Study on Ketalization Reaction of Poly(vinyl alcohol) by Ketones. VII. Reaction Between Poly(vinyl alcohol) and Aromatic Ketones and Behavior of Poly(vinyl ketal) in Water

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SYNOPSIS

The ketalization reaction of poly(vinyl alcohol) (PVA) by aromatic ketones, with dimethylsulfoxide (DMSO) as solvent, under the presence of an acidic catalyst in a homogeneous system, was carried out. The synthesis of poly(vinyl ketal) (PVKL) for the case of phenylacetone and benzylacetone was thus successfully performed, but for the case of acetophenone was performed only with a ketalization degree of a few molecular percent, and for the case of benzophenone it could not be performed at all. It seems that these different behaviors in synthesis are due to steric hindrance of the bulky side chain of ketones. The equilibrium constant at 40°C was ca. 0.12 in the case of phenylacetone and benzylacetone, and the value is somewhat higher compared with that of aliphatic ketones, but somewhat lower compared with the case of cyclic ketones. Because the heat of reaction is 7.5 kcal/mol in these two aromatic ketones, all ketalization reactions are considered to proceed by the same reaction mechanism. The rate of hydrolysis, contact angle, surface free energy, moisture regain, and water vapor permeability of PVKL films were measured. All results show that PVKL obtained from phenylacetone is nearly equal to PVKL obtained from methyl n-butyl ketone. However PVKL obtained from benzylacetone shows different behavior compared with other ketones, because the side chain of benzylacetone is flexible and bulky. The hydrophobicity of PVKL seems to depend upon the kind of the original ketones and the flexibility of the side chain. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

As described in the previous reports,[1-4] poly(vinyl ketal) (PVKL) with any ketalization degree can be successfully obtained from the reaction between poly(vinyl alcohol) (PVA) and aliphatic ketones or cyclic ketones in a homogeneous system. The values of the equilibrium constant of ketalization (K) at 40°C are ca. 0.01-0.07 for aliphatic ketones and ca. 0.35-0.50 for cyclic ketones. Steric hindrance of the bulky side chain of the ketones seems to affect the equilibrium. The heat of reaction for all cases is 7.5 kcal/mol including acetalization reaction, and all reactions are considered to proceed by an identical mechanism. It becomes clear that PVKL films are deketalized easily and dissolved in acidic water,[4-5] and the hydrolysis of PVKL films proceeds in the following order:

acetone > MEK > nPK > Pent > iPK

$$\dot{=} \; nBK > iBK > Hex > tBK$$

where MEK = methyl ethyl ketone, nPK = methyl n-propyl ketone, Pent = cyclopentanone, iPK = methyl i-propyl ketone, nBK = methyl n-butyl ketone, iBK = methyl i-butyl ketone, Hex = cyclohexanone, and tBK = methyl t-butyl ketone.

This order seems to be affected by the hydrophobicity of the film surface, which depends upon the kind of the original ketones.[3,4] The hydrophobicity of the PVKL film was made clear by measurements of the contact angle, the moisture regain, and the water vapor permeability.[4-6]

This article is concerned with the acid catalyzed synthesis of PVKL from aromatic ketones, such as phenylacetone (PhA), benzylacetone (BzA), acetophenone, and benzophenone in a homogeneous system. The values of K and solubilities in various

Table I   Equivalent Constant of Ketalization Reaction by Aromatic Ketones

Ketones	Temp. (°C)	Ketone Equivalent	Ketalization Degree (mol %)	K
PhA	40	6.00	54.2	0.11[8]
PhA	40	3.00	42.0	0.11[8]
PhA	40	1.00	25.7	0.12[0]
PhA	40	0.50	17.0	0.10[6]
BzA	40	6.00	55.3	0.12[6]
BzA	40	3.00	41.7	0.11[5]
BzA	40	1.50	31.5	0.12[2]
BzA	40	1.00	26.3	0.12[7]
BzA	40	0.50	17.6	0.11[6]
BzA	40	0.20	8.9	(0.07[8])
Acetophenone	40	6.00	5.9	0.0006
Benzophenone	40	6.00	0	0
Acetone[1]	40	6.00	46.0	0.07[0]
tBK[3]	40	6.00	20.8	0.009[4]
Hex[6]	40	1.50	50.0	0.50[0]
Pent[6]	40	1.50	45.1	0.35[3]
PhA	50	6.00	47.6	0.07[8]
BzA	50	6.00	47.5	0.07[8]
PhA	30	6.00	61.5	0.18[2]
BzA	30	6.00	54.7	(0.12[1])
BzA	30	3.00	48.3	0.17[9]

Note: all superior numbers are references. PVA initial concn. 0.3–0.6 mol/L, PTS concn. 2.5 g/L.

solvents for the PVKL were determined. To confirm the difference between these aromatic ketones, de-ketalization, contact angle, moisture regain, and water vapor permeability were studied. These behaviors were also compared with those of PVKL from aliphatic ketones and cyclic ketones.

EXPERIMENTAL

Samples and Reagents

PVA of average degree of polymerization, 1800, saponification degree above 99.4% (NH-18 from Nihon Gohsei Co., Ltd) was used. Dimethylsulfoxide (DMSO, water content 0.05%), p-toluene sulfonic acid (PTS), BzA, acetophenone, and benzohenone guaranteed reagent (Nacalai Tesque Inc.) were used without further purification. Because phenylacetone cannot be purchased as a raw material, the synthesis of PhA was performed in the following steps[7] under the permission of the Minister of Welfare. Phenyl acetic acid was dissolved in acetic anhydride, sodium acetate was added and heated, then neutralized and extracted by ethylether. PhA was distilled under vacuum (bp 123–125°C/46 mmHg); this value of bp coincides with that of Ref. 7.

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 the beginning to the end proceeds in a homogeneous system. Prescribed hours later, the reaction mixture was neutralized by 1N 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 the iodoform method, the quantitative analysis of ketone released by perfect deketalization of PVKL, as previously described. In the case of benzophenone, the analysis was done by ultraviolet spectrum.

Solubility in Organic Solvents

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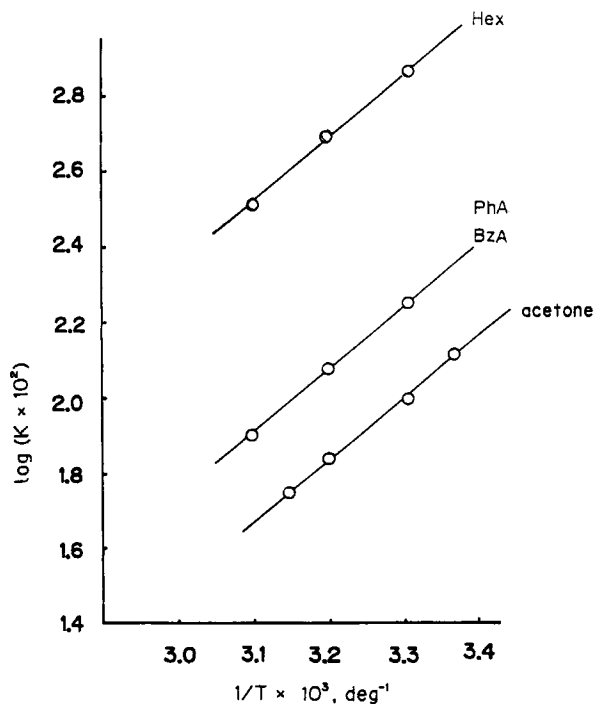

Figure 1   Temperature dependency of equilibrium constant, K.

Table II   Effect of Substituent of Ketone on Ketalization Reaction

	PhA	BzA	Acetophenone	Benzophenone	Acetone	tBK	Hex
Maximum ketalization degree (mol %)	63.5	55.3	6.5	0	68.5	34.7	80

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.[5]

Behavior of PVKL in Water

Samples were soaked in water of various pH values kept at the prescribed temperature. The time needed for complete dissolution of the film and deketalization degree were measured according to the method previously described.[5]

Measurement of Contact Angle

As previously reported,[6] the contact angle by water and methylene iodide (MI) were measured by the droplet method. From these data, surface free energy γ_s (hydrophobic component: γ_s^d; hydrophilic component: γ_s^P) were calculated.

Measurement of Moisture Regain

After hanging the film at 25°C in a desiccator with relative humidity (RH) of 100%, moisture regain was measured, as previously reported.[6]

Measurement of Water Vapor Permeability

According to previous studies,[6] 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 PVA and Ketones

The reaction between PVA and ketones proceeds as follows:
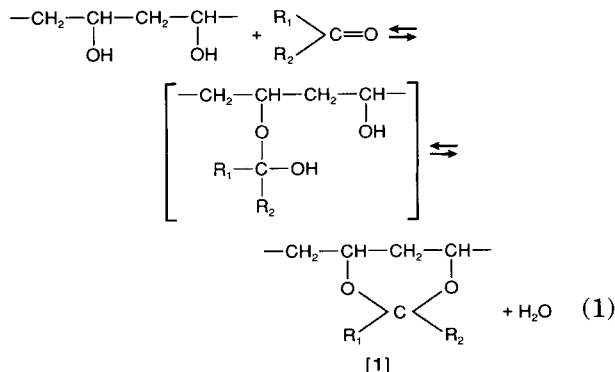
Table III   Solubilities of Various PVKL

		PhA						BzA						Acetophenone
						Ketalization Degree (mol %)								
Solvent	Temp. (°C)	7.0	11.9	17.0	27.5	42.0	54.6	4.5	8.9	17.6	26.3	41.7	55.3	6.5
100% ROH	20	X	X	X	X	X	X	X	X	X	X	X	X	X
	60	X	X	X	X	X	X	X	X	X	X	X	X	X
80% ROH	20	X	X	△	△	X	X	X	△	△	X	X	X	△
	60	△	O	O	O	X	X	X	△	O	O	X	X	△
50% ROH	20	△	△	△	X	X	X	X	△	X	X	X	X	△
	60	O	O	O	X	X	X	O	O	X	X	X	X	O
25% ROH	20	△	△	△	X	X	X	△	X	X	X	X	X	△
	60	O	△	△	X	X	X	O	X	X	X	X	X	△
DMSO	20	O	O	O	O	O	O	O	O	O	O	O	O	O
	60	O	O	O	O	O	O	O	O	O	O	O	O	O
DMF	20	△	△	△	△	O	O	X	△	△	△	O	O	△
	60	△	△	O	O	O	O	△	△	O	O	O	O	△
THF	20	X	X	X	X	X	X	X	X	X	X	△	△	X
	60	X	X	X	X	X	△	X	X	X	X	△	△	X
Dioxane	20	X	X	X	X	X	X	X	X	X	X	△	△	X
	60	X	X	X	X	X	△	X	X	X	X	△	△	X
Benzene	20	X	X	X	X	X	X	X	X	X	△	△	△	X
	60	X	X	X	X	X	X	X	X	X	△	△	△	X

ROH, alcohol; O, soluble; △, swelling; X, insoluble.

Table IV   Relation Between Complete Dissolution Time and pH with PVKL (PhA) at 37°C

Sample (mol %)		pH 2.00	3.00	3.50	4.00
7.0	t	NC	NC	NC	NC
	x	NC	NC	NC	NC
11.9	t	242	2641	10084	NC
	x	11.9	11.2	11.1	NC
17.0	t	456	4565	17783	NC
	x	15.5	15.7	17.6	NC
27.5	t	1300	12580	NC	
	x	28.0	31.0	NC	
38.0	t	14280	NC		
	x	38.5	NC		
57.6	t	NC			
	x	NC			

t, dissolution time (min); x, deketalization degree (mol %); NC, no complete dissolution.

Table V   Relation Between Complete Dissolution Time and pH with PVKL (BzA)

Sample (mol %)		pH 2.00	3.00	3.50	4.00
4.5	t	NC	NC	NC	NC
	x	NC	NC	NC	NC
8.9	t	218	2920	11042	
	x	8.0	7.3	8.0	
17.6	t	1256	11417	48479	NC
	x	15.8	15.4	16.2	NC
26.3	t	2658	35400	150802	NC
	x	23.7	24.9	27.9	NC
31.5	t	3900	40560	159640	NC
	x	29.7	29.9	29.6	NC
41.7	t	9711	127980	NC	
	x	41.7	39.0	NC	
55.3	t	18534	NC		
	x	53.7	NC		

t, dissolution time (min); x, deketalization degree (mol %); NC, no complete dissolution.

$$-CH_2-CH-CH_2-CH- \quad + \quad {R_1 \atop R_2}{>}C{=}O \rightleftharpoons$$

$$\left[\begin{array}{c} -CH_2-CH-CH_2-CH- \\ | \quad\quad\quad | \\ O \quad\quad\quad OH \\ | \\ R_1-C-OH \\ | \\ R_2 \end{array} \right] \rightleftharpoons$$

$$-CH_2-CH-CH_2-CH- $$
$$R_1{>}C{<}R_2 \quad + H_2O \quad (1)$$

[1]

Because no PVKL was formed in the reaction system using water as solvent, the ketalization reaction between PVA and ketones was carried out in a homogeneous system in DMSO. The ketalization reaction proceeds rather rapidly, and it was found that in 24 h equilibrium was 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. The 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 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 PVA mol).

The values of K for PhA and BzA are ca. 0.12 at 40°C. This value is higher than the values for aliphatic ketones, 0.01–0.07,[3] and smaller than the values for cyclic ketones, 0.35–0.50.[4] However in the case of acetophenone, maximum ketalization degree is only a few molecular percent and the ketalization reaction with benzophenone does not proceed at all. Steric hindrance of bulky side chain of ketones, such as a benzene ring combined to carbonyl group di-
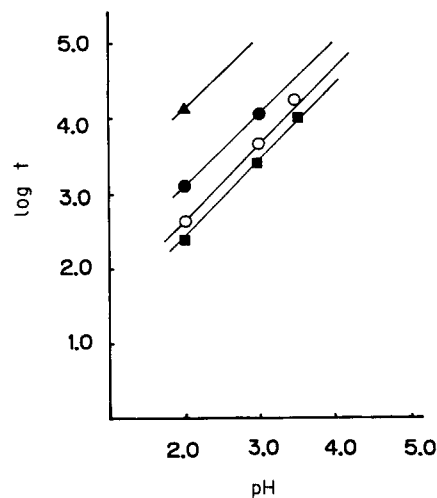

Figure 2 Dependency of hydrolysis rate in the case of PVKL (PhA) at various pH at 37°C: (■) 11.9 mol %; (○) 17.0 mol %; (●) 27.5 mol %; (▲) 38.0 mol %.
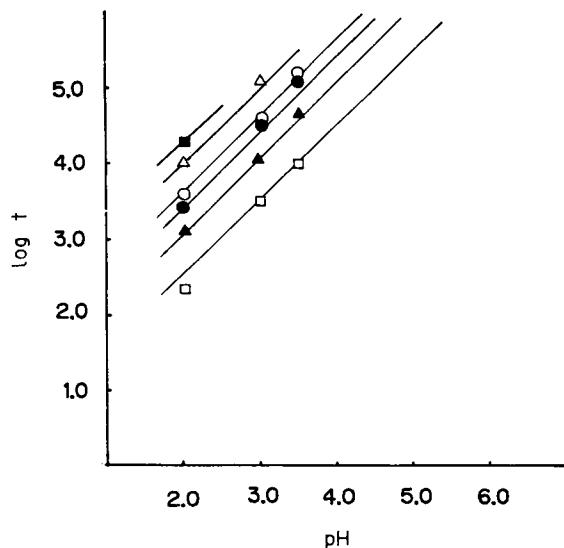
Figure 3 Dependency of hydrolysis rate in the case of PVKL (BzA) at various pH at 37°C: (□) 8.9 mol %; (▲) 17.6 mol %; (●) 26.3 mol %; (○) 31.5 mol %; (△) 41.7 mol %; (■) 55.3 mol %.

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

To obtain the maximum ketalization degree of PVKL, the ketalization reaction was carried out at 25°C with ketone equivalent 36.00, for 100 h, and the results are listed in Table II. As previously mentioned,[1,3] in the case of acetone the ketalization degree was ca. 70 mol %, in the case of tBK it was ca. 35 mol % for steric hindrance of bulky side chain of ketones. In the case of aromatic ketones, ketalization degree for PhA is higher than that for BzA. Because the side chain of BzA is flexible, it seems to interfere with the ketalization reaction between neighboring OH groups. Also as shown in Table I, in the case of ketalization reaction by BzA at 30°C with ketone equivalent 6.00, ketalization degree was 54.7 mol %, then the value of K was only 0.12 and smaller than the value 0.18 expected. Clearly, this is due to the maximum ketalization degree of ca. 55 mol %.

Solubility in Various Solvents

The solubilities of various PVKL in various solvents are listed in Table III. All ketal samples and PVA dissolved in DMSO, which shows it is the best solvent for carrying out a homogeneous reaction. The solubilities of PVKL (aromatic ketones) were different from those of PVKL (aliphatic ketones).

Methanol and ethanol give identical results. Therefore, these will be expressed as alcohol in the following: PVKL (aromatic ketones) of ketalization degree 5–10 mol % dissolved in 50% alcohol, 20–30
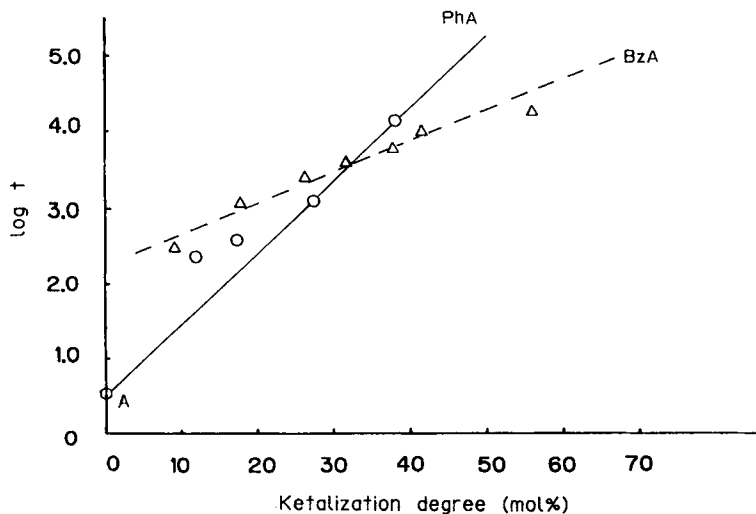
rectly, seems to affect the ketalization reaction. Figure 1 shows the temperature dependence of the equilibrium constant. The heat of reaction determined from the slope of the line is 7.5 kcal/mol, the same as that of aliphatic ketones, cyclic ketones, or various aldehydes. It can be interpreted that the ketalization reaction of aromatic ketones proceeds according to an identical mechanism as the ketalization reaction of aliphatic ketones, cyclic ketones, and the acetalization reaction of various aldehydes.[1-4]

Figure 4 Relation between hydrolysis rate and ketalization degree at pH 2.00 and 37°C: (○) PhA and (△) BzA.
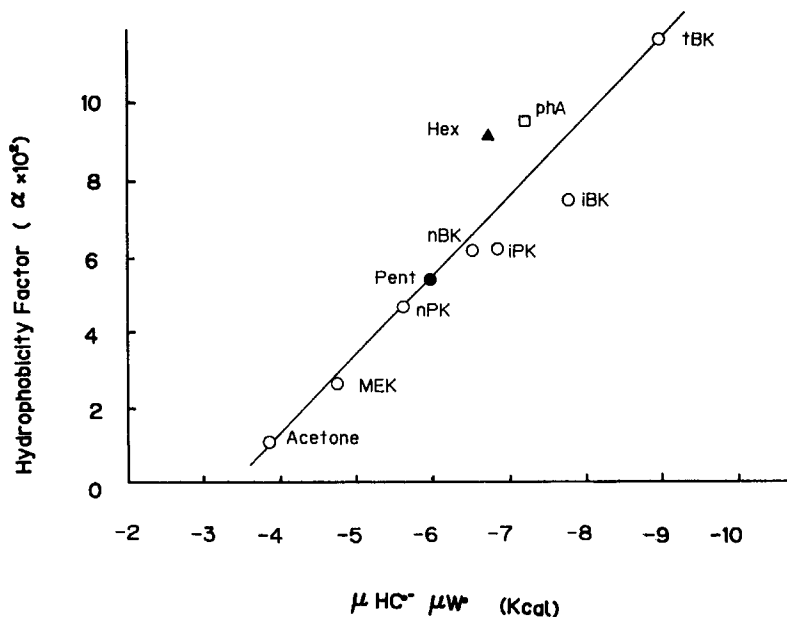
Figure 5 Relation between hydrophobicity factor α and the difference between the free energy of interactions with the solvents of the corresponding alkanes and aromatic and cyclic hydrocarbons.

mol % in 80% alcohol. This behavior is nearly equal to that of PVKL (aliphatic ketones).

When the ketalization degree is above 40 mol %, PVKL (aromatic ketones) did not dissolve in 100% alcohol at all. This behavior is nearly equal to that of PVKL (cyclic ketones).

PVKL (aromatic ketones) of high ketalization degree, dissolved in dimethylformamide (DMF) but did not dissolve in tetrahydrofuran (THF), dioxane, benzene.

In nonpolar solvents such as acetone, ether, ethyl acetate, etc., all samples are insoluble.

Effect of Acidity on Hydrolysis of PVKL

The relation 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 (PhA) are listed in Table IV and those of PVKL (BzA) are listed in Table V.

In Figures 2 and 3, in accordance with the results in Tables IV and V, respectively, the logarithm of dissolution time is plotted against pH values, as reported previously.[2-5]

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

$$\log t = pH + \text{const.} \tag{3}$$

These linearities indicate that the deketalization reaction rate is proportional to hydrogen ion con-

centration [H$^+$], in a manner similar to that of aliphatic ketones.

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.

In the case of PhA, even though there is some deviation at low ketalization degree, linear line of slope = α was obtained, which can be expressed as

$$\log t = \alpha X + \text{const} \tag{4}$$

where X = ketalization degree, α = hydrophobicity factor, and const = logarithm of dissolution time of ideal complete amorphous PVA. The reason for deviation at low ketalization degree is mentioned later. This linearity indicates that the deketalization reaction rate is proportional to the hydrophobicity of ketones; α seems to represent the hydrophobicity factor of ketones. This linear line comes across to point A and this point indicates the logarithm of dissolution time of ideal complete amorphous PVA film. This result coincides with that of aliphatic ketones and cyclic ketones. The α value of PVKL (PhA) is 9.5×10^{-2}.

On the contrary, in the case of BzA, a linear line of slope of α was obtained. However, this linear line did not come across to point A. PVKL (BzA) with high ketalization degree is hydrolyzed easily and that with low ketalization degree is not hydrolyzed

Table VI   Contact Angle and Surface Free Energy (erg cm⁻¹) of Various PVKL at 25°C

Sample	Ketalization Degree (mol %)	θH_2O	θMI	γ_s^d	γ_s^p	γ_s
PVA	0	40.7	31.9	31.2	28.1	59.3
PhA	7.0	45.9	41.2	27.6	27.1	54.7
	17.0	57.8	43.9	28.4	18.7	47.1
	25.7	61.2	46.8	27.5	17.0	44.5
	27.5	59.4	44.1	28.7	17.6	46.3
	38.0	65.0	35.0	34.8	11.5	46.3
	42.0	63.0	33.0	35.2	12.5	47.7
	54.2	64.8	31.7	36.3	11.1	47.4
	61.5	67.3	29.9	37.8	9.3	47.1
BzA	4.5	62.8	40.5	31.4	14.2	45.6
	8.9	59.0	48.0	26.4	19.0	45.4
	17.6	60.5	40.7	30.8	15.9	46.7
	26.3	60.1	42.1	30.1	16.4	46.5
	31.5	58.0	36.4	32.4	16.6	49.0
	41.7	59.5	42.1	29.8	16.9	46.7
	55.3	60.3	42.0	30.0	16.3	46.3
Acetophenone	6.5	59.8	41.2	30.3	16.5	46.8

easily compared with PVKL (PhA). The reason is not clear. It seems that the attack of [H⁺] to the ketal group is difficult, because the side chain ($-CH_2-CH_2-\phi$) of BzA is flexible at a low ketalization degree, whereas the bulky side chain of BzA seems to become inflexible for the steric hindrance at a high ketalization degree, to cause easy hydrolysis. In the case of PhA, although the flexibility of the side chain is less than that of BzA, the same phenomenon may occur to a small degree. Thus some deviation from linearity in Figure 4 at a low ketalization degree is recognized.

The hydrophobicity of hydrocarbon is evaluated in terms of the transfer of hydrocarbon molecules from water to a purely hydrocarbon solvent.[9] In Fig-
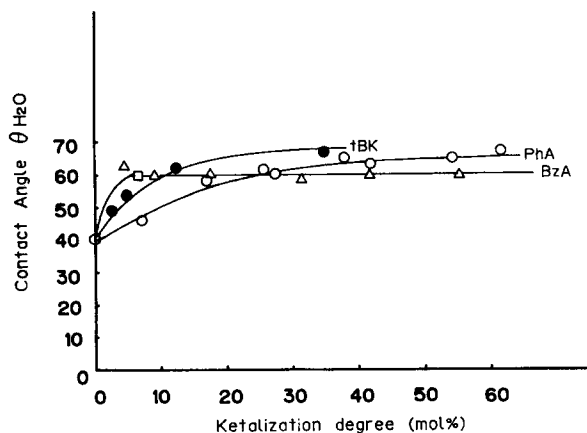
ure 5, in accordance with the above result and the results of aliphatic ketones and cyclic ketones,[4] hydrophobicity factor α is plotted against $\mu \hat{H} C - \mu \mathring{W}$ (difference between the free energy of interaction with the solvent for the corresponding alkanes).[9] The value of PhA, −7194 cal/mol, was calculated from the value of toluene, −5430 cal/mol.[9]

Even though the α value of PhA was a little higher than that of the value expected for $\mu \hat{H} C$-$\mu \mathring{W}$ for all aliphatic ketones, cyclic ketones, and aromatic ketones except BzA, a linear line was obtained. This linearity indicates that α values are proportional to the hydrophobicity of ketones.
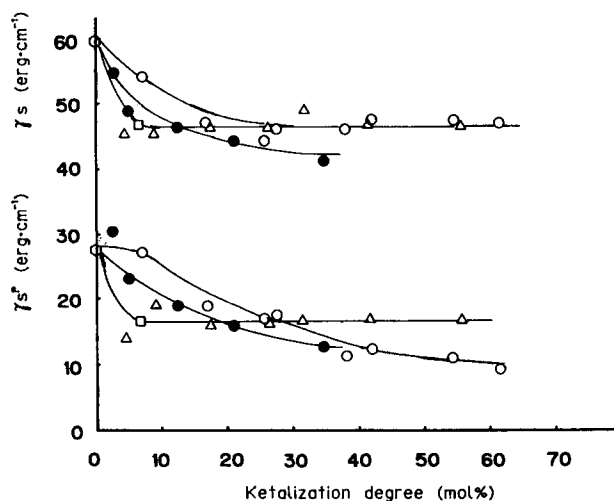

Figure 6   Contact angle (H_2O) of various PVKL at 25°C: (O) PhA; (△) BzA; (□) acetophenone; (●) tBK.

Figure 7 γ_s and γ_s^p of various PVKL at 25°C: (O) PhA; (△) BzA; (□) acetophenone; (●) tBK.
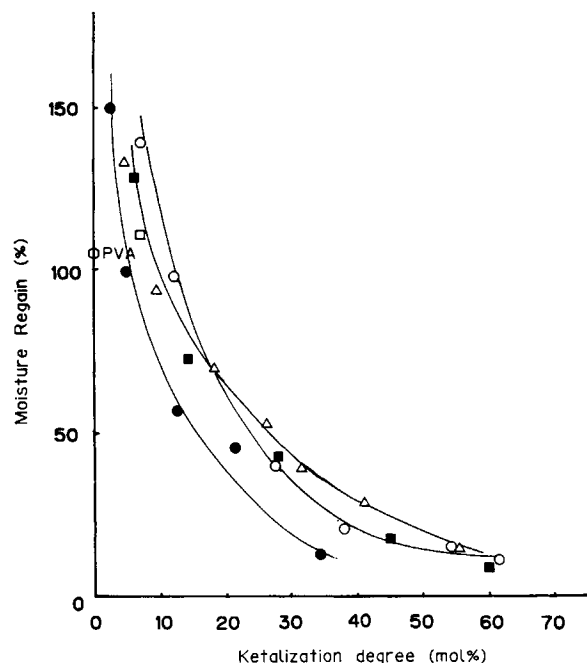
Figure 8   Moisture regain of various PVKL at 25°C, RH 100%: (O) PhA; (△) BzA; (□) acetophenone; (■) nBK; (●) tBK.

However, for Hex and PhA, α values were not laid on the straight line and were not higher than the values expected for $\mu \mathring{H}C - \mu \mathring{W}$, which means that PVKL (Hex) and PVKL (PhA) are not hydrolyzed easily. This is explained by taking into account that the cyclohexane ring and side chain of PhA are flexible and the ketal ring for PVKL (Hex) and PVKL (PhA) are protected against the attack of [H$^+$].

The hydrolysis of PVKL film proceeds in the following order:

acetone > MEK > nPK > Pent > iPK $\doteqdot$ nBK

> iBK > Hex > PhA > tBK.
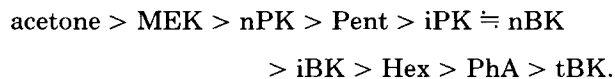
Contact Angle of Film Surface

The contact angle of the film surface by water (θH$_2$O) and MI (θMI) were measured. From θH$_2$O and θMI, surface free energy γ_s (hydrophobic component, γ_s^d; hydrophilic component, γ_s^p) were calculated. The results obtained are listed in Table VI. The relationship between ketalization degree and θH$_2$O are shown in Figure 6.

The θH$_2$O of PVKL (PhA) increased proportionally to the ketalization degree as well as for PVKL (aliphatic ketones)[6] and PVKL (cyclic ketones).[4] However, the θH$_2$O of PVKL (BzA) were constant as ketalization degree increased. To confirm this result, the relationship between ketalization degree and γ_s and γ_s^p are shown in Figure 7.

For comparison with PVKL (aliphatic ketones), the values of PVKL (tBK) are also plotted. In the case of PVKL (PhA), γ_s decreased as ketalization degree increased. γ_s^p showed the same tendency except the ketalization degree of ca. 5 mol % as that of PVKL (aliphatic ketones) and PVKL (cyclic ketones). However, the γ_s^p of PVKL (BzA) are nearly constant in spite of any ketalization degree. These phenomena show that hydrophobicity of PVKL (BzA) film surfaces is not high, even at a high ketalization degree. This result coinciding with that the hydrolysis of PVKL (BzA), is not in accord with eq. (4). The reason is not clear, but it seems that water molecules attack the ketal group easily because the side chain of BzA becomes inflexible for the steric hindrance at a high ketalization degree.
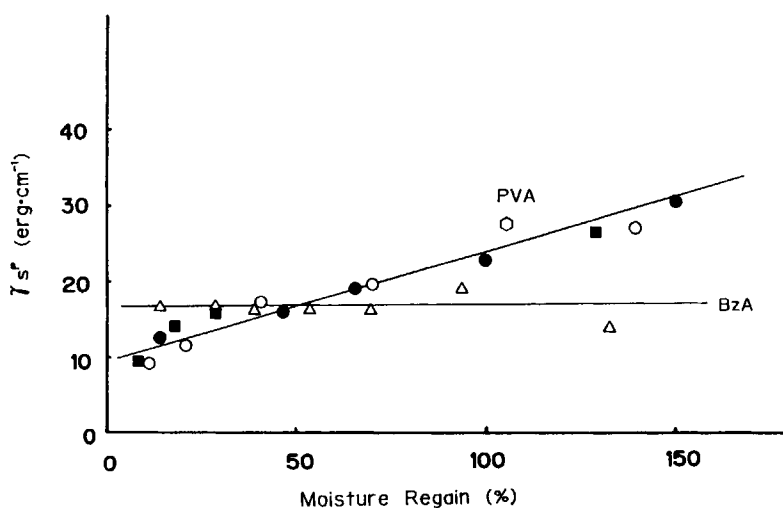

Figure 9   Relation between moisture regain and γ_s^p: (O) PhA; (△) BzA; (■) nBK; (●) tBK.
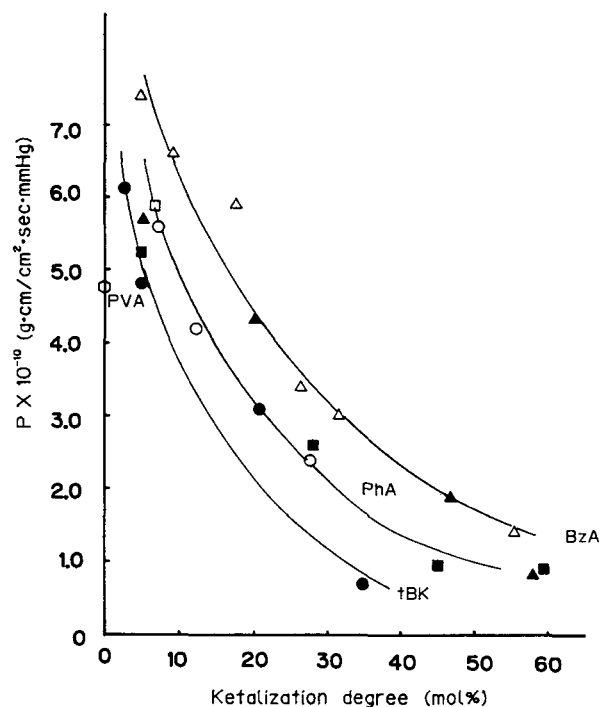
Figure 10 Water vapor permeability coefficient (P) of various PVKL at 25°C: (O) PhA; (△) BzA; (□) aceto-phenone; (▲) nPK; (■) nBK; (●) tBK.

Moisture Regain

The moisture regain of various PVKL (aromatic 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 PVA. This is consistent with that for PVKL (aliphatic ketones)[5] and PVKL (cyclic ketones),[4] except for PVKL (acetone, MEK).

The moisture regain of PVKL (PhA) and PVKL (BzA) are nearly equal to that of PVKL (nBK). However, at low ketalization degree the moisture regain of PVKL (PhA) is a little higher than that of PVKL (BzA) and at high ketalization degree reverse results are obtained.

As previously reported,[6] the values for moisture regain of various PVKL are plotted against γ_s^p in Figure 9. The relationship between γ_s^p and moisture regain is represented by the same straight line ir-

respective of the kind of PVKL and ketalization degree. Clearly, γ_s^p decreases as the hydrophobicity of polymer increases. However, in the case of PVKL (BzA), the values of γ_s^p are constant as the moisture regain changed. These results are similar to those for hydrolysis as mentioned in the introduction.

Water Vapor Permeability

The water vapor permeabilities of various PVKL are shown in Figure 10. The P values of all PVKL with low ketalization degree are higher than that of PVA, which is consistent with the fact that the moisture regains of those PVKL are higher than of PVA. As expected, the water vapor permeability decreased as ketalization degree increased. The P values of PVKL (PhA) is nearly equal to that of PVKL (nBK), the P values of PVKL (BzA) is nearly equal to that of PVKL (nPK), and the P values of PVKL (BzA) is higher than that of PVKL (PhA).

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