The typical results are listed in Figures 2–4. In the case of the PVKL with about 20 mol % of ketalization degree, the deketalization rate of no. 125 PVKL (tBK) (20.8 mol %) is slow, and those of no. 98 PVKL (nPK) (20.0 mol %) and no. 100 PVKL (iPK) (17.5 mol %) are fast, as shown in Figure 2. In the case of the PVKL with maximum ketalization degree such as no. 99 PVKL (nPK) (58.0 mol %), and no. 101 PVKL (iPK) (51.8 mol %), no. 103 PVKL (nBK) (59.5 mol %), no. 109 PVKL (tBK) (34.7 mol %), except no. 89 PVKL (iBK) (32.4 mol %), hydrolysis does not proceed at all after 72 h and only 10% of conversion is observed after 100 days. It is clear that hydrolysis reaction of these ketals becomes difficult compared to those of PVKL (acetone) and PVKL (MEK).

Solubility and degree of swell of PVKL in Figures 4 and 5, are similar to deketalization. The PVKL such as no. 99, no. 101, no. 103, and no. 109 are not soluble at all and the degree of swell is only about 1.10 after 72 h. It seems that these ketals are hydrophobic compared to PVA, PVKL (acetone), and PVKL (MEK). To confirm this point, the next experiment was carried out.

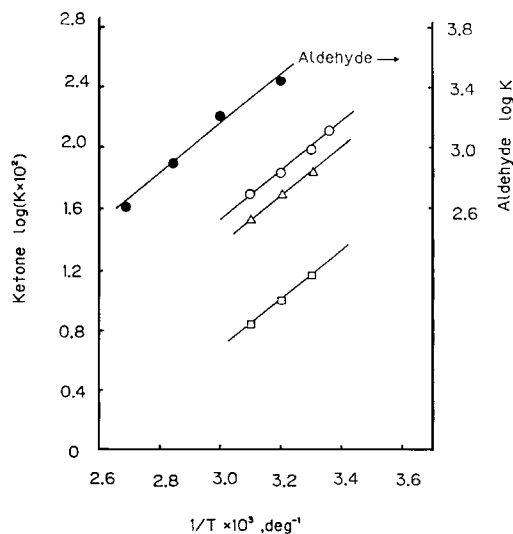
**Figure 1** Temperature dependency of equilibrium constant K : (○) nPK, nBK; (△) iPK; (□) iBK, tBK; (●) aldehyde.

Table IV Solubilities of Various Polyvinylketals^a

Kind of PVKL	Temp (°C)	Ketalization Degree (mol %)														
		nPK			iPK			nBK			iBK			tBK		
Solvent		20.0	46.6	58.0	17.5	34.7	51.8	28.0	44.9	59.5	11.1	24.9	32.4 ^b	12.5	20.8	34.7
100% ROH	20	△	△	○	△	△	○	△	△	△	×	×	△	×	△	△
	60	△	△	○	△	△	○	△	○	○	△	△	△	△	△	○
80% aq ROH	20	△	△	△	△	△	×	△	△	×	△	△	△	△	△	×
	60	○	○	△	○	○	×	○	△	×	△	○	△	△	○	×
50% aq ROH	20	△	×	×	△	×	×	△	×	×	△	×	×	△	×	×
	60	○	×	×	△	×	×	△	△	×	○	△	×	○	×	×
25% aq ROH	20	△	×	×	△	×	×	△	×	×	△	×	×	△	×	×
	60	△	×	×	△	×	×	△	×	×	△	×	×	△	×	×
DMSO	20	○	○	○	○	○	○	△	○	△	○	○	△	○	○	○
	60	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
DMF	20	△	△	○	△	△	○	△	○	○	△	△	△	△	△	○
	60	○	○	○	○	○	○	○	○	○	△	△	○	△	○	○
THF	20	×	×	△	×	×	△	△	△	△	×	×	△	×	×	△
	60	×	×	△	×	×	△	△	△	△	×	×	△	×	×	△
Dioxane	20	×	△	△	×	△	△	×	△	△	×	×	△	×	×	△
	60	×	△	△	×	△	△	△	△	△	×	×	△	×	×	△

^a ROH = alcohol, ○ = soluble, △ = swelling, × = insoluble.

^b PVKL (iBK) ketalization degree 32.4% dissolved in 90% aq ROH at 60°C.

Effect of Acidity on Hydrolysis of PVKL

The relationship between the time needed for the complete dissolution of PVKL film and pH value of water was examined.

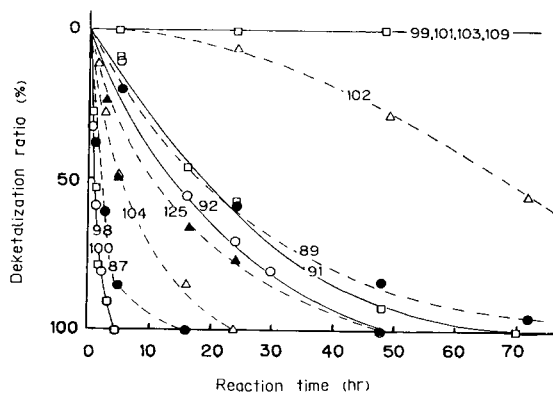


Figure 2 Hydrolysis of various PVKLs in water of pH 3.00 at 37°C: (□) nPK: no. 98 (20.0 mol %); no. 91 (46.6 mol %); no. 99 (58.0 mol %); (○) iPK: no. 100 (17.5 mol %); no. 92 (34.7 mol %); no. 101 (51.8 mol %); (△) nBK: no. 104 (28.0 mol %); no. 102 (44.9 mol %); no. 103 (59.5 mol %); (●) iBK: no. 87 (24.9 mol %); no. 89 (32.4 mol %); (▲) tBK: no. 125 (20.8 mol %); no. 109 (34.7 mol %).

Case of PVKL (Propyl Ketones)

The results of PVKL of propyl ketones are listed in Table V. In Figure 5, in accordance with results in Table V, the logarithm of dissolution time is plotted against pH values, as reported previously.^{2,3} For all samples, linear lines of the gradient = 1 are obtained except no. 148 (5.0 mol %) and can be expressed as

$$\log t = \text{pH} + \text{const} \quad (3)$$

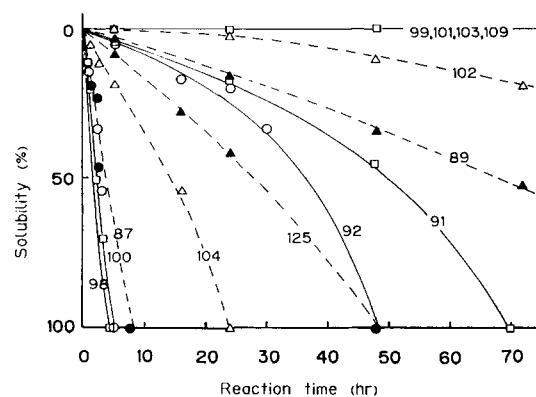


Figure 3 Solubility of various PVKLs in water of pH 3.00 at 37°C: (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.

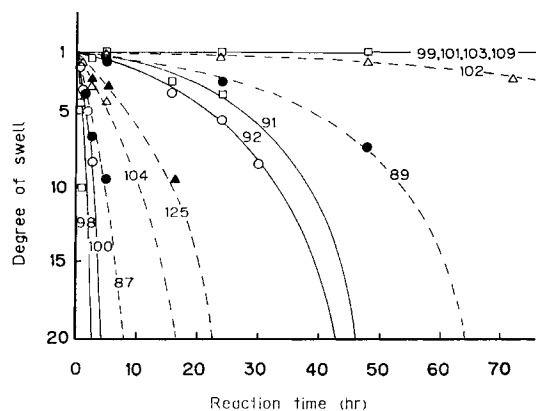


Figure 4 Degree of swell of various PVKLs in water of pH 3.00 at 37°C: (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.

These linearities indicate that the deketalization reaction rate is proportional to hydrogen ion concentration $[H^+]$, in a manner similar to that of acetone.

However, the data for no. 148 (5.0 mol %) cannot be expressed in eq. (3). As reported previously,³ PVKL (nPK) of ketalization degree of less than ca. 5 mol % dissolves in water at higher than pH 5.00 at 37°C without any hydrolysis.

But the samples no. 114 (11.0 mol %) and no. 98

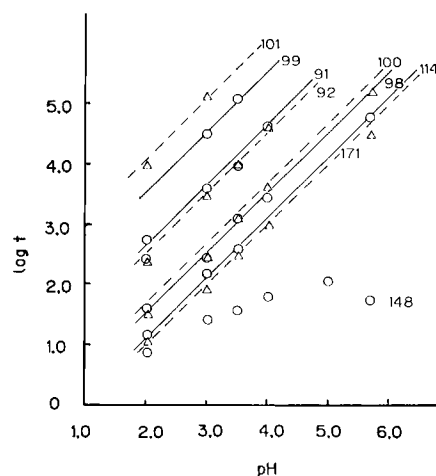


Figure 5 Dependency of hydrolysis rate in case of PVKL (propyl ketones) on various pH at 37°C: (—○) nPK: no. 148 (5.0 mol %); no. 114 (11.0 mol %); no. 98 (20.0 mol %); no. 91 (46.6 mol %); no. 99 (58.0 mol %); (---△) iPK: no. 171 (6.7 mol %); no. 100 (17.5 mol %); no. 92 (34.7 mol %); no. 101 (51.8 mol %).

(20.0 mol %) dissolve in neutral water with complete hydrolysis, within experimental error. This phenomenon is not similar as those found with acetone and MEK.^{2,3} To confirm the reason, the sample no. 148 (5.0 mol %) was dissolved in water of pH 5.70

Table V Relation between Complete Dissolution Time and pH with Various PVKLs (Propylketones) at 37°C^a

Kind of PVKL	Sample	pH	pH					
			2.00	3.00	3.50	4.00	5.00	5.70
nPK	No. 148 5.0%	<i>t</i>	8.0	25.6	41.5	68.0	116.5	60.0
		<i>x</i>	4.7	5.2	5.3	3.9	0.5	0
	No. 114 11.0%	<i>t</i>	14.7	145.6	402			54,750
		<i>x</i>	12.0	11.1	12.4			8.6
	No. 98 20.0%	<i>t</i>	39.3	279	1313	2813		54,888
		<i>x</i>	19.1	16.5	19.1	22.3		17.8
	No. 91 46.6%	<i>t</i>	249	4195	9854	48,832		
		<i>x</i>	47.3	42.3	42.5	44.3	○	○
		<i>t</i>	578	35,933	129,267		○	△
No. 99 58.0%	<i>x</i>	60.5	58.7	59.8				
	<i>t</i>	11.3	76.1	315	1020		31,830	
	<i>x</i>	6.5	6.3	6.6	5.7		6.0	
iPK	No. 100 17.5%	<i>t</i>	32.5	279.5	1402	4234		150,000
		<i>x</i>	19.8	19.8	18.0	18.5		17.7
	No. 92 34.7%	<i>t</i>	224.8	2878	9694	47,617		
		<i>x</i>	33.6	35.1	33.5	36.6	○	○
	No. 101 51.8%	<i>t</i>	10,137	140,996			△	△
<i>x</i>	52.5	52.1						

^a *t* = dissolution time (min); *x* = deketalization degree (mol %); ○ = no complete dissolution; △ = insoluble.

Table VI After Dissolution of PVKL (5.0 mol %), Deketalization Reaction in Water of pH 5.70 at 37°C

Reaction Time (h)	0	48	240	480	648
Deketalization degree (mol %)	0	0.3	2.5	4.5	5.1
Deketalization rate (%)	0	6	50	90	100

at 37°C; then the deketalization degree was determined after long time, results of which are listed in Table VI.

It is made clear that deketalization reaction of PVKL (nPK) is proceeding in neutral water and after 500–600 h is hydrolyzed completely. Since it took a long time (500–2500 h) to dissolve the samples no. 114 and no. 98 in neutral water, these polymers are hydrolyzed completely.

On the contrary, in the case of PVKL (iPK), the deketalization reaction of all samples proceeds completely, and the film is soluble in water. It can be understood to take a longer time for water to penetrate into film of PVKL (iPK) than that from PVKL (nPK), since iPK has more hydrophobicity than nPK.

Case of PVKL (Butyl Ketones)

The results of PVKL of butyl ketones are listed in Table VII and Figure 6. For all samples except high ketalization degree linear lines of the gradient = 1 are obtained and can be expressed as eq. (3) in a manner similar to those of acetone, MEK, and propyl ketones. PVKL (butyl ketones) are hydrolyzed completely and thus soluble in water. It can be understood that this is the same phenomenon as the case of PVKL (propyl ketones), since butyl ketones have more hydrophobicity than nPK.

For the similar reason, the samples no. 103 PVKL (nBK) (59.5 mol %) and no. 89 PVKL (iBK) (32.4 mol %) are not dissolved completely in water of pH 4.00 and no. 109 PVKL (tBK) (34.7 mol %)

Table VII Relation between Complete Dissolution Time and pH with Various PVKL (Butyl Ketones) at 37°C^a

Kind of PVKL	Sample	pH	pH					
			2.00	3.00	3.50	4.00	5.00	5.70
nBK	No. 177	<i>t</i>	24.0	116.8	331.1	982	12,840	57,240
	5.8%	<i>x</i>	6.2	5.6	5.1	5.7	5.8	5.7
	No. 104	<i>t</i>	160	1420	4234	18,000	○	○
	28.0%	<i>x</i>	30.5	25.3	28.8	27.2	○	○
	No. 102	<i>t</i>	1380	11,059	50,446	○	○	△
	44.9%	<i>x</i>	45.3	46.7	49.1	○	○	○
iBK	No. 103	<i>t</i>	34,523	○	○	○	○	△
	59.5%	<i>x</i>	64.3	○	○	○	○	○
	No. 88	<i>t</i>	22.6	92.3	430	1,020	○	29,060
	11.1%	<i>x</i>	11.0	9.6	10.0	8.2	○	9.1
tBK	No. 87	<i>t</i>	138.8	1411	4234	12,590	○	○
	24.9%	<i>x</i>	22.7	25.6	23.6	24.4	○	○
	No. 89	<i>t</i>	1283	5447	30,306	○	○	△
	32.4%	<i>x</i>	31.5	34.1	33.1	○	○	○
tBK	No. 108	<i>t</i>	19.3	350	112	230	3160	18,000
	4.9%	<i>x</i>	4.9	5.1	3.7	4.8	5.1	4.2
	No. 107	<i>t</i>	85.7	1363	4010	24,327	○	○
	12.5%	<i>x</i>	11.8	12.3	11.3	12.8	○	○
	No. 125	<i>t</i>	209.1	6900	14,488	○	○	△
	20.8%	<i>x</i>	19.1	20.1	17.9	○	○	○
	No. 109	<i>t</i>	○	○	○	○	△	△
34.7%	<i>x</i>	○	○	○	○	○	○	

^a *t* = dissolution time (min); ○ = no complete dissolution; *x* = deketalization degree (mol %); △ = insoluble.

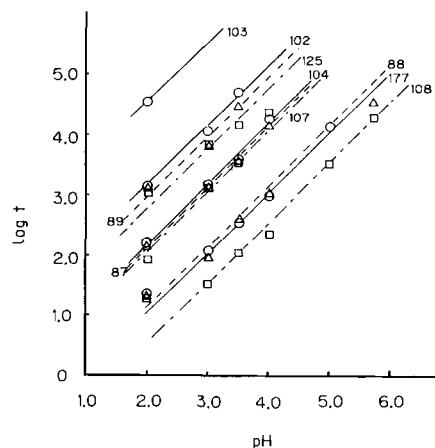


Figure 6 Dependency of hydrolysis rate in case of PVKL (butyl ketones) on various pH at 37°C: (—○) nBK: no. 177 (5.8 mol %); no. 104 (28.0 mol %); no. 102 (44.9 mol %); no. 103 (59.5 mol %); (---△) iBK: no. 88 (11.1 mol %); no. 87 (24.9 mol %); no. 89 (32.4 mol %); (—□) tBK: no. 108 (4.9 mol %); no. 107 (12.5 mol %); no. 125 (20.8 mol %).

is not dissolved completely in water of any pH values.

Difference of Hydrolysis of Various PVKLs

In order to confirm the difference of hydrolysis of various PVKL films, the logarithm of dissolution time, $\log t$, (apparent hydrolysis rate constant) at pH 2.00 is plotted against the ketalization degree of various PVKLs as shown in Figure 7. For each PVKL, linear lines of gradient = α were obtained, which can be expressed as

$$\log t = \alpha X + \text{const} \quad (4)$$

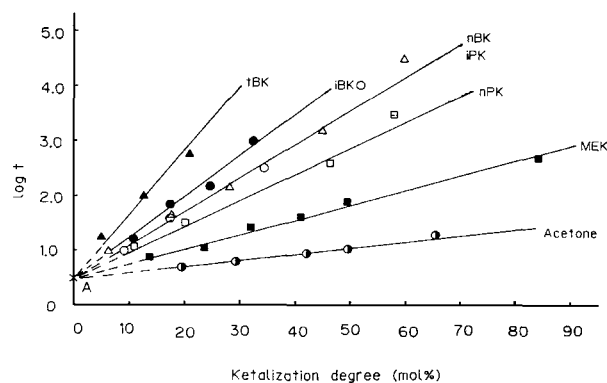


Figure 7 Reaction between hydrolysis rate and ketalization degree with various PVKL at pH 2.00 and 37°C: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.

where X = ketalization degree, α = hydrophobicity factor, and const = logarithm of dissolution time of ideal complete amorphous PVA. These linearities indicate that the deketalization reaction rate is proportional to hydrophobicity of ketones; α seems to represent hydrophobicity factor of ketones. All linear lines come across each other to point A and this point indicates the logarithm of dissolution time of ideal complete amorphous PVA film. The α values are listed in Table VIII. As listed in Figure 7 and Table VIII, it is made clear that the hydrolysis of PVKL film proceeds in the order as follows:

acetone > MEK > nPK > iPK

≡ nBK > iBK > tBK

In general, the stronger the electroreleasing substituent of ketone and aldehyde, the easier the hydrolysis of ketal and acetal in homogeneous state proceeds.^{4,5} On the contrary, in a heterogeneous reaction such as deketalization of the film, it can be understood to take a long time for water to penetrate into film due to hydrophobicity of the film surface, which depends upon the kind of ketones. The hydrolysis reaction of the film proceeds slowly.

The hydrophobicity of hydrocarbon is evaluated in terms of transfer of hydrocarbon molecules from water to a purely hydrocarbon solvent.⁶ In Figure 8, in accordance with the results in Table VIII, hydrophobicity factor α is plotted against $\mu_{\text{HC}} - \mu_{\text{W}}$ (difference between the free energy of interactions with the solvent for the corresponding alkanes).⁶ How-

ever, as values for $\begin{array}{c} | \\ -\text{CH}- \\ | \end{array}$ and $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$ are not

described in the literature, then in the case of iPK, iBK, and tBK the value for $-\text{CH}_2-$ were used

instead of the values for $\begin{array}{c} | \\ -\text{CH}- \\ | \end{array}$ and $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$.

Hence, the values for iPK, iBK, and tBK may be slightly larger than the true values. For all samples a linear line was obtained. This linearity indicates that α values are proportional to hydrophobicity of ketones.

On the other hand, the solubility parameter seems to indicate hydrophobicity of ketones. Since a solubility parameter is defined as (cohesive coagulation energy/mol)^{1/2}, a small solubility parameter indicates a small molecular interaction force. Therefore, a small solubility parameter indicates nonpolar. The values of solubility parameter of various ketones are calculated,⁷ and, in Figure 9, hydrophobicity factor

Table VIII α Value of Various PVKL

Ketone	Acetone	MEK	nPK	iPK	nBK	iBK	tBK
$\alpha \times 10^2$	1.1	2.6	4.7	6.2	6.2	7.5	11.7

is plotted against solubility parameter. As was expected, for all samples a linear line was obtained. It is made clear that α values are proportional to hydrophobicity of ketones.

CONCLUSION

Ketalization reaction of PVA by aliphatic ketones—acetone,^{1,3} MEK,² nPK, iPK, nBK, iBK, and tBK—were carried out and the reaction of polyvinylketal in water was carried out. These conclusions are as follows.

- (1) This reaction proceeds in bimolecular reaction, the equilibrium constant K is roughly 10^{-5} less compared with the acetalization reaction between PVA and aldehydes, synthesis in aqueous media is difficult.
- (2) The values of K are ca. 0.07 for acetone, MEK, nPK, and nBK, ca. 0.05 for iPK, and ca. 0.01 for iBK and tBK at 40°C. Steric hindrance of bulky side chain of ketones seems to affect the equilibrium.
- (3) Maximum ketalization degree of PVKL of ca. 70 mol % for acetone, ca. 60 mol % for

nPK and nBK, ca. 50 mol % for iPK, and ca. 35 mol % for iBK and tBK can be explained from the similar reason. But the reason of a little higher value of ca. 80 mol % for MEK is not clear.

- (4) The heat of reaction for all cases is 7.5 kcal/mol including acetalization reaction, and all reactions are considered to proceed in an identical reaction mechanism.
- (5) The reaction of the PVKL film with water, in acidic side, as deketalization reaction proceeds, the film dissolves in water. Dissolution time is controlled by both ketalization degree and pH of water which reveals that deketalization reaction proceeds proportional to proton concentration.
- (6) In all PVKLs, the following relation was obtained between ketalization degree and logarithm of dissolution time ($\log t$). The parameter α is considered to indicate hydrophobicity of ketones:

$$\log t = \alpha X + \text{const}$$

It is difficult for water to penetrate into the film due to the hydrophobicity of the film surface, which depends upon the kind of ke-

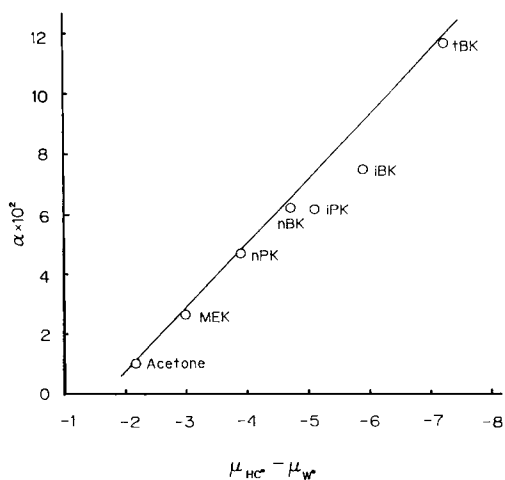


Figure 8 Relation between hydrophobicity factor α and difference between the free energy of interaction with the solvent for the corresponding alkanes.

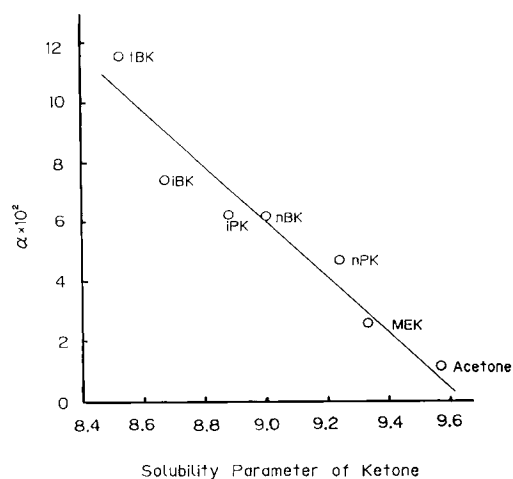
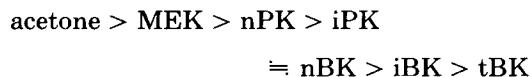


Figure 9 Relation between hydrophobicity factor α and solubility parameter of ketones.

tones. The deketalization reaction of PVKL film proceeds in the order as follows



- (7) On the other hand, the PVKL (acetone) of ketalization degree 5–20 mol %, PVKL (MEK) 3–15 mol %, and PVKL (nPK) ca. 5 mol % dissolve in neutral water at 37°C, without any hydrolysis.

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