Study on Ketalization Reaction of Polyvinylalcohol by Ketones. III. Reaction between Polyvinylalcohol and Methyl Ethyl Ketone and Behavior of Polyvinylketal in Water

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Synopsis

Ketalization reaction of polyvinylalcohol (PVA) by methyl ethyl ketone (MEK), dimethyl-sulfoxide (DMSO) as solvent, under the presence of acidic catalyst, in homogeneous system was carried out, and the synthesis of polyvinylketal with any ketalization degree was successfully performed. The reaction mechanism of PVA with MEK is identical with that with acetone: for both cases, the equilibrium constant is ca. 0.07 at 40°C and the heat of reaction is 7.5 kcal/mol. Films prepared from the polyvinylketal were soaked in water and degree of swell, solubility, and hydrolysis of films were measured. The reaction of film with water, in acidic side, easily proceeds, and at first the film swells; then, as deketalization reaction proceeds, the film dissolves in water. With polyvinylketal of the ketalization degree of above 15 mol %, dissolution time is controlled by both ketalization degree and pH of water, which reveals that deketalization reaction proceeds proportionally to proton concentration at 37°C. On the other hand, in the neutral condition where hydrolysis does not proceed at all, polyvinylketal of ketalization degree of 10–40 mol % dissolves in water at 0°C. The polyvinylketal obtained by MEK is more stable in water than that from acetone since MEK has hydrophobicity.

INTRODUCTION

As mentioned in the previous report,[1] polyvinylketal with any ketalization degree was successfully obtained from PVA and acetone, 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). It became clear as well[2] that polyvinylketal films deketalyzed easily and dissolved in acidic water, while in neutral or alkaline conditions hydrolysis did not proceed at all.

This paper is concerned with the acid-catalyzed synthesis of polyvinylketal from MEK, as another ketone, in homogeneous system, the solubilities in various solvents, and the deketalization reaction in acidic water. Also, these behaviors are compared with that of polyvinylketal from acetone.

EXPERIMENTAL

Samples and Reagents

PVA of average degree of polymerization 1800, saponification degree above 99.4% (NH-18 from Nihon Gosei Co., Ltd.) was used. DMSO (water content 0.05%), *p*-toluenesulfonic acid (PTS), and methyl ethyl ketone (MEK), all guaranteed reagents (Nakarai Kagaku Co., Ltd.), were used without further purification. 2-Ethyl-2,4-dimethyl-1,3-dioxane, as a model compound for structural analysis, was obtained from 1,3-butanediol and MEK.[3]

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 MEK were added, and the mixture was kept at the prescribed temperature under vigorous shaking. The reaction from beginning to end proceeds in homogeneous system. After a certain period, the reaction mixture was neutralized by a $1N$ NaOH aqueous solution, and then the reaction product was precipitated with either ethyl acetate or water, and dried under vacuum. The polymer thus obtained was dissolved in methanol (refer to Table II), precipitated by either ethyl acetate or water, and dried. This procedure was carried out twice.

Analysis Method

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

Solubility in Organic Solvents

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

Structure of Reaction Products

The structure of the products was determined by ^{1}H- (90 MHz) and ^{13}C-NMR (22.5 MHz) spectroscopy (JNM-FX90Q) in $(CD_3)_2SO$.

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.[2] During film preparation, hydrolysis of PVKL is not observed.
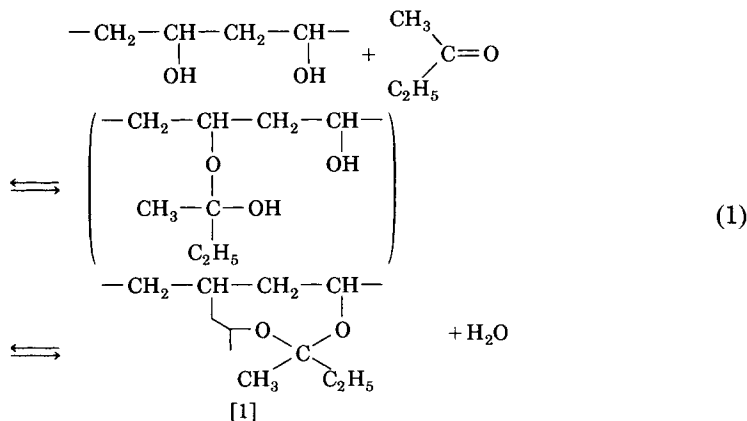
Behavior of PVKL in Water

Samples were soaked in water of various pHs kept at prescribed temperatures. Prescribed hours later, the film is removed from water and the degree of swell, solubility, deketalization degree, and the time needed for complete

dissolution of film were measured according to the method described previously.[2]

RESULTS AND DISCUSSION

Mechanism of Ketalization Reaction between PVA and MEK

The reaction between PVA and MEK seems to proceed as follows.

$$
\begin{array}{l}
-CH_2-CH-CH_2-CH- \quad \overset{CH_3}{\underset{C_2H_5}{\diagdown}}C{=}O \\
\qquad\quad OH \qquad\quad OH \\
\\
\left(\begin{array}{l}
-CH_2-CH-CH_2-CH- \\
\qquad\quad O \qquad\qquad OH \\
\\
\quad CH_3-C-OH \\
\qquad\quad C_2H_5
\end{array}\right) \\
\\
-CH_2-CH-CH_2-CH- \\
\qquad\qquad\diagdown O\diagup C\diagdown O \\
\qquad\quad CH_3 \quad C_2H_5 \\
\qquad\qquad [1]
\end{array}
\quad +H_2O
$$

(1)

Since in the reaction system using water as solvent, no PVKL was formed, the ketalization reaction between PVA and MEK was carried out in homogeneous system in DMSO. The ketalization reaction proceeds rather rapidly, and it was found that in 2–3 h equilibrium is reached. The reactions were further carried out for more than 24 h, reaction equilibrium was confirmed, and the equilibrium ketalization degrees were determined. From the values, in accordance with eq. (2), the equilibrium constant K was calculated. Results

TABLE I
Equilibrium Constants of Ketalization Reaction

Temp (°C)	PVA (mol/L)	MEK (eq)	PTS (g/L)	Ketalization[a] (mol %)	K[b]
40	0544	0.397	2.90	13.6	0.082
	0.520	0.450	2.51	15.8	0.102
	0.395	1.30	2.55	23.2	0.066
	0.434	2.97	7.07	35.4	0.074
	0.354	5.50	9.77	41.3	0.057
	0.359	6.52	2.30	49.2	0.079
	0.248	36.0	2.71	71.1	0.050
30	0.494	1.50	2.47	31.7	0.108
	0.420	3.00	2.04	40.0	0.111
	0.476	6.00	2.49	51.7	0.101
25	0.377	6.00	6.07	55.4	0.126
	0.180	36.0	1.19	84.2	0.128
50	0.374	6.00	6.05	41.5	0.053

[a] Equilibrium ketalization degree.
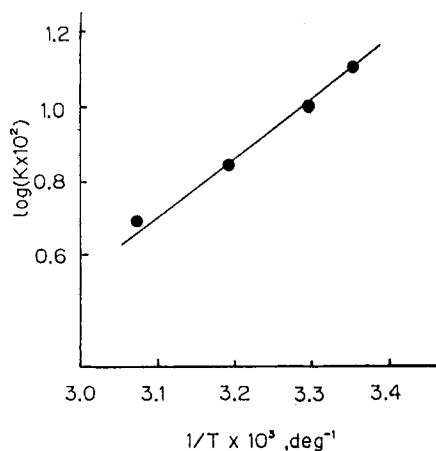[b] Equilibrium constant.

Fig. 1. Temperature dependency of equilibrium constant K.

obtained are listed in Table I:

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

Suppose a (mol/L) = PVA initial concentration [value obtained against two basic PVAs (mol)], b (mol/L) = MEK initial concentration, x (mol/L) = PVKL concentration, $X = x/a$, ketalization degree, and $E = b/a$, MEK equivalent [mole ratio MEK against two basic PVAs (mol)]. The values of K for MEK are ca. 0.05 at 50°C, ca. 0.07 at 40°C, ca. 0.10 at 30°C, and ca. 0.13 at 25°C, which are equal to that for acetone.

Figure 1 shows the temperature dependence of the equilibrium constant of the reaction between PVA and MEK. 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 MEK proceeds according to identical mechanisms with the ketalization of acetone and acetalization reactions of various aldehydes.[1]

Structural Analysis by ^{1}H- and ^{13}C-NMR Measurement

To confirm that ketalization reaction of PVA by MEK was carried out shown eq. (1), the structure of the product was examined.

Figure 2 shows the ^{1}H-NMR spectra of PVA (A) and the ketalization product (B) ketalization degree 84.2 mol %. Upon ketalization the absorption of the hydroxyl groups (4.74, 4.56, and 4.32 ppm) decreased, and the absorption attributed to methyl and ethly groups of the ketal unit [~0.9 ppm

$(-\overset{|}{\underset{|}{C}} - CH_2CH_3)$ 1.3–1.5 ppm $(CH_3 - \overset{|}{\underset{|}{C}} - CH_2CH_3)$] in turn appeared, and

no signals assignable to other structures could be detected. The ^{13}C-NMR spectrum of the ketalization product was identical with that of the corresponding model (2-ethyl-2,4-dimethyl-1,3-dioxane). According to these NMR results, the structure of the ketalization product was confirmed to be [1] in eq.
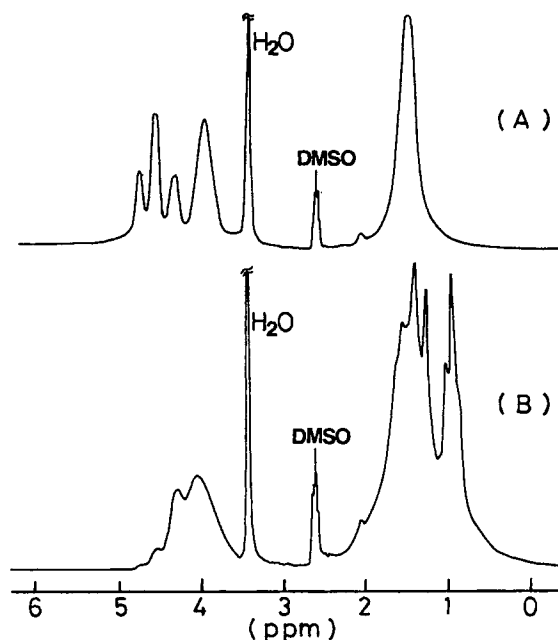
Fig. 2. ^{1}H-NMR spectrum of PVA and polyvinylketal: (A) PVA; (B) polyvinylketal (MEK) (ketalization degree 84.2 mol %).

(1). Moreover, we confirm that hemiketals which were produced by addition of a MEK molecule to each OH group did not exist, since quaternary carbon atoms of hemiketal [$-O-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-OH$ (ca. 91 ppm)] were not detected, by means of a ^{13}C-NMR spectrum of product.

Solubility in Various Solvents

The solubilities of PVKL of various ketalization degrees (2.9–84.2 mol %) and PVA in various solvents are listed in Table II.

In DMSO, all ketal samples excluding PVA dissolved, which shows it is the best solvent for carrying out homogeneous reaction; in DMF, all samples dissolved at high temperature (60°C). In nonpolar solvents such as acetone, ether, petroleumether, ethyl acetate, methylenechloride, carbontetrachlorid, cyclohexane, benzene, etc., all samples are insoluble. 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 determind. As it is clear from Table II, PVKL becomes soluble in alcohol while the proportion of OH groups in the polymer decreases. As alcohols, both methanol and ethanol were tried; identical behavior was observed. At the same ketalization degree, PVKL of MEK [PVKL(MEK)] appears to have lower solubilities in organic solvent as compared with PVKL of acetone [PVKL(acetone)].

TABLE II
Solubilities of Various Polyvinylketals

Solvent	Temp (°C)	Ketalization degree (mol %)[a]									
		0	2.9	15.8	23.8	31.7	39.1	49.5	77.1	84.2	49.4[b]
100% ROH[c]	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] ○ = soluble; △ = swelling; × = insoluble.
[b] PVKL(acetone).
[c] ROH; alcohol.

Behavior of PVKL(MEK) of Different Degrees of Ketalization in Acidic Water

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

The results listed in Figures 3–5 are similar with case of PVKL(acetone).[2] The behavior of the film in water depends strongly on ketalization degree, and
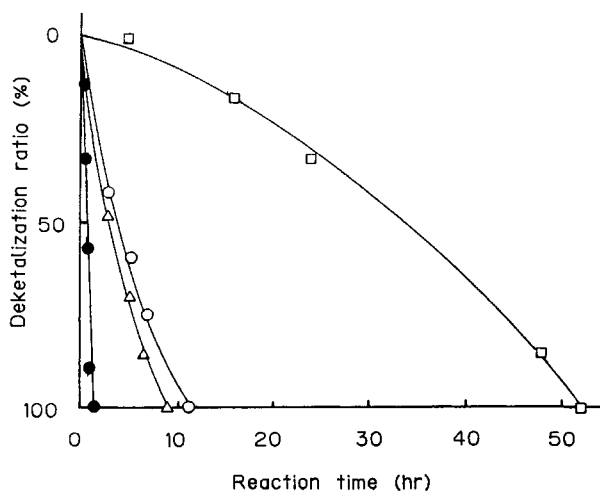

Fig. 3. Hydrolysis of various PVKL in water of pH 3.00 at 37°C: (△) PVKL(MEK) 41.3 mol %; (○) PVKL(MEK) 49.2 mol %; (□) PVKL(MEK) 84.2 mol %; (●) PVKL(acetone) 49.4 mol %.
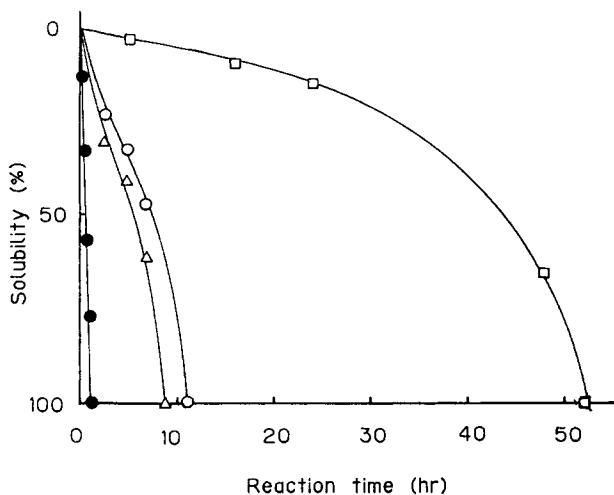
Fig. 4. Solubility of various PVKL in water of pH 3.00 at 37°C: (△) PVKL(MEK) 41.3 mol %; (○) PVKL(MEK) 49.2 mol %; (□) PVKL(MEK) 84.2 mol %; (●) PVKL(acetone) 49.4 mol %.

it is clear that in comparison with PVKL(MEK) of ketalization degree below 50 mol %, the deketalization rate of no. 4 (84.2 mol %) is extremely slow; then after 50 h the film is dissolved. It is considered that as with the PVKL reaction to the maxinum ketalization degree region, because swell and dissolution by water proceed with difficulty, also the proceeding of the hydrolysis reaction becomes difficult.

It turns out from Figures 3–5 that no. 25, PVKL(acetone), swell, deketalizes, and dissolves more rapidly than no. 15, PVKL(MEK), at the same
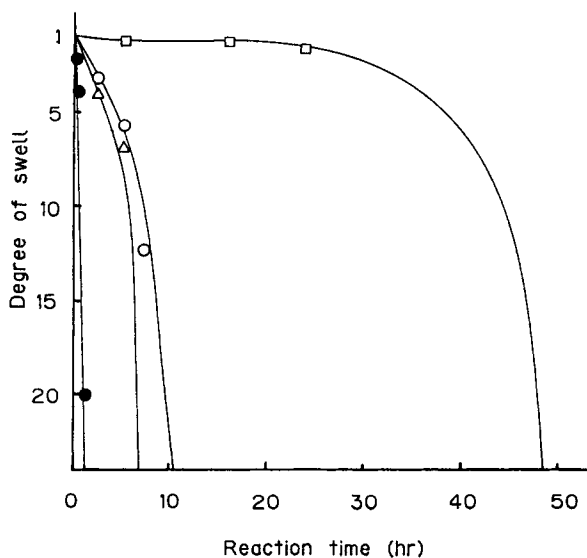

Fig. 5. Degree of swell of various PVKL in water of pH 3.00 at 37°C: (△) PVKL(MEK) 41.3 mol %; (○) PVKL(MEK) 49.2 mol %; (□) PVKL(MEK) 84.2 mol %; (●) PVKL(acetone) 49.4 mol %.

TABLE III

Reaction between Complete Dissolution Time and with Various PVKLs at 37°C[a]

Sample \ pH	2.00	3.00	3.50	4.00	5.00	5.70	12.00
No. 97 t	15.3	43		180		430	△
2.9% x	2.7	2.2		3.0		0	
No. 46 t	6.85	19.75	26.7	58.7	600	600	△
13.6% x	17.1	13.8	12.5	9.0	1.0	0.2	
No. 14 t	9.31	51.2	223.5	1232	10,240	44,460	△
23.2% x	22.4	22.2	24.3	21.9	14.3	14.8	
No. 71 t	25.0	263.9	960	2474	30,240	10,1580	△
31.7% x	29.1	26.9	26.4	27.4	24.1	23.8	
No. 18 t	41.5	540	1716	17,640	○	○	△
41.3% x	40.3	40.8	42.8	38.0			
No. 15 t	45.1	660	3810	28,680	○	○	△
49.2% x	50.6	50.0	46.1	46.5			
No. 4 t	480	3120	10,080	42,120	○	△	△
84.2% x	84.2	83.9	80.0	77.6			
No. 25[b] t	9.87	69.3	265	685	34,560	49,773	△
49.4% x	51.2	50.3	50.6	48.5	40.2	39.3	

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

[b] PVKL(acetone).

ketalization degree (ca. 50 mol %). The PVKL(MEK) is more stable in water than that from acetone since MEK has hydrophobicity.

Effect of Acidity on Hydrolysis of PVKL

The reaction between the time needed for the complete dissolution of PVKL film and pH value of water is listed in Table III. In Figure 6, in accordance with results in Table III, the logarithm of dissolution time is plotted against pH values, as reported previously.[2]

For all samples of ketalization degree above 15 mol %, linear lines of the gradient = 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 concentration [H+], in a manner similar to that of acetone. However, with samples of ketalization degree less than 15 mol %, the data cannot be expressed in eq. (3).

As reported previously,[2] it is made clear that PVKL(MEK) of ketalization degree of less than ca. 15 mol % dissolves in water at higher than pH 5.00 at 37°C without any hydrolysis, and that of 23.2 mol % of 31.7 mol % dissolves in water under the same condition accompanying with incomplete hydrolysis, when PVKL is deketalized to the residual ketalization degree of less than 10 mol %. The phenomenon is similar to that found with acetone.

In the case of acetone, PVKL of less than 20 mol % ketalization degree is complete soluble in neutral water without any hydrolysis. PVKL of less than 66 mol %, which is the maximum value of ketalization degree we could obtain,
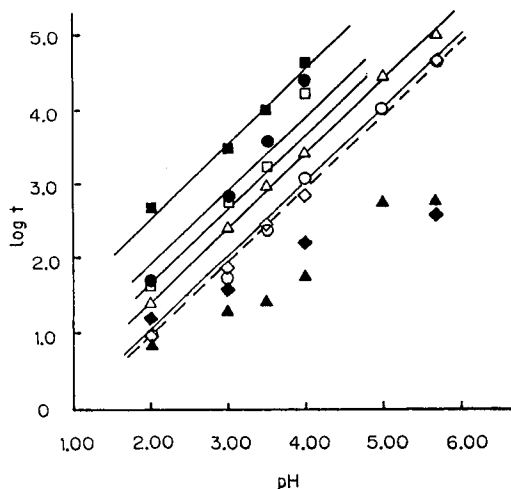
Fig. 6.   Dependency of hydrolysis rate on pH values at 37°C: (◆) No. 97 (2.9 mol %); (▲) No. 46 (13.6 mol %); (○) No. 14 (23.2 mol %); (△) No. 71 (31.7 mol %); (□) No. 18 (41.3 mol %); (●) No. 15 (49.2 mol %); (■) No. 4 (84.2 mol %); (◇) No. 25 acetone (49.4 mol %).

become soluble in neutral water with incomplete hydrolysis.[2] Whereas that from MEK of more than 40 mol % is not soluble in neutral water, the PVKL(MEK) is more stable in water than that from acetone since MEK has hydrophobicity.

However, PVKL(MEK) no. 97 (2.9 mol %) at ketalization degree less than 5 mol % is completely soluble in water, different from PVKL(acetone) at the same ketalization degree. In the cases of PVKL(MEK), because some MEK groups are added to PVA, crystallinity is lower than that made with acetone.

Effect of Temperature on the Rate of Hydrolysis

In order to study the effect of temperature for the case of dissolution accompanied by hydrolysis, dissolution of PVKL in water of pH value of 3.50 was studied at various temperatures. In Figure 7 logarithms of reciprocal of dissolution times, as a function of deketalization reaction rate, are plotted against temperature. The apparent activation energies of deketalization reactions obtained are as follows: no. 46, 7.8 kcal/mol; no. 18, 18.3 kcal/mol; no. 4, 20.9 kcal/mol. It can be observed that, in such heterogeneous reactions, the lower the initial ketalization degree, the easier the deketalization proceeds, and apparent activation energy of PVKL(MEK) is higher than that of PVKL(acetone) at the same ketalization degree.

Effect of Temperature on the Solubility in Neutral Water

As described in the previous paper,[2] in water close to neutral, PVKL(acetone) dissolves without hydrolysis. Figure 8 shows the solubility in water of pH 5.70 and the cloud point of various PVKL(MEK). The area within points A, B, C, and D is the region where PVKL(MEK) dissolves in water without being hydrolyzed. Comparison with the region where PVKL (acetone) dissolves in water without hydrolysis, the area within points A, E, F,
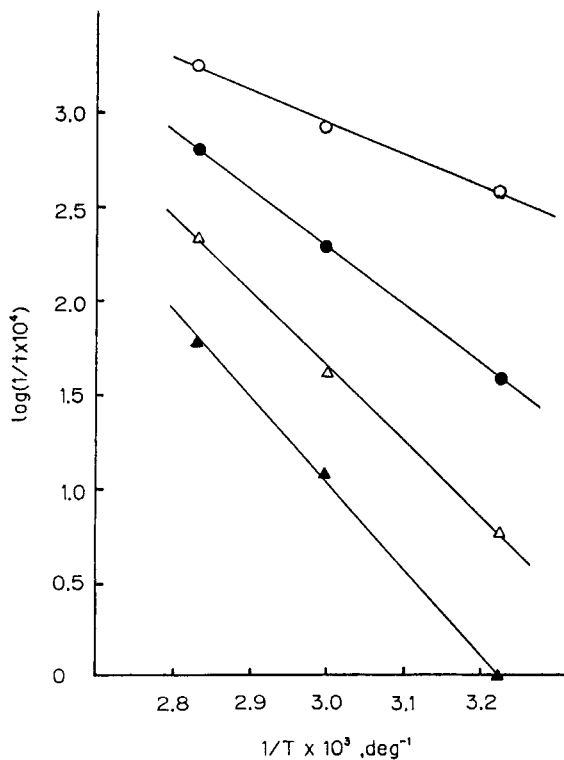
Fig. 7.   Temperature dependency of deketalization reaction: (○) No. 46 (13.6 mol %); (△) No. 18 (41.3 mol %); (▲) No. 4 (84.2 mol %); (●) No. 25 acetone (49.4 mol %).
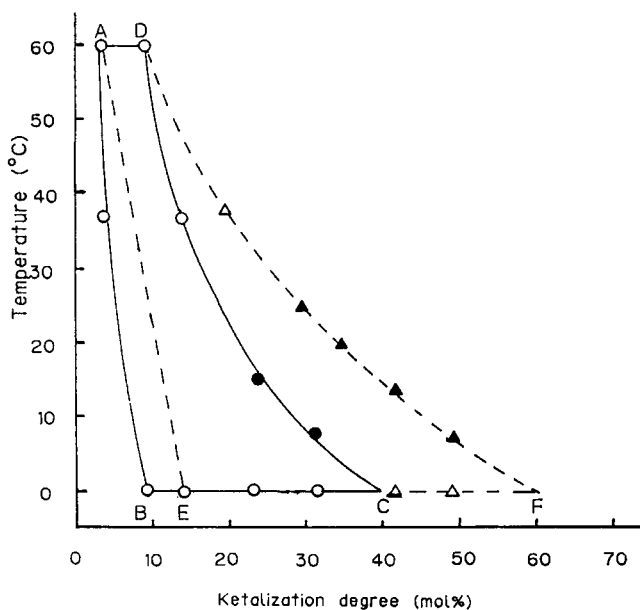

Fig. 8.   PVKL vs. dissolution temperature (case of dissolution proceeding without any hydrolysis): (○) dissolution (MEK); (●) cloud point (MEK); (△) dissolution (acetone); (▲) cloud point (acetone).

and D indicates that PVKL(MEK) exhibited lower solubilities in water than PVKL(acetone). But in the case of lower ketalization degree (5–10 mol %) PVKL(MEK) dissolves in water and PVKL(acetone) does not dissolve in water at low temperatures. The reason why PVKL(MEK) is more soluble is because crystallinity of PVKL(MEK) is lower than that of PVKL(acetone) due to the asymmetric structure of MEK.

There are several speculative explanations for this, but an established theory has not been accepted. The interesting facts that PVKL dissolves in slightly acidic water, even at a relatively low temperature of 37°C, and in water close to neutral without any deketalization at 0°C were made clear.

References

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