

# Study on Ketalization Reaction of Polyvinylalcohol by Ketones. V. The Film Properties of Polyvinylketals Obtained by Aliphatic Ketones

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## SYNOPSIS

The physical and chemical properties of polyvinylketals (PVKL) prepared from seven aliphatic ketones [acetone, methyl ethyl ketone (MEK), methyl *n*-propyl ketone (nPK), methyl *i*-propyl ketone (iPK), methyl *n*-butyl ketone (nBK), methyl *i*-butyl ketone (iBK), methyl *t*-butyl ketone (tBK)] were studied. The moisture regain and water vapor permeability of PVKL films decrease in the following order: acetone > MEK > nPK > iPK  $\approx$  nBK > iBK > tBK. The contact angle measurements revealed that this order is determined by the surface free energy of films, which depends upon the kind of the original ketones. PVKL (acetone) with low ketalization degree was not soluble in neutral water and had lower moisture regain than PVA. As shown in X-ray analysis, the molecular orientation was not random, the crystalline part of PVA remaining. Thus, it becomes clear that behavior of PVKL in water is affected not only by the hydrophobicity of film surface, but also by the crystallinity of PVKL.

## INTRODUCTION

As mentioned in the previous reports,<sup>1-4</sup> PVKLs with any ketalization degree were successfully obtained from PVA and aliphatic ketones in homogeneous system. It becomes clear that PVKL films are deketalized easily when dissolved in acidic water and the hydrolysis of PVKL films proceeds in the following order:

acetone > MEK > nPK  
> iPK  $\approx$  nBK > iBK > tBK

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

In order to confirm the hydrophobicity of the film surface, the contact angle, the moisture regain, and the water vapor permeability were studied. In order

to clarify the reason why PVKL (acetone) with the low ketalization degree is not soluble in water completely, the crystallinity of PVKL was estimated by the means of X-ray analysis. Also, the solubility in neutral water and the cloud point of various PVKLs at low temperature were determined.

## EXPERIMENTAL

### Samples

As mentioned previously,<sup>1-4</sup> various aliphatic PVKL films such as PVKL (acetone), PVKL (MEK), PVKL (nPK), PVKL (iPK), PVKL (nBK), PVKL (iBK), and PVKL (tBK), were prepared.

### Measurement of Contact Angle<sup>5</sup>

A water or methylene iodide (MI) droplet of 0.1–0.3 mm diameter was put on the film. The diameter ( $\phi$ ) and height ( $h$ ) of the droplet were displayed on a TV monitor; as the droplet was increased or decreased, a microscope was used to take readings from

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the monitor. From these data, the advancing contact angle ( $\theta_a$ ) or receiving contact angle ( $\theta_r$ ) were calculated using eq. (1), and the true contact angle ( $\theta$ ) was calculated using eq. (2) from  $\theta_a$  and  $\theta_r$ :

$$\theta_a \text{ or } \theta_r = \begin{cases} 2 \tan^{-1}(h/x) [x = \phi/2, \theta \leq 90^\circ] \\ 90^\circ + \cos^{-1}(\phi h/h^2 + x^2) \\ [x = \phi/2, \theta > 90^\circ] \end{cases} \quad (1)$$

$$\theta = \cos^{-1}[(\cos \theta_a + \cos \theta_r)/2] \quad (2)$$

### Measurement of Moisture Regain

After hanging the film for a week at 25°C in a desiccator with various relative humidities regulated by various concentrations of H<sub>2</sub>SO<sub>4</sub>, the film was weighed,  $W_2$  (g), dried at 105°C for 2 h, and then weighed again,  $W_1$  (g). Moisture regain (%) is given as

$$\text{moisture regain (\%)} = \bar{W}_2 - \bar{W}_1 / \bar{W}_1 \times 100 \quad (3)$$

The relative humidity (RH) and the concentration of H<sub>2</sub>SO<sub>4</sub> in the desiccator are as follows<sup>6</sup>:

H <sub>2</sub> SO <sub>4</sub> (%)	0	10	20	35	50
RH (%)	100	94	88	66	36

These RH values were confirmed using a Yokogawa-Hokushin type 2577 hygrometer.

### Measurement of Water Vapor Permeability

Two pieces of the film, ca. 0.05 mm thick, cut into ca. 2.0 cm  $\phi$ , were put on the tops of two glass vessels, A [ $A_1$  (g)] and B [ $B_1$  (g)] separately (cf. Fig. 1). Vessel A contained CaCl<sub>2</sub> on the bottom. These vessels were kept in the desiccator with RH 100% at 25°C, and weighed periodically at 0.5–1 h intervals. Taking  $A_2$  (g) and  $B_2$  (g) as the weights, respectively, the value  $a = A_2 - A_1$  indicates the summation of the moisture regain of the film and the amount of water transmitted through the film. On the other hand, the value  $b = B_2 - B_1$  indicates the net moisture regain of the film. Therefore, the water vapor transmission of the film is given as  $a - b$ . The water vapor transmission  $H$  was calculated as follows:

$$H = (a - b)d/F \quad (\text{mg cm/cm}^2) \quad (4)$$

where  $d$  = thickness of the film and  $F$  = area of the film.

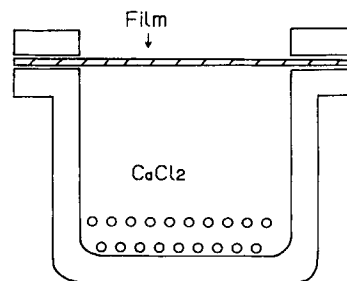


Figure 1 Apparatus for measurement of water vapor permeability.

### Behavior in Neutral Water

Films, ca. 0.05 mm thick, cut into 1.5 × 3.0 cm pieces, were taken as samples. These samples were soaked in neutral water (pH 5.70) at 0°C and 37°C; later, the films were removed from the water and the de-ketalization degree, solubility, and degree of swell were measured, as described previously.<sup>2</sup>

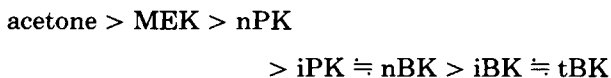
### X-Ray Measurement

The X-ray measurements were made with a Rigakudenki D-3F diffractometer using Ni-filtered Cu-K  $\alpha$  radiation (38 kV, 18 mA). The diffractometer curve ( $2\theta = 45-5^\circ$ ) of the PVKL films was obtained with a Geiger-Müller counter.

## RESULTS AND DISCUSSION

### Contact Angle of Film Surface

In order to confirm the difference of hydrophobicity of the surface for various PVKL films, at first the contact angle of film surface by water ( $\theta_{\text{H}_2\text{O}}$ ) was measured. The results are listed in Table I and Figure 2.  $\theta_{\text{H}_2\text{O}}$ 's of various PVKLs are decreased proportional to the hydrophobicity, which depends upon kind of the original ketones in the following order:



As expected, this result consists of the case of hydrolysis of PVKL.<sup>4</sup> However, ( $\theta_{\text{H}_2\text{O}}$ ) of PVKL-(acetone) and PVKL(MEK) with a ketalization degree less than 5 mol % are higher than that of PVA. In this region of low ketalization degree, since molecular orientation is not random, the crystalline part of PVA remains as discussed later in the measurement of X-ray. On the contrary, ( $\theta_{\text{H}_2\text{O}}$ )'s of

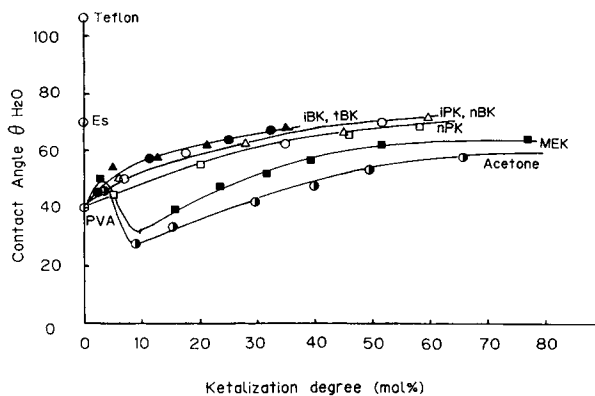
**Table I Contact Angle and Surface Free Energy (erg cm<sup>-1</sup>) of Various PVKLs at 25°C**

	X <sup>a</sup>	θ H <sub>2</sub> O	θ MI	γ <sub>s</sub> <sup>d</sup>	γ <sub>s</sub> <sup>p</sup>	γ <sub>s</sub>
PVA	0	40.7	31.9	31.2	28.1	59.3
Acetone	3.5	47.2	50.2	23.1	29.4	52.5
	8.9	27.6	70.2	20.6	44.2	64.8
	15.6	34.2	49.3	21.7	39.3	61.0
	29.4	42.8	51.2	21.8	33.4	55.2
	40.0	49.2	50.1	23.5	27.7	51.2
	49.4	53.6	50.6	23.9	24.5	48.4
	65.6	57.9	50.0	25.0	20.6	45.6
MEK	2.9	49.9	48.3	24.5	26.4	50.9
	15.8	39.2	48.3	22.9	35.0	57.9
	23.2	48.1	48.1	24.3	27.8	52.1
	31.7	52.1	47.5	25.4	24.4	49.8
	39.1	56.3	47.4	26.2	21.0	47.2
	51.7	62.4	47.6	27.3	16.3	43.6
	77.1	63.9	46.9	28.0	15.0	43.0
nPK	5.0	44.7	48.6	23.5	30.8	54.3
	20.0	55.4	46.0	26.8	21.2	48.0
	46.6	65.2	47.9	27.7	14.4	42.1
	58.0	68.5	42.2	31.7	10.8	42.5
iPK	6.7	50.7	46.5	25.7	25.1	50.8
	17.5	59.2	46.9	27.1	18.5	45.6
	34.7	62.9	48.8	26.7	16.3	43.0
	51.8	69.1	46.7	29.3	11.4	40.7
nBK	5.8	50.4	44.3	26.8	24.6	51.4
	28.0	62.9	48.5	26.9	16.2	43.1
	44.9	65.8	48.1	27.8	14.0	41.8
	59.5	72.0	45.8	30.5	9.4	39.9
iBK	2.4	45.5	46.5	24.8	29.3	54.1
	11.1	57.1	52.3	23.6	22.0	45.6
	24.9	63.2	51.7	25.1	17.0	42.1
	32.4	67.0	52.7	25.3	14.4	39.7
tBK	4.9	53.8	47.8	25.5	23.1	48.6
	12.5	57.7	45.2	27.7	19.2	46.9
	20.8	62.1	44.8	28.8	15.8	44.6
	34.7	67.7	48.1	28.2	12.7	40.9

<sup>a</sup> X = ketalization degree (mol %).

PVKL (acetone) with a 5–25 mol % ketalization degree and PVKL (MEK) with a 5–15 mol % ketalization degree are less than that of PVA, of which the molecular orientation is random and the hydrophobicity low. This is not the case for PVKL (nPK), PVKL (iPK), PVKL (nBK), PVKL (iBK), and PVKL (tBK), because the hydrophobicity, which depends upon the original ketones, is high.

The contact angle of film surface by MI (θ<sub>MI</sub>) was measured. From (θ<sub>H<sub>2</sub>O</sub>) and θ<sub>MI</sub>, surface free energy



**Figure 2** Contact angle (H<sub>2</sub>O) of various PVKLs at 25°C: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.

γ<sub>s</sub> (hydrophobic component = γ<sub>s</sub><sup>d</sup>, hydrophilic component = γ<sub>s</sub><sup>p</sup>) were calculated by eqs. (5) and (6). Results obtained are listed in Table I. In accordance with Fowkes' equation,<sup>7</sup> Owens' equation,<sup>8</sup> and Young's equation, eqs. (5) and (6) can be given as

$$(1 + \cos \theta) \cdot \gamma_L / 2 = (\gamma_s^d \cdot \gamma_L^d)^{1/2} + (\gamma_s^p \cdot \gamma_L^p)^{1/2} \quad (5)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (6)$$

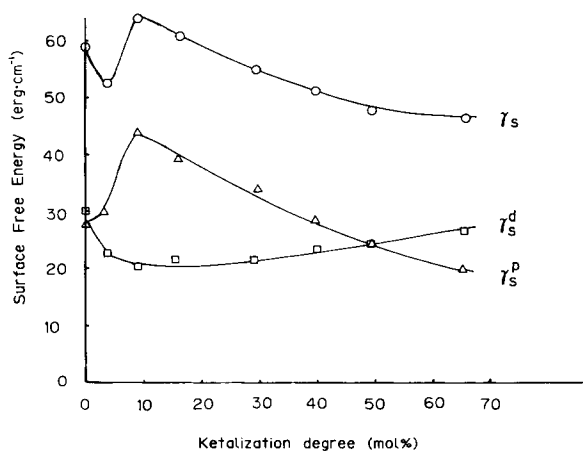
Suppose<sup>9</sup>

γ<sub>L</sub> = surface tension of contact liquid

γ<sub>L</sub><sup>d</sup> = hydrophobic component of γ<sub>L</sub>

γ<sub>L</sub><sup>p</sup> = hydrophilic component of γ<sub>L</sub>

In the case of PVKL (acetone), the relationships



**Figure 3** Surface free energy of PVKL (acetone) at 25°C.

between ketalization degree and the values  $\gamma_s$ ,  $\gamma_s^p$ , and  $\gamma_s^d$  are shown in Figure 3.

$\gamma_s$  reaches its lowest value at ca. 5 mol % ketalization degree, its highest value at ca. 10 mol %, and then decreases gradually. The behavior of  $\gamma_s^p$  is almost the same as that of  $\gamma_s$ .  $\gamma_s^d$  reaches its lowest values at ca. 10 mol %, and then increases gradually. It can be interpreted that PVKL (ca. 5 mol %) remains the crystalline part, but in the case of PVKL with a higher ketalization degree, molecular orientation is random and hydrophobicity high.

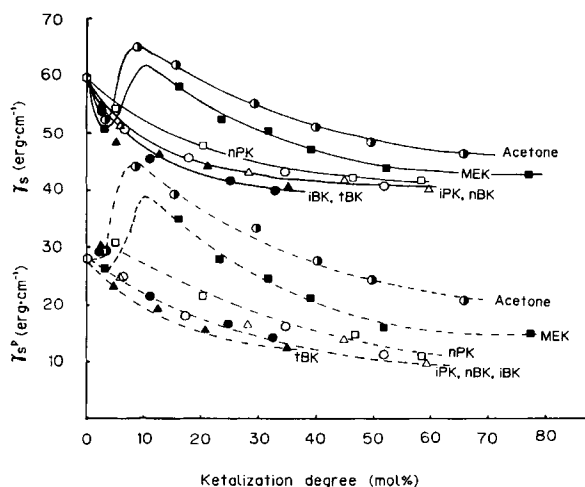
$\gamma_s$  and  $\gamma_s^p$  of various PVKLs are plotted against ketalization degree in Figure 4. The surface free energy of PVKL (acetone) and PVKL (MEK) with ca. 5 mol % is shown to be lower than that of PVA, and the highest value is seen at ca. 10 mol %. But  $\gamma_s$  of PVKL obtained by the other aliphatic ketone decreases gradually as ketalization degree increases.  $\gamma_s^p$ 's at same ketalization degree are in the following order:

$$\text{acetone} > \text{MEK} > \text{nPK} \\ > \text{iPK} \approx \text{nBK} \approx \text{iBK} > \text{tBK}$$

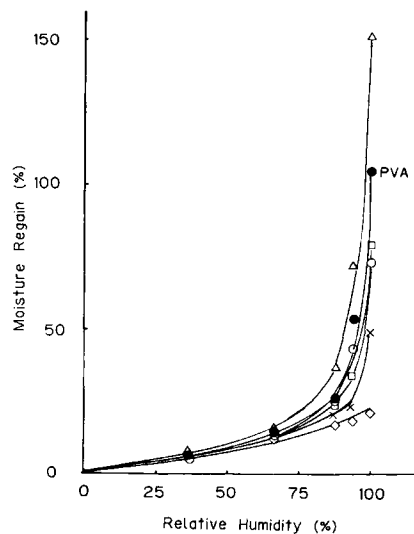
This order is in accordance with the hydrophobicity of PVKL.

**Moisture Regain**

The adsorption isotherms of PVKL (acetone) are shown in Figure 5 at 25°C. The moisture regain of PVKL 8.9 mol % is higher than that of PVA and that of PVKL 3.5 mol % is lower than that of PVA.



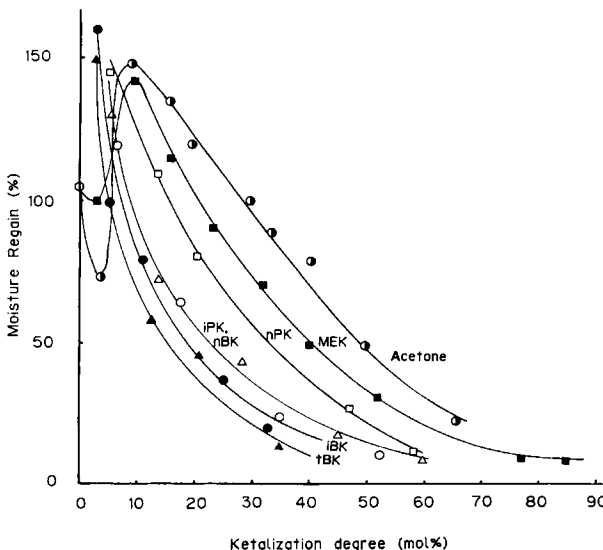
**Figure 4**  $\gamma_s$  and  $\gamma_s^p$  of various PVKLs at 25°C: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.



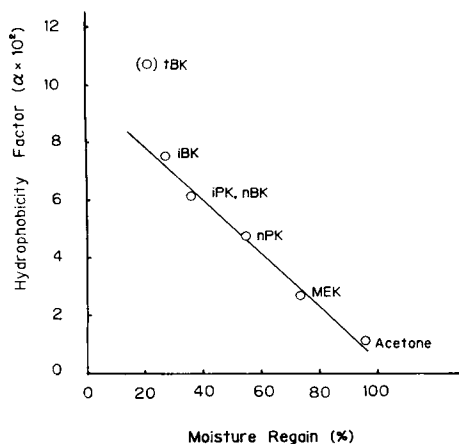
**Figure 5** Absorption Isotherms of PVKL (acetone) at 25°C: (●) PVA; (○) 3.5 mol %; (△) 8.9 mol %; (□) 40.0 mol %; (X) 49.4 mol %; (◇) 65.6 mol %.

These phenomena are consistent with those for the contact angle, and the results supporting the above-mentioned forecast are obtained. As expected, the moisture regain becomes lower as ketalization degree increases.

Finally, the moisture regain of various PVKL at RH 100% is plotted against ketalization degree, as shown in Figure 6. The moisture regain is in the following order:



**Figure 6** Moisture regain of various PVKLs at 25°C, RH 100%: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.



**Figure 7** Relation between hydrophobicity factor  $\alpha$  and moisture regain of PVKL film (30 mol %).

acetone > MEK > nPK

> iPK  $\approx$  nBK > iBK > tBK

This order consists with that for the hydrolysis of PVKL film.<sup>4</sup> To confirm this point, the moisture regain of various PVKL (30 mol %) is plotted against the hydrophobicity factor  $\alpha^4$  in Figure 7.

The linear line is obtained, except PVKL (tBK), and it can be shown that the moisture regain of PVKL is proportional to hydrophobicity of ketone. As can be seen from Figure 6, in the cases of PVKL (acetone) and PVKL (MEK), the moisture regains in the region of ca. 5 mol % are lower than that of PVA, and in the region of ca. 10 mol % are higher than that of PVA. These phenomena are consistent with those of  $\theta_{H_2O}$ ,  $\gamma_s$ , and  $\gamma_s^p$ . To confirm

this point, the values for the moisture regain of various PVKL are plotted against  $\gamma_s$  and  $\gamma_s^p$  in Figure 8.

Even with some deviation with PVKL (acetone), PVKL (MEK), PVKL (nPK), and PVKL (the other ketones), including PVA, respectively, linear lines are obtained irrespective of ketalization degree. It is clear that  $\gamma_s^p$  decreases as the hydrophobicity of polymer increases. Almost the same results at  $\gamma_s$  have been obtained. It is suggested that the molecular structure of the film surface is the same as that inside the film.

### Water Vapor Permeability

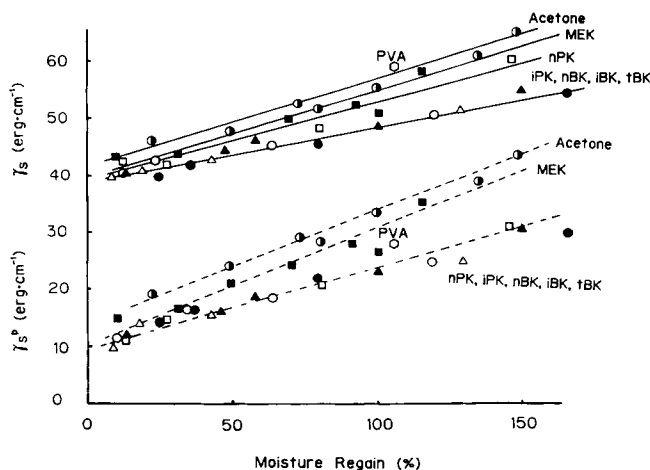
Recent studies on the vapor permeability of functional polymer films have been carried out.<sup>10-12</sup> Water vapor permeability of various PVKL has been studied. At first, the water vapor transmission  $H$  of PVKL (acetone), 65.6 mol %, as a representative sample, was determined. The results are shown in Figure 9. After 3 h, linear correlations between  $H$  and time were obtained. The water vapor transmission rate  $H_v$  was calculated using eq. (7) and water vapor permeability  $P$  was calculated using eq. (8):

$$H_v = H/t \quad (\text{mg cm/cm}^2 \text{ h}) \quad (7)$$

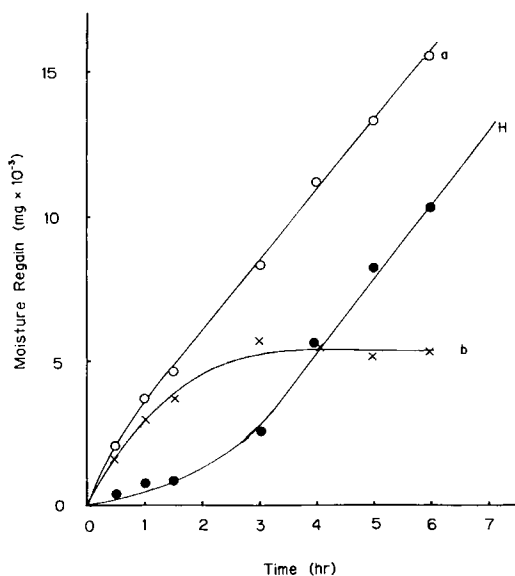
$$P = H_v/P_1 - P_2 \quad (8)$$

Suppose<sup>6</sup>

$$P_1 = 2.3755 \text{ cm Hg}$$



**Figure 8** Relation between moisture regain and  $\gamma_s$ ,  $\gamma_s^p$ .



**Figure 9** Water vapor transmission of PVKL(acetone) film (65.6 mol %): (O)  $a = A_1 - A_2$ ; (X)  $b = B_2 - B_1$ ; (●)  $H = (a - b)d/F$ . For details, see the text.

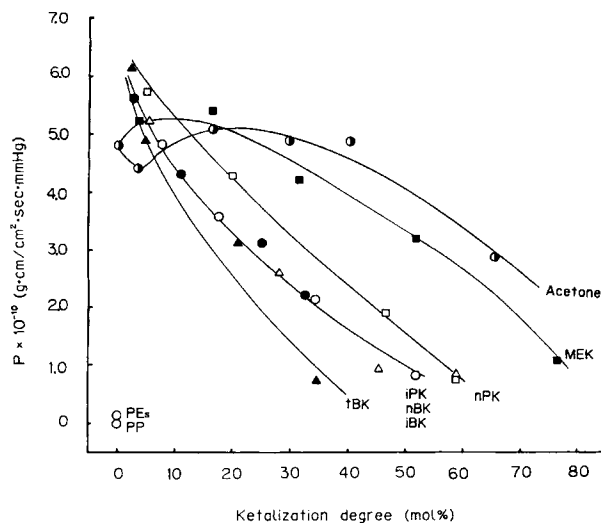
with partial vapor pressure, RH 100% at 25°C in the upper part of the film,

$$P_2 = 0$$

**Table II** Water Vapor Permeability Coefficient [ $P \times 10^{-10}$  (g cm/cm<sup>2</sup> s mm Hg)] at 25°C of Various PVKLS

PVKL	Symbol	$P$	Ketalization degree (mol %)			
PVA	P	4.8				
Acetone	X <sup>a</sup>	3.5	15.6	29.4	40.0	49.4
	P	4.4	5.1	4.9	4.9	4.8
MEK	X	2.9	15.8	31.7	51.7	77.1
	P	5.3	5.4	4.2	3.2	1.1
nPK	X	5.0	20.0	46.6	58.0	
	P	5.7	4.3	1.9	0.79	
iPK	X	6.7	17.5	34.7	51.8	
	P	4.9	3.6	2.1	0.83	
nBK	X	4.9	28.0	44.9	59.5	
	P	5.2	2.6	0.95	0.89	
iBK	X	2.4	11.1	24.9	32.4	
	P	5.6	4.3	3.1	2.2	
tBK	X	2.4	4.8	20.8	34.7	
	P	6.1	4.8	3.1	0.71	
PEs	P	0.18				
PP	P	0.016				

<sup>a</sup> X = ketalization degree (mol %).



**Figure 10** Water vapor permeability coefficient ( $P$ ) of various PVKLS: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.

with partial vapor pressure with CaCl<sub>2</sub> at 25°C in the lower part of film,

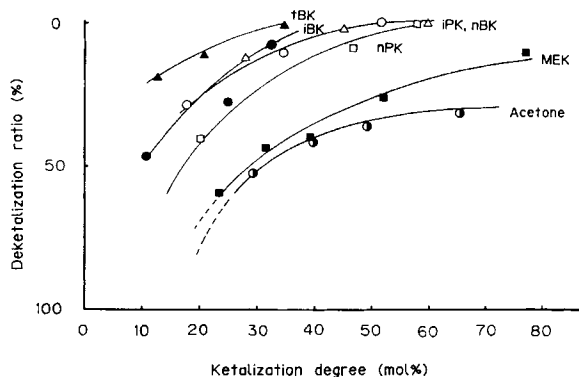
$$P = H_v \times 1.17 \times 10^{-10} \text{ (g cm/cm}^2 \text{ s mm Hg)} \quad (9)$$

$P$ 's of various PVKLS are listed in Table II and Figure 10. The order for  $P$  is as follows:

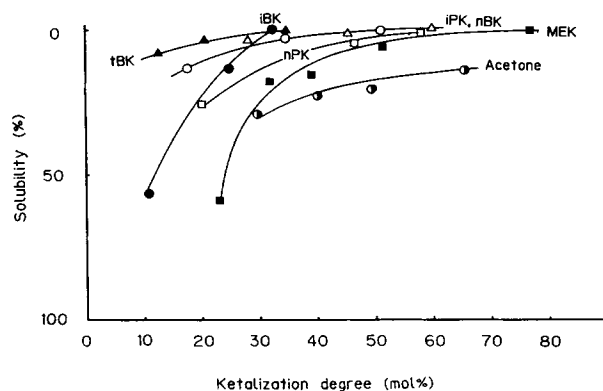
acetone > MEK > nPK

> iPK  $\approx$  nBK  $\approx$  iBK > tBK

It is understood that this order is in accordance with that for the hydrophobicity of PVKL. The lowest  $P$  value obtained for PVKL(tBK) 34.7 mol % is



**Figure 11** Hydrolysis of various PVKLS after 100 h soaking in water of pH 5.70 at 37°C: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.



**Figure 12** Solubility of various PVKs after 100 h soaking in water of pH 5.70 at 37°C: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.

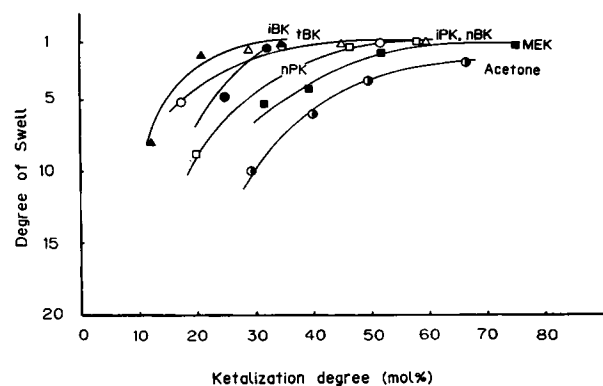
roughly 4 times larger than that of polyester and 50 times larger than that of polypropylene.

**Behavior in Neutral Water**

**Behavior with Accompanying Hydrolysis**

As reported previously,<sup>2-4</sup> PVKs are dissolved in water close to neutral with accompanying hydrolysis. In order to confirm this phenomenon, various PVKs were soaked in neutral water at 37°C for 100 h and deketalization degree, solubility, and degree of swell were determined. The results are listed in Figures 11-13.

It is clear that PVK(acetone)<sup>2</sup> and PVK(MEK)<sup>3</sup> are dissolved in neutral water at ca. 15 mol % and ca. 8 mol % residual ketalization degrees, respectively. Then the deketalization degree of those two PVKs was calculated based on



**Figure 13** Degree of swell of various PVKs after 100 h soaking in water of pH 5.70 at 37°C: (●) acetone; (■) MEK; (□) nPK; (○) iPK; (△) nBK; (●) iBK; (▲) tBK.

$$\text{corrected deketalization ratio PVK(acetone)} = \frac{\text{deketalization degree}}{\text{initial ketalization degree} - 15.0} \times 100$$

$$\text{corrected deketalization ratio PVK(MEK)} = \frac{\text{deketalization degree}}{\text{initial ketalization degree} - 8.0} \times 100$$

As shown in Figure 11, the deketalization reaction proceeds in the following order:

acetone > MEK > nPK  
> iPK = nBK = iBK > tBK

It is understood that the rate of deketalization reaction in the heterogeneous system depends on the hydrophobicity of PVK.

**Table III** Case of Dissolution without Accompanying Hydrolysis at 0°C, pH 5.70

	X (mol %)	Solubility (%)	Degree of Swell	Deketalization Degree (mol %)
Acetone	3.5	7.1	4.09	0.2
	15.6	100	∞	0
	49.4	100	∞	0
	65.6	0	1.64	0
MEK	2.9	26.3	10.5	0
	9.6	100	∞	0
	31.7	100	∞	0
	51.7	0	1.65	0
nPK	5.0	100	∞	0
	10.9	100	∞	0
	20.0	59.2	11.0	0.3
	46.6	0	1.26	0
iPK	6.7	71.2	29.5	0
	17.5	13.3	4.06	0.5
	34.7	0	1.22	0
nBK	5.8	68.5	26.2	0.7
	28.0	0	1.83	0.5
	59.5	0	1.04	0
iBK	4.5	44.2	25.7	0
	24.9	4.1	2.21	0.7
	32.4	0	1.52	0
tBK	4.9	15.9	10.8	0.6
	12.5	4.5	4.19	0
	34.7	0	1.20	0

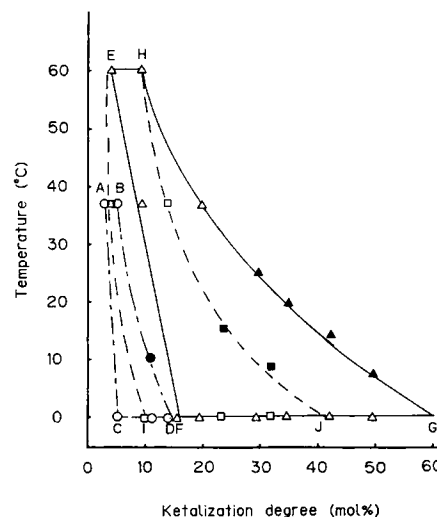
<sup>a</sup> X = ketalization degree (mol %).

As can be seen in Figures 12 and 13, almost the same results at solubility and degree of swell were obtained, except PVKL(iBK) with low ketalization degree. The reason for higher solubility and swelling for PVKL(iBK) is not clear. But it seems that the water molecule has penetrated into the film completely, and PVKL(iBK) is deketalized more easily than PVKL(nBK) in the homogeneous system because PVKL(iBK) has a strong electroreleasing substituent.

### Behavior without Accompanying Hydrolysis

As reported previously, it has been made clear that, at low temperature, PVKL(acetone)<sup>2</sup> and PVKL(MEK)<sup>3</sup> dissolve without any hydrolysis in neutral water. Then, various PVKLs obtained by the other aliphatic ketones were soaked in neutral water at 0°C for 500–600 h, and deketalization degree, degree of swell, and solubility were determined. The results are listed in Table III.

As is clear from Table III, PVKL(acetone), 15–60 mol %, PVKL(MEK), 10–40 mol %, and PVKL(nPK), 5–11 mol %, are dissolved without hydrolysis. On the other hand, PVKL(iPK),



**Figure 14** PVKL vs. dissolution temperature without any hydrolysis: ( $\Delta$ ) dissolution (acetone); ( $\blacktriangle$ ) cloud point (acetone); ( $\square$ ) dissolution (MEK); ( $\blacksquare$ ) cloud point (MEK); ( $\circ$ ) dissolution (nPK); ( $\bullet$ ) cloud point (nPK).

PVKL(nBK), PVKL(iBK), and PVKL(tBK) do not dissolve completely. The solubility in neutral water and the cloud point of PVKL were determined under the conditions where no hydrolysis proceeds

**Table IV** Water Solubility of PVKL with Lower Ketalization Degree at 37°C, pH 5.7

	$X^a$	RT <sup>b</sup> (h)	Solubility (%)	Degree of Swell	Deketalization Degree (mol %)
PVA	0	100	59.7	19.8	—
Acetone	3.5	100	51.2	14.5	0
MEK	2.9	7.2	100	$\infty$	0.2
nPK	3.2	2.0	100	$\infty$	0
	5.0	1.7	100	$\infty$	0
iPK	2.0	307	96.1	78.5	1.9
	3.5	3.0	100	$\infty$	1.1
	6.7	530	100	$\infty$	4.8
nBK	2.7	360	59.3	43.6	0
	3.6	43	100	$\infty$	1.4
	5.8	954	100	$\infty$	5.7
iBK	2.4	307	96.0	34.7	0.4
	4.5	409	100	$\infty$	4.2
tBK	2.4	307	71.8	21.1	0.7
	3.6	1948	75.5	41.6	2.0
	4.9	300	100	$\infty$	3.2

<sup>a</sup>  $X$  = ketalization degree (mol %).

<sup>b</sup> RT = reaction time (h).



and are plotted against ketalization degree, as shown in Figure 14.

The area within points A, B, C, and D is the region where PVKL (nPK) dissolves in water without being hydrolyzed, the area within points E, F, G, and H is the region where PVKL (acetone) dissolves, and the area within points E, I, J, and H is the region where PVKL (MEK) dissolves. It is understood that the order of solubility in neutral water is in accordance with that for the hydrophobicity of PVKL.

### Solubility of PVKL with Low Ketalization Degree in Water

Finally, discussion of solubility of PVKL with ketalization degree of less than 5 mol % in neutral water is given. The results in neutral water at 37°C are shown in Table IV. Complete dissolution of PVA and PVKL (acetone), 3.5 mol %, are not observed and its solubility is almost 50%. On the contrary, PVKL (MEK), 2.9 mol %, PVKL (nPK), 3.2 mol %, and PVKL (nPK) 5.0 mol % dissolve without hydrolysis within short period. However, PVKL (iPK), 2.0 mol %, PVKL (nBK), 2.7 mol %, PVKL (iBK), 2.4 mol %, and PVKL (tBK), 2.4 mol %, do not dissolve completely. It is considered that these phenomena depend upon the crystallinity of the polymer, which will be discussed below.

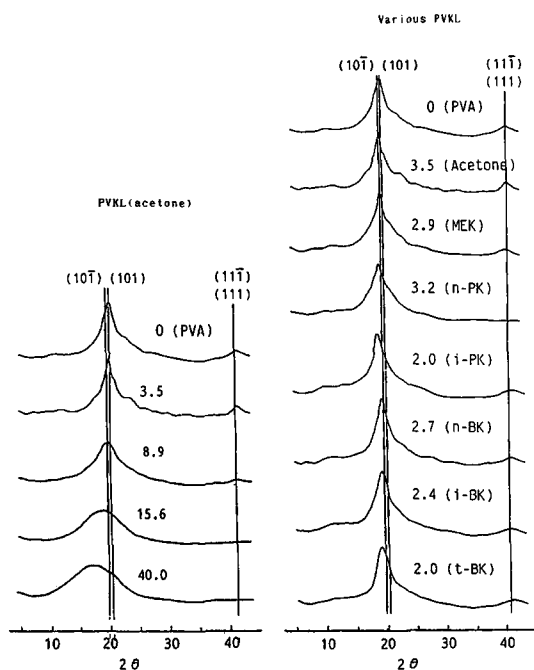


Figure 15 X-ray diffraction curves of various PVKLs.

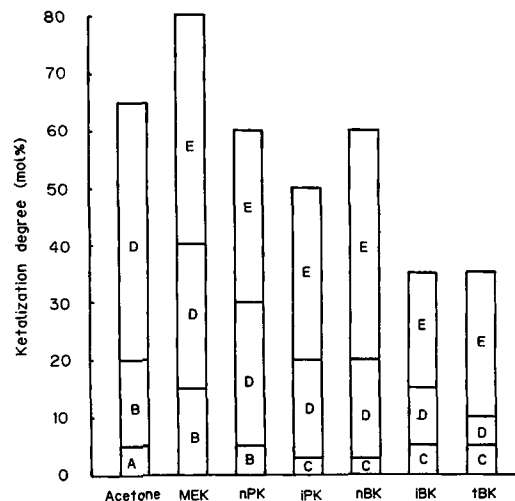


Figure 16 Relation between hydrophobicity and crystallinity of various PVKLs for A, B, C, D, and E; see the text.

### Crystallinity of PVKL

At first, X-ray diffractometer curves of PVA and PVKL (acetone), as a representative PVKL, were determined. The results are shown in Figure 15. In the case of the PVKL with a low ketalization degree such as 3.5 mol %, crystallinity is similar to that of PVA, since the diffractograms of the (101) and (10 $\bar{1}$ ) crystalline peaks at  $2\theta = 19.7\text{--}20.3^\circ$  are detected as are those of the (111) and (11 $\bar{1}$ ) peaks at  $2\theta = 40.9^\circ$ . However, in the case of the PVKL with higher ketalization degree such as 8.9 mol %, the crystallinity is lower while the proportion of OH groups in the polymer decreases since the diffractometer curve is broad.

X-ray diffractometer curves of various PVKL with less than 5 mol % ketalization degree were determined, and the results are shown in Figure 15. The crystallinities of the PVKLs are decreased proportionally to the bulky side chain, which depends upon the kind of the original ketones. The crystallinity of PVKL is in the following order:

$$\text{acetone} > \text{MEK} > \text{nPK} \\ > \text{iPK} \cong \text{nBK} > \text{iBK} > \text{tBK}$$

As expected, these results are consistent with the case of PVKL in water.

### CONCLUSION

The relationship between hydrophobicity and crystallinity of various PVKLs are shown in Figure 16.

### A Region

This region is seen for PVKL(acetone) with less than 5 mol % ketalization degree. At A region,  $\theta_{\text{H}_2\text{O}}$  is larger than that of PVA and the moisture regain is smaller than that of PVA, because its crystallinity is similar to that of PVA and its hydrophobicity larger than that of PVA. In other words, the crystallinity is the highest and the hydrophobicity the lowest.

Then this sample is insoluble in water as PVKL and it does not dissolve completely even when subjected to deketalization. Since the crystalline parts of PVA remain, molecular orientation is not randomly disposed.

### B Region

This region is seen for PVKL (acetone), 5–20 mol %, PVKL (MEK) up to 15 mol %, and PVKL (nPK) up to 5 mol %. Because the crystallinity is medium and the hydrophobicity is slightly low, at B region, these samples dissolve in water as PVKL.

### C Region

This region is seen for PVKL (iPK) up to 3 mol %, PVKL (nBK) up to 3 mol %, PVKL (iBK) up to 5 mol %, and PVKL (tBK) up to 5 mol %. Because the crystallinity is medium and the hydrophobicity medium, at C region, these samples are insoluble in water as PVKL and they do not dissolve in water upon hydrolysis.

### D Region

This region is seen for PVKL (acetone), 20–65 mol %, PVKL (MEK), 15–40 mol %, PVKL (nPK), 5–30 mol %, PVKL (iPK), 5–20 mol %, PVKL (nBK), 3–20 mol %, PVKL (iBK), 3–15 mol %, and PVKL (tBK), 5–10 mol %. Because the crystallinity is low and the hydrophobicity is high at D region, these samples are insoluble in water as PVKL, but dissolve in water upon hydrolysis.

### E Region

This region is seen for PVKL (MEK) above 40 mol %, PVKL (nPK) above 30 mol %, PVKL (iPK) above 20 mol %, PVKL (nBK) above 20 mol %, PVKL (iBK) above 15 mol %, and PVKL (tBK)

above 10 mol %. Because the crystallinity is the lowest and the hydrophobicity the highest at E region, these samples are insoluble in water as PVKL. It is difficult to hydrolyze them in water, and they did not dissolve in water completely after standing for 100 days. Especially, PVKL with maximum ketalization degree such as PVKL (nPK), 58.0 mol %, PVKL (iPK), 51.8 mol %, PVKL (nBK), 59.5 mol %, PVKL (iBK), 32.4 mol % and PVKL (tBK), 34.7 mol %, did not dissolve in water at all after standing for 100 days. In order to dissolve these samples in water, theoretically it would be necessary to soak them for almost 20 years.

The physical and chemical properties of polyvinylketals from aliphatic ketones in water have been made clear. The polyvinylketals shown here can be used either for the hydrophilic or for the hydrophobic polymer, depending on the ketalization degree and the starting ketone.

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