

# Study of Ketalization Reaction of Poly(vinyl alcohol) by Ketones. VI. Reaction Between Poly(vinyl alcohol) and Cyclic Ketones and Behavior of Poly(vinyl ketal) in Water

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## SYNOPSIS

The ketalization reaction of poly(vinyl alcohol) (PVAL) by cyclic ketones, with dimethyl sulfoxide (DMSO) as solvent, in the presence of an acidic catalyst in homogeneous system, was carried out. The synthesis of poly(vinyl ketals) was thus successfully performed, except for the case of poly(vinyl ketal) highly ketalized by cyclohexanone; these poly(vinyl ketals) with a ketalization degree of more than 60 mol % were insoluble in DMSO, and, thus, the reaction could not be carried out in a homogeneous system. The equilibrium constant at 40°C was ca. 0.50 in the case of cyclohexanone and ca. 0.35 in the case of cyclopentanone, some 10–50 times higher compared with the case of aliphatic ketones. Because the heat of reaction is 7.5 kcal/mol in all ketones, all ketalization reactions are considered to proceed by the same reaction mechanism. Films prepared from the poly(vinyl ketals) were soaked in water, and hydrolysis, degree of swell, and solubility were measured. The dissolution time of films is affected by the kind of the ketones, ketalization degree, and the pH of water, which reveals that deketalization reaction proceeds proportionally to the proton concentration. It is more difficult to dissolve poly(vinyl ketal) obtained by cyclohexanone than that by cyclopentanone. The rate of hydrolysis of poly(vinyl ketal) film obtained by cyclohexanone is nearly equal to that by methyl butyl ketone, and that by cyclopentanone is nearly equal to that by methyl propyl ketone. The contact angle, surface free energy, moisture regain, and water permeability of poly(vinyl ketal) films were measured. All the results show that poly(vinyl ketal) obtained from cyclohexanone is a more hydrophobic polymer than that from cyclopentanone. The hydrophobicity seems to depend upon the kind of the original ketones and the flexibility of the ring. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

As described in the previous reports,<sup>1–3</sup> poly(vinyl ketals) (PVKL) with any ketalization degree can be successfully obtained from poly(vinyl alcohol) (PVAL) and aliphatic ketones in a homogeneous system. The values of the equilibrium constant of ketalization ( $K$ ) at 40°C are ca. 0.07 for acetone, methyl ethyl ketone (MEK), methyl *n*-propyl ketone (*n*PK), and methyl *n*-butyl ketone (*n*BK), ca. 0.05 for methyl *i*-propyl ketone (*i*PK), and ca. 0.01 for methyl *i*-butyl ketone (*i*BK) and methyl *t*-butyl ketone (*t*BK). Steric hindrance by a bulky side chain of ketones seems to affect the equilibrium.

Maximum ketalization degrees of PVKL were ca. 70 mol % for acetone, ca. 60 mol % for *n*PK and *n*BK, ca. 50 mol % for *i*PK, and ca. 35 mol % for *i*BK and *t*BK. The heat of reaction for all cases is 7.5 kcal/mol including the acetalization reaction, and all reactions are considered to proceed by an identical reaction mechanism. It becomes clear that PVKL films are deketalized easily and dissolved in acidic water,<sup>4</sup> and the hydrolysis of PVKL films proceeds in the following order:

acetone > MEK > *n*PK > *i*PK

≡ *n*BK > *i*BK > *t*BK

This order seems to be affected by the hydrophobicity of the film surface, which depends upon the

kind of the original ketones.<sup>3</sup> The hydrophobicity of the film surface was made clear by measurements of the contact angle, the moisture regain, and the water vapor permeability.<sup>5</sup>

On the other hand, reports on ketalization by cyclic ketones are not known outside of an old patent by I.G. Farben AG<sup>6</sup> and by Noma and Kou,<sup>7</sup> reporting successful results with only cyclohexanone. However, in such methods, maintaining the reaction system from the beginning to the end in a homogeneous system is difficult; therefore, neither a kinetic study nor a study of the physical properties of the PVKL was made.

This paper is concerned with the acid-catalyzed synthesis of PVKL from cyclic ketones, such as cyclohexanone (Hex) and cyclopentanone (Pent) in a homogeneous system. The values of  $K$  and solubilities in various solvents for the PVKLs were determined. To confirm the difference between these cyclic ketones, studies of the degree of swell, solubility, and deketalization degree with PVKL films soaked in water of several pH values were made, and the contact angle, moisture regain, and the water-vapor permeability were studied. Also, these behaviors were compared with those of PVKL from aliphatic ketones.

## EXPERIMENTAL

### Samples and Reagents

PVAL of an average degree of polymerization, 1800, saponification degree above 99.4% (NH-18 from Nihon Gohsei Co.) was used. DMSO (water content 0.05%), *p*-toluene sulfonic acid (PTS), and guaranteed reagent (Nacalai Tesque Inc.) were used without further purification. Cyclohexanone (Hex) and cyclopentanone (Pent) (guaranteed reagent, Nacalai Tesque Inc.) were dried over anhydrous sodium sulfate and distilled before use.

### Synthesis Method

PVAL 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 the beginning to the end proceeds in homogeneous system, except when a large amount of Hex is used. Prescribed hours later, the reaction mixture was neutralized by 1*N* aqueous NaOH and then the reaction

product was precipitated with ethyl acetate. The polymer thus obtained was purified by extraction with ethyl acetate for 4 days, using a Soxhlet extractor.

### Analysis Method

The ketalization degree of PVKL was determined by dissolving the sample in *N*/10 aqueous HCl at 60°C, which was accompanied by complete hydrolysis. The cyclic ketone thus obtained was quantitatively determined by steam gas chromatography using an Ohkurariken SSC-1. In the case of Hex, the following conditions were used: injection temperature 180°C, column temperature 150°C, steam speed 10  $\mu$ L/min, column composition A-1-3 (chromosorb P-AW), and *n*-butyl alcohol as internal standard. The conditions of Pent were as follows: column composition F-0 (Tenax GC), dioxane as internal standard, and the other conditions the same as those for Hex.

### Solubility in Organic Solvents

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

### Film Preparation Method

To obtain transparent film, PVKL dissolved in 50% aqueous ethanol or DMF (5 wt %) was gradually allowed to dry on a glass plate at room temperature (refer to Table II).<sup>4</sup>

### Behavior of PVKL in Water

Samples were soaked in water of various pH's kept at the prescribed temperature. A prescribed number of hours later, the film was removed from the water and the degree of swell, solubility, deketalization degree, and the time needed for complete dissolution of the film were measured according to the method previously described.<sup>4</sup>

### Measurement of Contact Angle

As previously reported,<sup>5</sup> the contact angle by water and methylene iodide (MI) were measured by the droplet method. From these data, surface free energy  $\gamma_s$  (hydrophobic component:  $\gamma_s^d$ ; hydrophilic component:  $\gamma_s^p$ ) were calculated.

### Measurement of Moisture Regain

As previously reported,<sup>5</sup> after hanging the film at 25°C in a desiccator with relative humidity (RH) of 100%, moisture regain was measured.

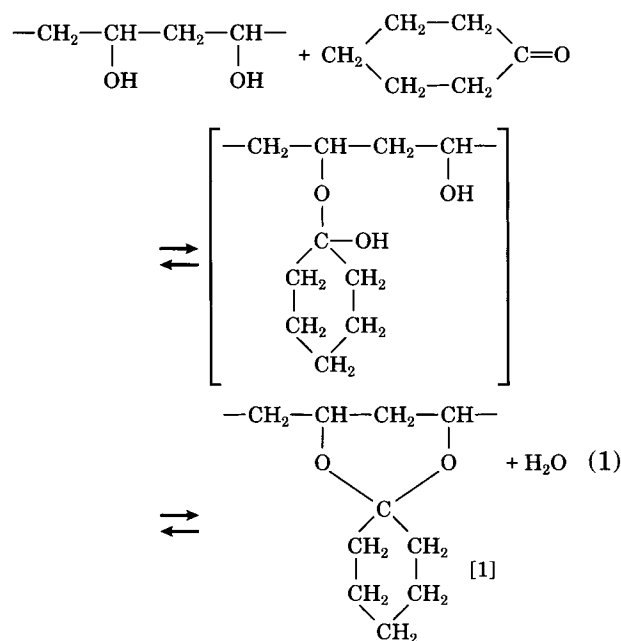
### Measurement of Water Vapor Permeability

As previously reported,<sup>5</sup> the film was put on the top of a glass vessel and this vessel was kept in a desiccator at RH 100% and 25°C; then, the timewise variation of weight was measured. From these data, water vapor permeability was calculated.

## RESULTS AND DISCUSSION

### Mechanism of Ketalization Reaction between PVAL and Ketones

The reaction between PVAL and Hex proceeds as follows:



A similar reaction takes place for Pent. The ketalization reaction between PVAL and ketones was carried out in a homogeneous system in DMSO. The ketalization reaction proceeded rather rapidly, and it was found that in 24 h equilibrium was reached. The reactions were further carried out for an additional 24 h, reaction equilibrium was confirmed, and the equilibrium ketalization degrees were determined. When Hex concentration was three times more than the ketone equivalent, the reaction could not be carried out in a homogeneous system and

**Table I** Equilibrium Constants of Ketalization Reaction by Cyclic Ketones<sup>a</sup>

Temp (°C)	Ketone	Ketone Equivalent	Ketalization <sup>b</sup> Degree (mol %)	K
40	Hex	0.06	5.4	0.51
40	Hex	0.12	9.8	0.48
40	Hex	0.25	17.2	0.46
40	Hex	0.50	28.5	0.53
40	Hex	1.00	41.4	0.50
40	Hex	1.50	50.0	0.50
40	Hex	3.00	59.9 <sup>c</sup>	(0.37)
40	Hex	6.00	70.7 <sup>c</sup>	(0.32)
40	Pent	0.25	16.3	0.36
40	Pent	0.50	25.4	0.35
40	Pent	1.00	35.9	0.31
40	Pent	1.50	45.1	0.35
40	Pent	3.00	56.3	0.30
40	Pent	6.00	56.9	(0.14)
40	Pent	12.00	61.5	(0.08)
30	Hex	1.50	55.6	0.74
30	Pent	1.00	40.6	0.47
50	Hex	1.50	44.6	0.34
50	Pent	1.00	32.5	0.23

<sup>a</sup> PVAL initial concentration 0.35–0.6 mol/L; PTS concentration = 2.5 g/L.

<sup>b</sup> Equilibrium ketalization degree.

<sup>c</sup> Precipitation during reaction.

PVKL was precipitated during the ketalization reaction. This depends upon the solubility of PVKL (Hex) in organic solvents (refer to Table II). From the values, in accordance with eq. (2), equilibrium constant  $K$  was calculated (results obtained are listed in Table I):

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

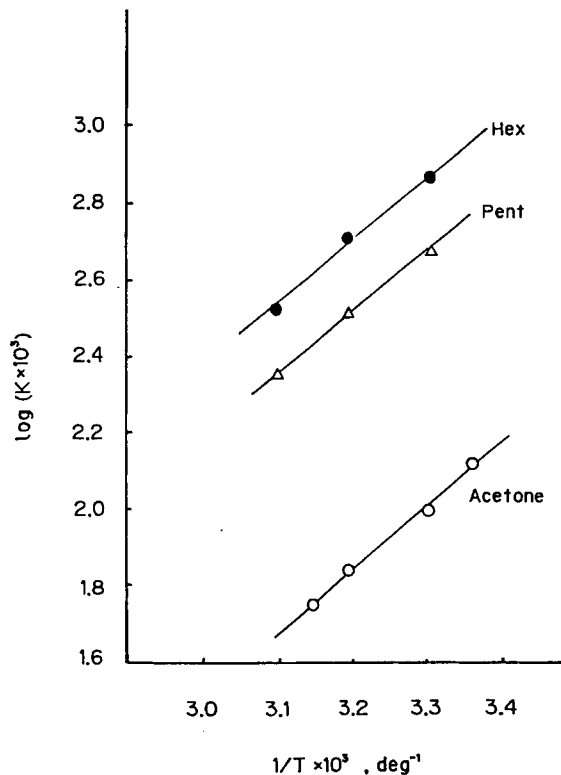
where  $a$  (mol/L) = PVAL initial concentration (value obtained against 2 basic PVAL mol),  $b$  (mol/L) = ketone initial concentration,  $x$  (mol/L) = PVKL concentration,  $X = x/a$  = ketalization degree, and  $E = b/a$  = ketone equivalent (mol ratio ketone against 2 basic PVAL mol).

The value of  $K$  for Hex is ca. 0.50 at 40°C, except for highly ketalized PVKL (ketalization degree more than 60 mol %). This value is higher than the values for aliphatic ketones 0.01–0.07.<sup>3</sup> Since the ring of Hex is flexible, it seems not to interfere with the ketalization. The value of  $K$  for Pent is ca. 0.35,

which is a little lower than that for Hex, perhaps due to the interference of the rigid ring with the ketalization reaction.

To confirm this explanation, a ketalization reaction by Pent was carried out at 25°C with a ketone equivalent of 36.00 for 100 h, and PVKL with the ketalization degree of 65.4 mol % was obtained. This value is the maximum ketalization degree for Pent and is lower than the reported value for Hex attainable as the maximum ketalization degree (ca. 80 mol %).<sup>7</sup> This result shows the effect of ring flexibility as described above.

Clearly, the values of  $K$  for cyclic ketones are roughly 10–50 times higher than for aliphatic ketones. This shows that the ketalization reaction proceeds in the presence of a small amount of water. In fact, Känzlein revealed that the ketalization reaction with Hex proceeded smoothly in the presence of water.<sup>6</sup> He did not measure the ketalization degree of the PVKL (Hex), but the value is assumed to be a few mol % due to the solubility in organic solvents. Figure 1 shows the temperature dependence of the equilibrium constant. The heat of reaction determined from the slope of line is 7.5 kcal/mol, which is same as that of aliphatic ketones or various al-



**Figure 1** Temperature dependency of equilibrium constant,  $K$ : (●) Hex; (△) Pent; (○) acetone.

dehydes. It can be assumed that the ketalization reaction of cyclic ketones proceeds by an identical mechanism with the ketalization reaction of aliphatic ketones and acetalization reactions of various aldehydes.<sup>1</sup>

Based on <sup>1</sup>H- and <sup>13</sup>C-NMR measurement, as previously described,<sup>1</sup> 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 II. The solubilities of PVKL (cyclic ketones) were different from those of PVKL (aliphatic ketones), and there are some differences between PVKL (Hex) and PVKL (Pent), as is clear in Table II:

1. Methanol and ethanol gave identical results; therefore, these will be expressed as alcohol in the following. PVKL (cyclic ketones) of ketalization degree above 5 mol % dissolved in 25% alcohol; above 10 mol %, in 50% alcohol; and of 30–40 mol %, in 80% alcohol. This behavior is nearly equal to that of PVKL (aliphatic ketones).
2. But when the ketalization degree is above 40 mol %, PVKL (Hex) did not dissolve in 100% alcohol, while PVKL (Pent) dissolved in 100% alcohol.
3. PVKL (cyclic ketones) of ketalization degree above 50 mol % did not dissolve in 100% alcohol. There is a difference between PVKL (cyclic ketones) and PVKL (aliphatic ketones). In THF and dioxane, PVKL (Hex) dissolved, while PVKL (Pent) did not dissolve.
4. PVKL (Pent) of ketalization degree above 60 mol % dissolved also in THF and dioxane. PVKL (Hex) dissolved in benzene and methylene chloride, while PVKL (Pent) did not dissolve.
5. The largest difference in solubility between PVKL (Hex) and PVKL (Pent) is as follows: PVKL (Hex) of ketalization degree above 60 mol % did not dissolve in DMSO and precipitated during the ketalization reaction. But the PVKL (Hex) of ketalization degree above 70 mol % dissolved in Hex; thus, the reaction mixture becomes homogeneous at the end of the reaction when a large amount of Hex is used.<sup>7</sup>
6. In nonpolar solvents such as acetone, ether, ethyl acetate, etc., all samples are insoluble.

**Table II Solubilities of Various PVKLs**

Solvent	Temp (°C)	Kind of PVKL														
		Hex							Pent							
		Ketalization Degree (mol %)														
		5.4	9.8	17.2	28.5	41.1	50.0	59.9	70.7	16.3	25.4	35.9	45.1	51.5	56.9	61.5
100% ROH	20	×	×	×	△	△	△	△	×	△	△	△	△	△	△	△
	60	×	×	△	△	△	△	△	×	△	△	△	○	△	△	△
80% ROH	20	△	△	△	△	△	×	×	×	△	△	△	△	△	△	△
	60	△	○	○	○	△	×	×	×	○	○	○	○	△	△	△
50% ROH	20	△	△	△	×	×	×	×	×	△	×	×	×	×	×	×
	60	○	○	△	△	×	×	×	×	○	△	×	×	×	×	×
25% ROH	20	△	△	△	×	×	×	×	×	△	×	×	×	×	×	×
	60	○	△	△	×	×	×	×	×	△	×	×	×	×	×	×
DMSO	20	○	○	○	○	○	○	△	×	○	○	○	○	○	○	○
	60	○	○	○	○	○	○	△	△	○	○	○	○	○	○	○
DMF	20	△	△	△	△	○	○	○	△	△	△	○	○	○	○	○
	60	△	△	○	○	○	○	○	○	○	○	○	○	○	○	○
THF	20	×	×	×	×	△	○	○	○	×	×	×	×	△	△	△
	60	×	×	×	△	△	○	○	○	×	×	×	△	△	△	○
Dioxane	20	×	×	×	×	△	△	○	○	×	×	×	×	×	△	△
	60	×	×	×	△	△	○	○	○	×	×	×	△	△	△	○
Benzene	20	×	×	×	×	×	△	△	○	×	×	×	×	×	△	△
	60	×	×	×	△	△	△	○	○	×	×	×	×	×	△	△
Methylene chloride	20	×	×	×	×	△	△	○	○	×	×	×	△	△	△	△

ROH, alcohol; ○, soluble; △, swelling; ×, insoluble.

### Effect of Acidity on Hydrolysis of PVKL

The relationship between the time needed for the complete dissolution of PVKL film due to hydrolysis and pH value of water was examined. The results of PVKL (Hex) are listed in Table III and those of PVKL (Pent) are listed in Table IV.

In Figures 2 and 3, in accordance with the results in Tables III and IV, respectively, the logarithm of dissolution time is plotted against pH values, as reported previously.<sup>2-4</sup>

For all samples, linear lines of the slope = 1 are obtained and can be expressed as

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

These linearities indicate that the deketalization reaction rate is proportional to hydrogen ion concentration  $[\text{H}^+]$ , in a manner similar to that of aliphatic ketones. The deketalization reaction of PVKL (Pent) proceeds more easily than that of PVKL (Hex), and PVKL (Hex) of ketalization degree 70.7 mol % are not hydrolyzed in water of pH

**Table III Relation between Complete Dissolution Time and pH with Various PVKLs (Hex) at 37°C**

Sample		pH			
		2	3	3.5	4
5.4	<i>t</i>	19.8	72.0	365.0	985.0
	X	5.4	5.6	5.4	5.3
9.8	<i>t</i>	45.2	364.0	986.0	5,820.0
	X	9.8	10.3	10.4	10.4
17.2	<i>t</i>	139.3	1,424.0	7,435.0	18,715.0
	X	17.1	17.8	17.5	16.4
28.5	<i>t</i>	1,339.0	11,347.0	51,740.0	○
	X	28.2	32.3	33.0	
41.4	<i>t</i>	7,140.0	129,780.0	○	
	X	41.9	43.7		
50.0	<i>t</i>	138,420.0	△		
	X	46.9			
70.7	<i>t</i>	△			
	X				

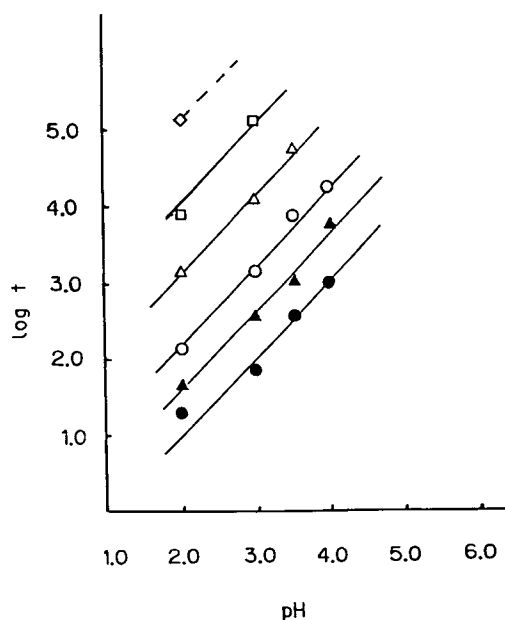
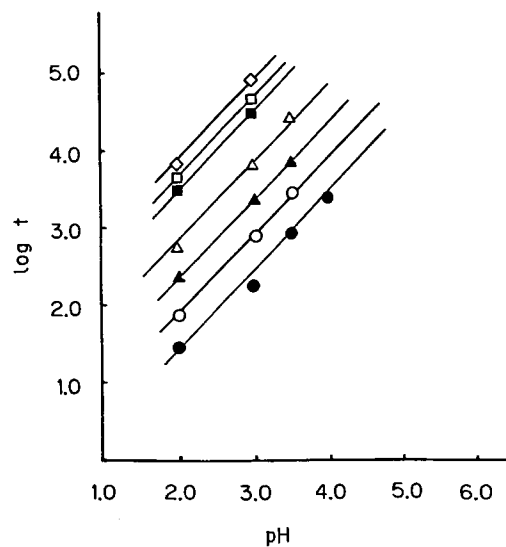
*t*, dissolution time (min); X, deketalization degree (mol %); ○, no complete dissolution; △, insoluble.

**Table IV** Relation between Complete Dissolution Time and pH with Various PVKLs (Pent) at 37°C

Sample		pH			
		2	3	3.5	4
16.3	<i>t</i>	28.5	166.0	960.0	2540.0
	<i>X</i>	15.3	18.0	16.5	14.1
25.4	<i>t</i>	75.3	780.0	2,950.0	
	<i>X</i>	28.3	28.6	27.8	
35.9	<i>t</i>	240.0	2,400.0	6,750.0	
	<i>X</i>	34.4	35.7	37.6	
45.1	<i>t</i>	562.0	6780.0	25,980.0	○
	<i>X</i>	45.3	45.7	44.9	
51.5	<i>t</i>	3010.0	31,920.0	○	
	<i>X</i>	52.0	51.1		
56.9	<i>t</i>	4320.0	48,810.0	○	
	<i>X</i>	59.9	58.7		
61.5	<i>t</i>	6840.0	85,140.0	○	
	<i>X</i>	63.8	62.6		

*t*, dissolution time (min); *X*, deketalization degree (mol %); ○, no complete dissolution.

2.00 even after 100 days. 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 PVKL, as shown in Figure 4.

**Figure 2** Dependency of hydrolysis rate in the case of PVKL (Hex) on various pH at 37°C: (●) 5.4 mol %; (▲) 9.8 mol %; (○) 17.2 mol %; (△) 28.5 mol %; (□) 41.4 mol %; (◇) 50.0 mol %.**Figure 3** Dependency of hydrolysis rate in the case of PVKL (Pent) on various pH at 37°C: (●) 16.3 mol %; (○) 25.4 mol %; (▲) 35.9 mol %; (△) 45.1 mol %; (■) 51.5 mol %; (□) 56.7 mol %; (◇) 61.5 mol %.

For each PVKL, linear lines of slope =  $\alpha$  were obtained, which can be expressed as

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

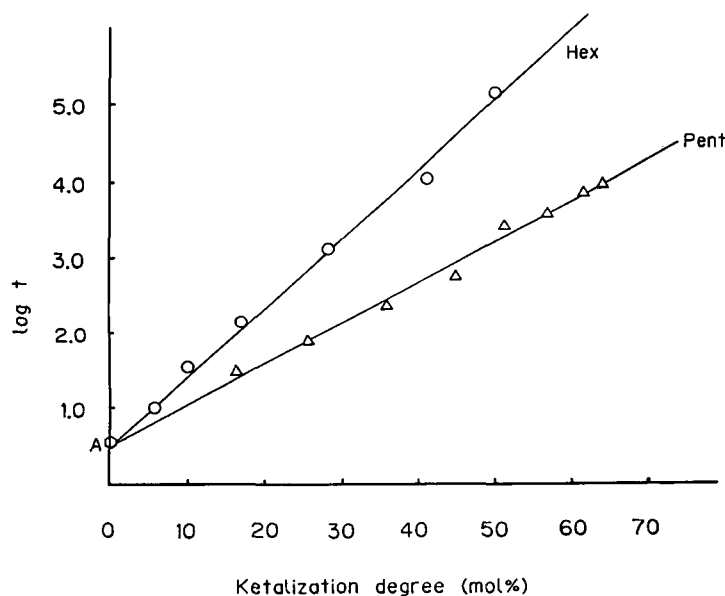
where  $X$  = ketalization degree,  $\alpha$  = hydrophobicity factor, and const = logarithm of dissolution time of ideal complete amorphous PVAL. These linearities indicate that the deketalization reaction rate is proportional to hydrophobicity of ketones;  $\alpha$  seems to represent hydrophobicity of ketones. All linear lines come across each other to point A, which indicates the logarithm of dissolution time of ideal complete amorphous PVAL film. The  $\alpha$  values are listed in Table V. The hydrolysis of PVKL film proceeds in the following order:

acetone > MEK > nPK > Pent > iPK

$\cong$  nBK > iBK > Hex > tBK

As described previously,<sup>3</sup> 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.<sup>8</sup> In Figure 5, in accordance with the results in Table V, hydrophobicity factor  $\alpha$  is plotted against  $\mu_{\text{HC}}^\circ - \mu_{\text{W}}^\circ$



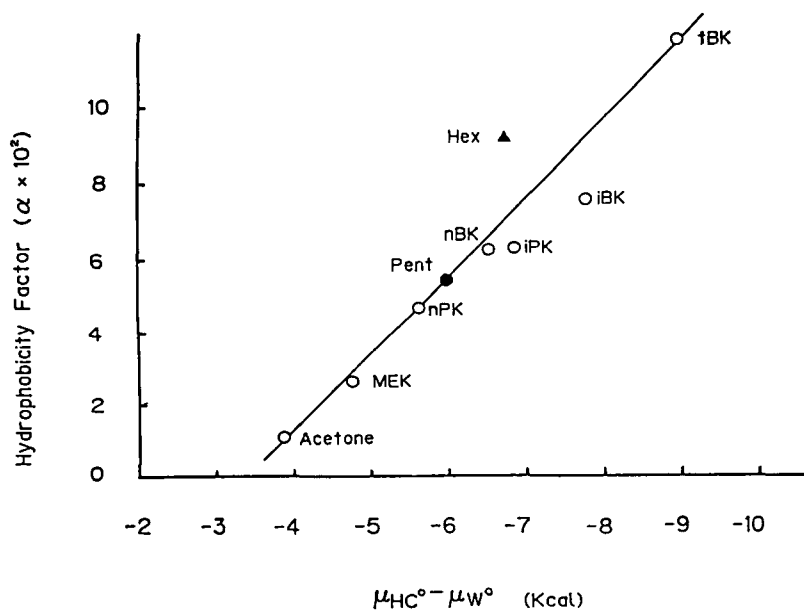
**Figure 4** Reaction between hydrolysis rate and ketalization degree at pH 2 and 37°C: (O) Hex; ( $\Delta$ ) Pent.

(difference between the free energy of interactions with the solvent for the corresponding alkanes and cyclic hydrocarbons).<sup>8</sup>

As reported previously,<sup>3</sup> the value for  $\text{CH}_3$  were neglected in all aliphatic ketones. Since there is the difference of  $-880$  cal/mol between 2,4-dimethyl pentane and 2-methyl pentane and between methyl cyclopentane and cyclopentane as reported by Tanford,<sup>8</sup>  $-880$  cal/mol can be taken as a value of  $\text{CH}_3$ .

Then, using this value,  $\mu_{\text{HC}}^\circ - \mu_{\text{W}}^\circ$  of aliphatic ketones were calculated again to compare them with cyclic ketone. The values for  $-\text{CH}_2-$  were used instead of the values for  $-\text{CH}-$  and  $-\text{C}-$ . The values  $-6730$  cal/mol and  $-6000$  cal/mol were used for Hex and Pent, respectively.<sup>8</sup>

As was expected, for all aliphatic ketones and



**Figure 5** Relation between hydrophobicity factor  $\alpha$  and difference between the free energy of interactions with the solvents for the corresponding alkanes and cyclic hydrocarbons.

**Table V**  $\alpha$  Value of Various PVKLs

Ketones	Hex	Pent	Acetone <sup>3</sup>	MEK <sup>3</sup>	nPK <sup>3</sup>	iPK <sup>3</sup>	nBK <sup>3</sup>	iBK <sup>3</sup>	tBK <sup>3</sup>
$\alpha \times 10^2$	9.0	5.4	1.1	2.6	4.7	6.2	6.2	7.5	11.7

Pent, a linear line was obtained. This linearity indicates that  $\alpha$  values are proportional to hydrophobicity of ketones. However, for Hex, a linear line was not obtained and the  $\alpha$  value was higher than that of the value expected for  $\mu\text{HC}^\circ - \mu\text{W}^\circ$ , which means that PVKL (Hex) is not hydrolyzed easily. This is well explained by taking into account that the cyclohexane ring is more flexible than the cyclopentane ring, and the ketal ring for PVKL (Hex) is protected against the attack of  $[\text{H}^+]$ .

### Behavior in Neutral Water

As reported previously,<sup>2-4</sup> PVKL are dissolved in water close to neutral with accompanying hydrolysis. To confirm this phenomenon, PVKL (cyclic ketones) were soaked in neutral water at 37 and 0°C for 100 h and deketalization degree, solubility, and degree of swell were determined. The results are listed in Table VI.

The deketalization ratio, solubility, and degree of swell decreased proportionally to the ketalization degree. But all samples did not dissolve completely within 100 h. PVKL (Hex) of ketalization degree above 40 mol % is not hydrolyzed at all at 0°C. On the contrary, all samples of PVKL (Pent) are hydrolyzed under the same conditions, and the solubility and the degree of swell are higher than those of PVKL (Hex). Clearly, the rate of the deketalization reaction in a heterogeneous system becomes high at high temperatures, while the solubility and the degree of swell are high at low temperatures. PVKL (Hex) is a more hydrophobic polymer than is PVKL (Pent).

### Contact Angle of Film Surface

The contact angle of the film surface by water ( $\theta\text{H}_2\text{O}$ ) and MI ( $\theta\text{MI}$ ) were measured. From  $\theta\text{H}_2\text{O}$  and  $\theta\text{MI}$ , surface free energy  $\gamma_s$  (hydrophobic com-

**Table VI** Behavior in Neutral Water (pH 5.7)

Kind of PVKL	Ketalization		Deketalization		Deketalization	Degree of Swell	Solubility (%)
	Degree (mol %)	Temp (°C)	Degree (mol %)	Ratio (%)			
Hex	17.2	37	5.2	30.2	3.26	11.1	
Hex	28.5	37	1.2	4.2	1.31	4.3	
Hex	41.4	37	0.0	0.0	1.13	2.6	
Hex	50.0	37	0.0	0.0	1.15	0.0	
Hex	70.7	37	0.0	0.0	1.04	0.0	
Pent	16.3	37	4.9	30.1	4.85	24.4	
Pent	25.4	37	5.4	21.3	1.95	8.5	
Pent	45.1	37	3.4	7.5	1.24	2.7	
Pent	51.5	37	3.5	6.5	1.17	0.0	
Pent	61.5	37	1.2	2.0	1.14	0.0	
Hex	17.2	0	0.0	0.0	4.62	27.6	
Hex	28.5	0	0.0	0.0	1.44	7.4	
Hex	41.4	0	0.0	0.0	1.25	3.1	
Hex	50.0	0	0.0	0.0	1.12	0.0	
Hex	70.7	0	0.0	0.0	1.07	0.0	
Pent	16.3	0	2.0	12.3	32.30	68.2	
Pent	25.4	0	2.1	8.3	4.04	15.4	
Pent	45.1	0	1.4	3.1	1.31	1.7	
Pent	51.5	0	1.3	2.5	1.19	0.0	
Pent	61.5	0	0.6	0.1	1.14	0.0	



**Table VII** Contact Angle and Surface Free Energy (erg cm<sup>-1</sup>) of Various PVKLs at 25°C

Kind of Ketone	Ketalization Degree (mol %)	$\theta$ (H <sub>2</sub> O)	$\theta$ (MI)	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$
PVAL	0.0	40.7	31.9	31.2	28.1	59.3
Hex	5.4	42.4	44.2	25.5	30.9	56.4
Hex	9.8	46.5	43.9	26.3	27.6	53.9
Hex	17.2	53.7	34.8	32.3	19.3	51.7
Hex	28.5	57.2	33.2	33.8	16.4	50.3
Hex	41.1	61.5	33.2	34.8	13.5	48.3
Hex	50.0	66.2	33.4	35.8	10.5	46.3
Hex	59.9	70.1	34.9	36.1	8.4	44.5
Hex	70.7	72.9	36.2	36.1	7.1	43.2
Pent	16.3	52.8	46.0	26.3	23.3	49.6
Pent	25.4	56.8	41.4	29.6	18.8	48.4
Pent	35.9	59.8	42.5	29.6	16.8	46.5
Pent	45.1	63.8	42.6	30.4	14.3	44.6
Pent	51.5	65.0	43.8	29.8	14.1	44.0
Pent	56.9	66.4	44.1	30.2	12.6	42.8
Pent	61.5	66.2	45.5	29.3	13.0	42.4

ponent:  $\gamma_s^d$ ; hydrophilic component:  $\gamma_s^p$ ) were calculated. Results obtained are listed in Table VII.

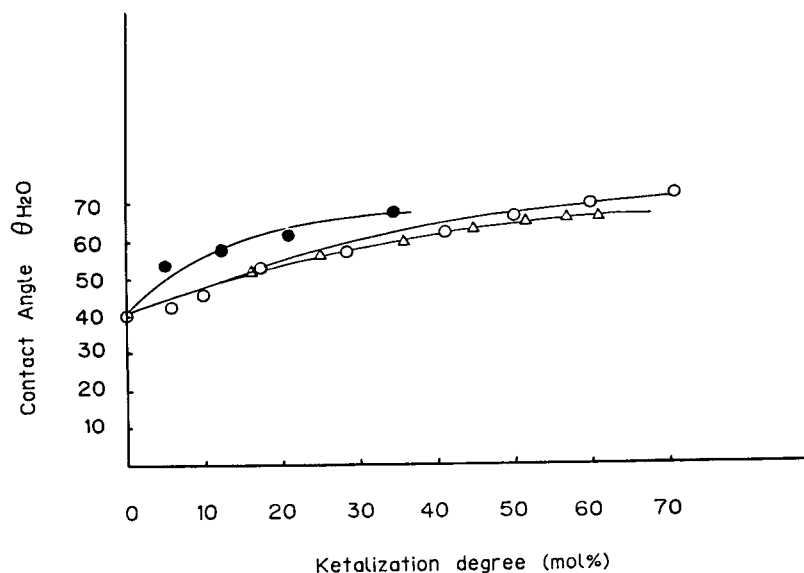
The relationships between ketalization degree and  $\theta_{H_2O}$  are shown in Figure 6 and values  $\gamma_s$  and  $\gamma_s^p$  are shown in Figure 7. For comparison with PVKL (aliphatic ketones), the values for PVKL (*t*BK) are also plotted.

The  $\theta_{H_2O}$  of PVKL (cyclic ketones) increased proportionally to the ketalization degree. Clearly, the PVKL (Hex) is a more hydrophobic polymer than is PVKL (Pent), as was expected.

$\gamma_s$  decreased gradually as ketalization degree increased.  $\gamma_s^p$  showed the same tendency except the ketalization degree of ca. 5 mol %, as above, and  $\gamma_s^p$ 's at same ketalization degree is in the following order:

$$\text{Pent} > \text{Hex} > t\text{BK}$$

The maximum ketalization degree of PVKL (*t*BK) is, however, ca. 35 mol %, <sup>3</sup> whereas that of PVKL (Hex) is ca. 80 mol %; therefore, PVKL

**Figure 6** Contact angle (H<sub>2</sub>O) of various PVKLs at 25°C: (○) Hex; (△) Pent; (●) *t*BK.

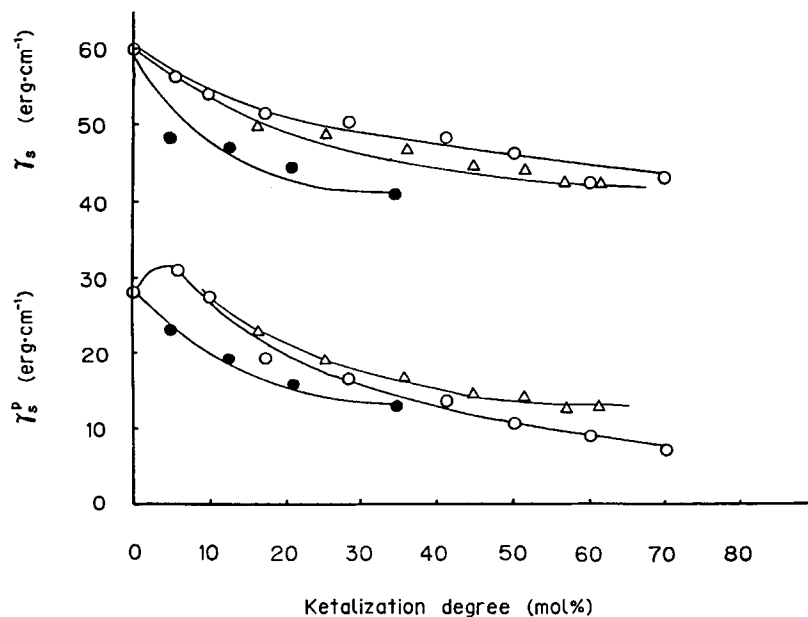


Figure 7  $\gamma_s$  and  $\gamma_s^p$  of various PVKLs at 25°C: (○) Hex; (△) Pent; (●) tBK.

(Hex) with more than a 70 mol % ketalization degree is a highly hydrophobic polymer.

#### Moisture Regain

The moisture regain of various PVKL (cyclic ketones) at RH 100% and 25°C is plotted against ketalization degree in Figure 8. The moisture regain

of PVKL with ketalization degree of ca. 5 mol % is higher than that of PVAL. This is consistent with that for PVKL (aliphatic ketones), except for PVKL (acetone, MEK).<sup>5</sup>

The moisture regain of PVKL (Hex) is nearly equal to that of PVKL (*n*BK) and PVKL (*i*BK). The moisture regain of PVKL (Pent) is nearly equal

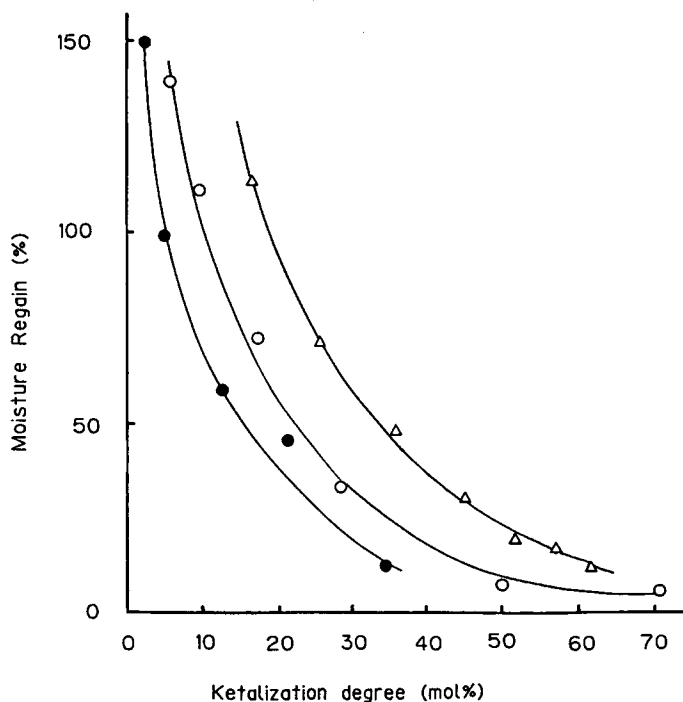


Figure 8 Moisture regain of various PVKLs at 25°C: (○) Hex; (△) Pent; (●) tBK.

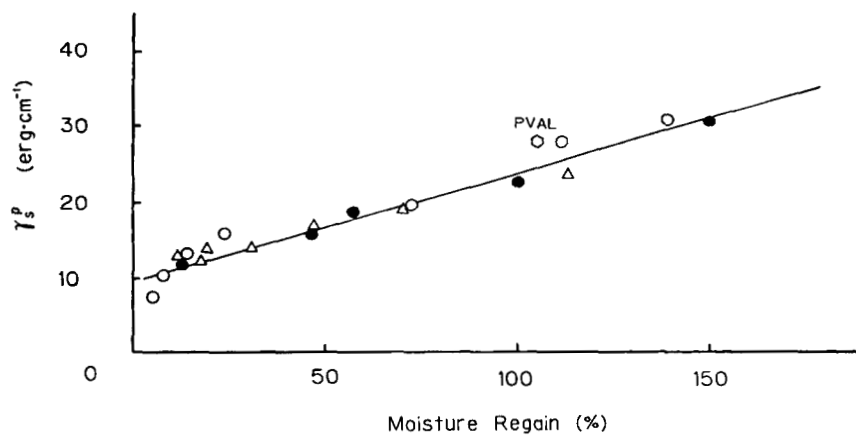


Figure 9 Relation between moisture regain and  $\gamma_s^p$ : (○) Hex; (△) Pent; (●) *t*BK.

to that of PVKL (*n*PK). These results are consistent with the relationships for hydrophobicity factor  $\alpha$  as shown in Figure 5 and the results obtained previously for contact angle.<sup>5</sup>

As previously reported,<sup>5</sup> the values for moisture regain of various PVKL are plotted against  $\gamma_s^p$  in Figure 9. The relationship between  $\gamma_s^p$  and moisture

regain is represented by a straight line irrespective of the kind of PVKL and ketalization degree. Clearly,  $\gamma_s^p$  decreases as the hydrophobicity of polymer increases. Almost the same tendency has been obtained for  $\gamma_s$ . This suggests that the molecular structure of surface of the film is the same as that inside of the film.

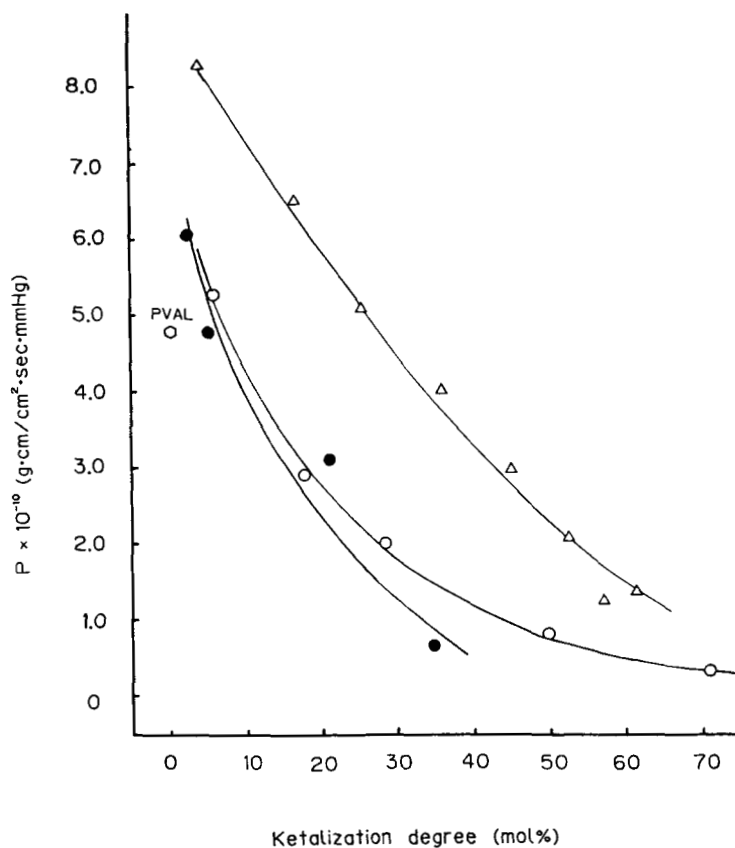


Figure 10 Water vapor permeability coefficient ( $P$ ) of various PVKLs: (○) Hex; (△) Pent; (●) *t*BK.

### Water Vapor Permeability

The water permeabilities are listed in Figure 10.

The  $P$  values of both PVKLs with low ketalization degree are higher than that of PVAL, which is consistent with the fact that the moisture regains of those PVKLs are higher than that of PVAL and support the forecast mentioned above. As expected, the water vapor permeability became lower as ketalization degree increased.

Although the  $P$  values of PVKL (Hex) is nearly equal to that of PVKL (*t*BK), the  $P$  values of PVKL (Pent) is higher than that of PVKL (Hex). This is explained by the water molecules being able to penetrate easily into PVKL (Pent) film, since the Pent ring does not protect nearest-neighbor OH groups for the penetration of the water molecules. This is in accordance with the rigidity of the Pent ring.

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