Study on Ketalization Reaction of Polyvinylalcohol by Ketones. I. Reaction between Polyvinylalcohol and Acetone

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Synopsis

Ketalization reaction of polyvinylalcohol (PVA) by acetone, dimethylsulfoxide (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. This reaction proceeds in bimolecular reaction, the equilibrium constant is ca. 0.07 at 40°C and roughly 10^{-5} less compared with the acetalization reaction between PVA and aldehydes. Synthesis in aqueous media is difficult. However, the heat of reaction for both cases is 7.5 kcal/mol and both reactions are considered to proceed in an identical reaction mechanism. Ketalization reaction starts from isotactic OH portion and proceeds finally to syndiotactic OH portion, however, 100% ketalization is extremely difficult. The effects of water on reaction was confirmed both from theoretical and experimental viewpoints, and even though the presence of water lowers the degree of ketalization, it was observed that the presence of water below 0.1 mol against 1 mol of PVA will not significantly affect final ketalization degree. Polyvinylketals thus obtained are soluble in DMSO, dimethylformamide (DMF), and alcohols.

INTRODUCTION

Recently studies on synthesis of functional high polymers with specific characteristics by reacting various low molecular weight compounds on polymers have been carried out.[1-4] As PVA has many OH groups bound on it, it is capable of reacting with various low molecular compounds, and therefore, various functional polymers can be obtained with relative ease in this way. One such representative way is the acetalization reaction with various aldehydes. Acetalization reaction with formaldehyde is utilized in the production of synthetic fiber "Vinylon" and PVA acetalized with butylaldehyde is presently widely used as adhesives for safety glass in the industry.

On the other hand, reports on ketalization reaction by ketones are not known outside of an old patent by I. G. Farben AG,[5] reporting successful results with ring ketones such as cyclohexanone. Except for this patent, as reacting ketones directly with PVA is difficult, only reports[6,7] reacting ketones as ketal of alcohol are known, synthesis of ketal monomers seems to be in a similar situation. However, in such methods, maintaining the reaction system from the beginning to the end in a homogeneous system is difficult, therefore, neither kinetic study nor study of the physical properties of the polyvinylketal obtained was made.

The author succeeded in synthesizing polyvinylketal of any ketalization degree through ketalizing PVA with acetone, as a representative ketone, DMSO as reaction media in homogeneous system. As the result, equilibrium

constant, as well as the effect of the presence of water to the reaction was determined and the difference between this ketalization reaction and the acetalization with aldehydes was made clear. Also, solubilities of polyvinyl-ketals in various solvents were studied.

EXPERIMENTAL PROCEDURES

Samples and Reagents

PVA of average degree of polymerization 1800, saponification degree above 99.4% (NH-18 from Nihon Gohsei Co. Ltd) was used. DMSO (Guaranteed reagent, Nakarai Kagaku Co. Ltd) as solvent was used. *p*-Toluene sulfonic acid (PTS) (Guaranteed reagent, Nakarai Kagaku Co. Ltd), thoroughly dried, was used. Acetone (Guaranteed reagent, Nakarai Kagaku Co. Ltd) was used. 2,2,4-Trimethyl 1,3-dioxane, used as model compound was obtained from 1,3-butanediol and acetone.[8]

Synthesis Method

PVA dried at 105°C for more than 2 hours was dissolved in DMSO. The concentration of the solution was prepared to be 4–5 wt%. Then the prescribed amount of catalyst (in most of the experiments PTS was used) was charged and dissolved in the solution. Prescribed amount of acetone being added onto the solution and the resulting solution was kept at prescribed temperature under vigorous shaking. The reaction from beginning to end proceeds in homogeneous system. Prescribed hours later, the reaction mixture was neutralized by 1N NaOH aqueous solution and then the reaction product was precipitated with either ethyl acetate or water and dried. Polymer thus obtained was dissolved in methanol (refer to Table I), precipitated by either

TABLE I
Solubilities of Various Polyvinylketals

Solvent	Temp. °C	Ketalization degree, mol%									
		0	3.5	8.9	15.4	19.5	29.4	34.8	42.0	49.4	65.6
ROH	20	×	×	×	△	△	○	○	○	○	○
	60	×	×	△	△	△	○	○	○	○	○
80% aq. ROH	20	×	×	△	△	○	○	○	○	○	○
	60	×	×	△	○	○	○	○	○	○	○
50% aq. ROH	20	×	×	○	○	○	○	○	○	△	△
	60	×	△	○	○	○	○	○	○	△	△
25% aq. ROH	20	×	△	△	○	○	○	×	×	×	×
	60	△	○	○	○	○	○	△	△	×	×
DMSO	20	△	○	○	○	○	○	○	○	○	○
	60	○	○	○	○	○	○	○	○	○	○
DMF	20	×	△	△	△	△	△	△	○	○	○
	60	△	○	○	○	○	○	○	○	○	○
THF	20	×	×	×	×	×	×	×	△	△	△
	60	×	×	×	×	×	×	×	△	△	○
Dioxane	20	×	×	×	×	×	×	×	×	△	△
	60	×	×	×	×	×	×	×	×	△	○

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

ethyl acetate or water and dried. This procedure was carried out twice. For confirmation, polymer thus purified was quantitatively analyzed with sulfur by the Karius method, but no sulfur was detected and it was verified that both solvent and catalyst were completely removed from the polymer. During polymer purification, the hydrolysis of polyvinylketal was not observed at all.

Analysis Method

The ketalization degree of polyvinylketal was determined by dissolving the sample in DMSO, after perfect deketalizing in acidic range, acetone was quantitatively determined by iodoform method.[9] The iodine consumed by PVA itself has to be deduced from the results. The analysis can be done by ultraviolet (UV) spectrum analysis, as well.

Solubility in Organic Solvents

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

Structure of Reaction Products

The structure of products was determined from nuclear magnetic resonance (NMR) measurement of ^{1}H and ^{13}C with a sample dissolved in $(CD_3)_2SO$, tetramethylsilan as internal standard, by NMR spectrophotometer, JEOL NMR FX90Q.

RESULTS AND DISCUSSION

As with the reaction between PVA and aldehydes,[10] a reaction between PVA and acetone seems to proceed as follows. In order to confirm this, the structure of the product was examined.
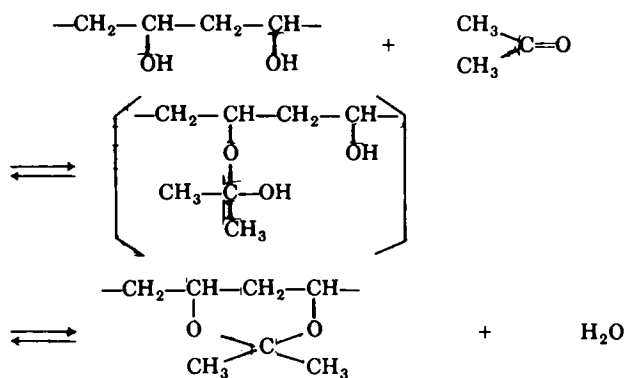
$$\tag{1}$$

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

^{1}H NMR spectrum of PVA, Figure 1(A), of polyvinylketal of different ketalization degrees, 37.4, 68.6 mol% (Fig. 1(B), (C)) are listed.
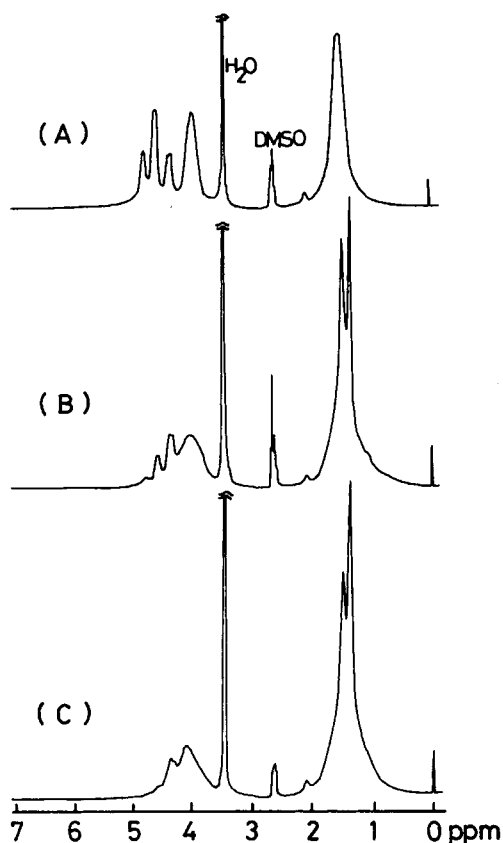
Fig. 1. ^{1}H NMR spectrum of PVA and polyvinylketals. (A) PVA; (B) polyvinylketal (ketalization degree 37.4 mol%); (C) polyvinylketal (ketalization degree 68.6 mol%).

Absorption attributed to —OH groups at 4.74, 4.56, and 4.32 ppm (isotactic, heterotactic, and syndiotactic structures, respectively)[11] decreased, instead at around 1.3 ppm, the absorption attributed to methyl groups of polyvinylketal appeared and thus the structure of the product is confirmed to be that of polyvinylketal in formula (1). The ketalization degree of sample (C) obtained from ratio of areas of absorption peaks is ca. 70 mol% and shows the satisfactory coincidence with 68.6 mol% determined by iodoform method.

From the change of —OH absorptions in 4.3–4.7 ppm, it is understood that the ketalization reaction starts from the isotactic portion and then at the latter stage of reaction takes place at the syndiotactic portion. The results from ^{13}C NMR spectrum coincides satisfactorily with that of product struc-
tures as shown in formula (1) [δ (ppm); 97.6 (—O— $\overset{|}{\underset{|}{C}}$ —O—), 63.6 (main chain, CH), 45.3 (main chain, CH$_2$), 30.4 (equatorial CH$_3$), 20.0 (axial CH$_3$)].

Moreover, we confirm that hemiketals which were produced by addition of an acetone molecule to each OH group did not exist, since quaternary carbon atoms of hemeketal [—O— $\overset{|}{\underset{|}{C}}$ —OH (ca. 89 ppm)] were not detected, by

means of a ^{13}C NMR spectrum of the product. However, in a ^{13}C NMR spectrum of highly ketalized polymers (e.g., the sample of Fig. 1(C)) small absorptions (99.5, 24.8 ppm) in addition to the absorptions mentioned above were observed. These absorptions are close to those quaternary carbon atoms and methyl groups of polyvinylketal. In comparison with a model compound (2,2-dimethoxypropan), these absorptions were assigned to quaternary carbon atoms and methyl groups of ketals produced with non-neighboring OH groups. The ketal seems to be produced intramolecularly but not intermolecularly, since the polyvinylketal was dissolved completely in various solvents as shown in Table I.

Solubility in Various Solvents

In order to establish a purification method of polyvinylketal and as the basic data for studying the procedure of film preparation as well, solubilities of polyvinylketals of various ketalization degrees (3.5–65.6 mol%) and PVA in various organic solvents were determined. The results are listed in Table I.

With certain solvents, solubility was determined at 20°C (room temperature) and 60°C. As is clear from Table I, in DMSO, even at lower temperatures, all ketal samples dissolved, which shows it is the best solvent for carrying out homogeneous reaction. In DMF, all samples excluding PVA dissolved at higher temperatures (60°C). As alcohols, both methanol and ethanol were tried, but identical behavior was observed, therefore, in Table I it is expressed as alcohol. As alcohol is the best solvent for purifying polymers and preparing film, solubilities at various concentrations were determined. In 100% alcohol, only polyvinylketal of ketalization degree above 30 mol% dissolved, in 80% alcohol, ketalization degree above 10 mol% dissolved. Polyvinylketal of ketalization degree of 5–10 mol% dissolves in 50% alcohol, degree of ketalization below 5 mol% in 25% alcohol. This shows that polyvinylketal becomes soluble in alcohol while OH groups in PVA decrease.

In nonpolar solvents such as acetone, ether, petroleum ether, ethyl acetate, methylenechloride, carbontetrachloride, cyclohexane, benzene, etc., all samples are insoluble. Rather interesting solubility behavior was found with water, the details of which will be reported in the following report.

Ketalization Reaction in Anhydrous State

The reaction between PVA and acetone proceeds in accordance with formula (1), however, in the reaction system using water as solvent, no polyvinylketal is formed. This is a big difference compared to the acetalization reaction between PVA and aldehydes. Keeping the above in mind, ketalization reaction between PVA and acetone was carried out in homogeneous system in DMSO with almost no water as the solvent. In order to determine the equilibrium state of the reaction, the time-wise variation of reaction was studied. The results obtained are listed in Table II.

As is clearly observed from Table II, the ketalization reaction proceeds rather rapidly and it was found that in 2–3 hours equilibrium is reached. The reactions were carried out for more than 24 hours, reaction equilibrium is confirmed and the equilibrium ketalization degrees are determined. From the

TABLE II
Timewise Variation of Ketalization Reaction

reaction time (h)	0.5	1	2.5	5	24
ketalization degree (mol%)	25.6	37.1	45.7	46.1	46.3

PVA initial concentration, 0.389 mol/L; PTS concentration, 6.08 g/L; equivalent of acetone against PVA, 6.00; reaction temperature, 40°C.

values, in accordance with formula (2), equilibrium constant, K, were calculated. Results obtained are listed in Table III.

Suppose,

a mol/l PVA initial concentration (value obtained against 2 basic PVA mol)

b mol/l acetone initial concentration

x mol/l polyvinylketal concentration

$X = x/a$ ketalization degree

$E = b/a$ acetone equivalent (mol ratio acetone against 2 basic PVA mol)

At equilibrium state, the equilibrium constant K is given as formula (2). Calculation of K is based on a decrease in the amount of OH groups in PVA. This K includes intramolecular reaction between non-neighboring OH groups in case of highly ketalized polymer (cf. structural analysis by NMR of ^1H and ^{13}C)

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

From reactions varying acetone equivalent from 0.2 to 36.0, ketals of increasing ketalization degree were obtained as the acetone equivalent is

TABLE III
Equilibrium Constants of Ketalization Reaction Anhydrous State[a]

PVA mol/L	Acetone equivalent	PTS g/L	Ketalization[b] mol%	K^c
0.433	0.200	10.0	8.9	0.078
0.481	0.403	6.53	14.3	0.092
0.531	0.446	2.83	15.6	0.099
0.406	1.23	8.18	26.2	0.096
0.846	3.00	2.50	37.4	0.085
0.398	6.06	2.44	46.0	0.070
0.313	10.0	2.78	51.5	0.058
0.278	13.7	3.28	53.0	0.045
0.312	15.4	3.22	56.5	0.050
0.146	20.5	4.05	59.9	0.045
0.208	30.0	1.34	65.6	0.043
0.125	36.0	2.09	68.6	0.043

[a]At 40°C.
[b]Equilibrium ketalization degree.
[c]Equilibrium constant.

TABLE IV
Equilibrium Constants of Acetalization Reactions by Various Aldehydes[a]

R in RCHO	Equiv. of RCHO	PVA mol/L	H_2SO_4 g/L	Ketalization[b] mol%	K^c
H	0.125	0.350	100	12.1	4750
Me	0.125	0.350	100	11.8	2780
	0.200	0.350	100	19.0	3250
	0.250	0.350	100	23.4	2620
Et	0.125	0.350	20	11.9	3140
Pr^n	0.125	0.350	20	11.8	2900
Pr^i	0.125	0.350	20	11.8	2900
$ClCH_2$	0.125	0.358	100	11.9	3020

[a]At 40°C.
[b]Equilibrium acetalization degree.
[c]Equilibrium constant.

increased and as result, samples having various ketalization degrees were synthesized. Equilibrium constant decreases with increase in ketalization degree. Once Flory,[12] from statistical treatment of maximum reaction yield of 1-3 polymer having sufficiently long molecular chain, obtained the value of $1 - 1/e^2 = 0.8647$ and pointed out that when the reverse reaction is accompanied the maximum yield will be higher than the above value. Sakaguchi,[13] from statistical means, obtained the rate of formation of isolated groups remaining unreacted and calculated a correction factor and stated that when such correction factor is applied the value of equilibrium constant coincides up to high reaction yield. When the correction factor is applied to equilibrium constants in Table III, up to certain high reaction yields, the value of equilibrium constant remains constant.

However, the K value for this reaction is ca. 0.07 and small, the reverse reaction tends to proceed easily, therefore, the probability of formation of isolated groups remaining unreacted is considered to be rather less. Accordingly, applying the correction factor by Sakaguchi may be not adequate. In the above, from ^{1}H NMR spectrum in Figure 1, it is shown that ketalization starts at isotactic OH and ketalization of syndiotactic OH takes place at the latter part of reaction, and intramolecular reactions between non-neighboring OH groups occasionally occurred. This may be because complete ketalization of syndiotatic OH portion is not feasible. Experiments on these structural factors are under way now.

In order to compare the case with aldehydes, in Table IV, equilibrium constants of acetalization by aldehydes[14] are listed.

As water is engaged as reaction medium, strictly speaking, the reaction conditions cannot be considered identical with those in this report, equilibrium constant of cases with aldehydes are very high (ca. 3000) and it is considered that almost no reverse reaction is proceeding. To keep the reaction system homogeneous, experiments are confined to low aldehyde concentration regions, however, it is clear that in comparison with the case with acetone, aldehydes are far more reactive toward PVA and exists stably even in the presence of water. On the contrary, with acetone, as listed in Table III, values of equilibrium constants are scattered within the range of 0.04–0.1, which

TABLE V
Temperature Dependency of Equilibrium Constants of Ketalization Reaction by Acetone

Temp. °C	PVA mol/L	Acetone equivalent	PTS g/L	Ketalization[a] mol%	K[b]
25	0.551	0.55	4.64	19.5	0.133
	0.442	3.02	4.18	44.3	0.137
	0.341	6.04	3.52	56.1	0.131
	0.361	10.1	3.85	62.7	0.111
	0.223	36.0	2.71	70.8	(0.049)
30	0.398	3.00	2.62	39.8	0.101
	0.368	5.80	2.41	49.4	0.091
	0.401	6.07	5.48	51.7	0.100
40	0.398	6.06	2.44	46.0	0.070
45	0.436	3.12	7.06	32.9	0.058

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

gives the simple mean value of 0.07, and it is 2×10^{-5} times more unstable compared with aldehydes. It is clear that synthesis of polyvinylketal reaction system with water as reaction medium is not possible.

Next the effect of temperature on reaction was studied and the results are listed in Table V.

The temperature dependency of equilibrium constant determined from the above results is plotted in Figure 2.

The gradient of lines for both aldehyde and ketone are the same and shows that in exothermic reaction of the heat of reaction of 7.5 kcal/mol. It can be interpreted that the acetalization reaction by aldehydes and ketones proceeds according to identical mechanisms. Cases with ketones in addition to acetone are to be reported in the following report and results in line with the present case are obtained.
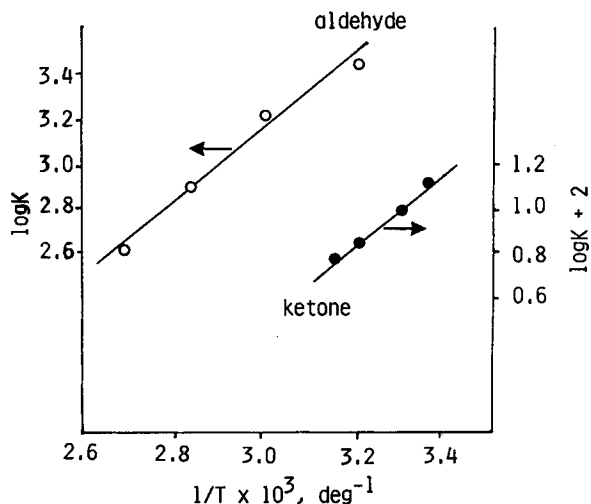

Fig. 2. Temperature dependency of equilibrium constant, K.

Ketalization Reaction in the Presence of Water

As the value of equilibrium constant is very low, it is necessary to carry out ketalization reaction of PVA by acetone under conditions with the least amount of water possible. How far the water in reaction system hinders the ketalization reaction was theoretically calculated and confirmed experimentally as well. From formula (1), when the initial concentration of water is supposed to C mol/l, then formula (3) is obtained.

$$K = \frac{x(c + x)}{(a - x)(b - x)} = \frac{X(c/a + X)}{(1 - X)(E - X)} \tag{3}$$

Accordingly, formula (4) is obtained.

$$X = \frac{-[c/a + K(E + 1)] + \sqrt{[c/a + K(E + 1)]^2 + 4(1 - K)KE}}{2(1 - K)} \tag{4}$$

As equilibrium constants, listed in Table III, vary appreciably with acetone equilibrium, in order to simplify the case, $K = 0.07$ is engaged here. When, suppose, $c/a + K(E + 1) = Q$ and substituting respective values in formula (4), formula (5) is obtained. Equilibrium ketalization degree, Xe,

$$Xe = \frac{-Q + \sqrt{Q^2 + 0.2604E}}{1.86} \tag{5}$$

In Figure 3, theoretical curves of equilibrium ketalization degree calculated from formula (5) are shown. Water in reaction system being expressed as initial concentration water/initial concentration PVA = c/a are given together with experimental results obtained. The coincidence of experimental
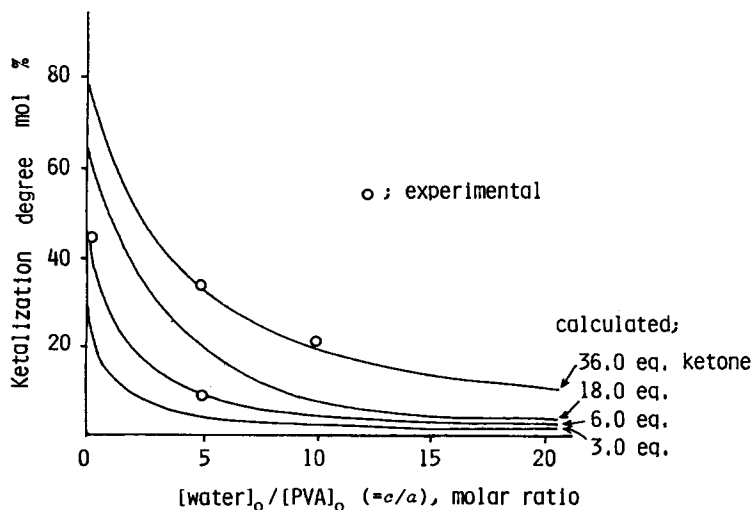

Fig. 3.   The effects of water in reagents on equilibrium ketalization degree.

results on theoretical curves shows the adequacy of the formulas. It is understood that the ketalization degree in this ketalization reaction rapidly decreases with the increase of water in the reaction system. When $c/a = 20$, as PVA initial conc., $a = 0.35$ mol/L, water in reaction system is 126 g/L. This shows that when more than 10 wt% of water exists in the reaction system, the ketalization reaction becomes appreciably difficult to achieve.

Effect of Water in Reagents Engaged

From the results given in Fig 3, it is clear that the ketalization reaction is hindered when water exists in the reaction system. However, as it is difficult to perfectly eliminate water from reagents engaged, the effect of the existence of very minor amount of water was studied.

Water content in DMSO, whose amount engaged in the reaction is the highest among reagents engaged, was quantitatively determined by Karl-Fischer method and its effect was studied. DMSO containing the least amount of water, which was dried even anhydrous potassium carbonate and distilled, was 0.01 wt%, but the DMSO (guaranteed reagent) engaged for experiments was in the level of 0.05 wt%. In experiments, frequently, against PVA 4.0 g, DMSO 100 cc was engaged and when water content in DMSO is supposed to be 0.05 wt%, $c/a = 0.06$.

On the other hand, one water molecule is bound, as crystal water, per one molecule of PTS and whether or not crystal water remains in thoroughly dried PTS is a point of debate. The case of PTS with crystal water amount of the possible highest content is taken here. Water content in PTS is calculated to be 9.5 wt%. The amount of PTS engaged in the reaction is in the range of 3 g/L, which is 0.035 in terms of c/a and this was taken as the maximum amount of water coming from PTS. As PVA and acetone were used after thorough dehydration, water content in these was neglected. The effects of water in reagents on equilibrium ketalization degree are listed in Table VI.

In other words, when water content of the range accompanied by reagents engaged in experiments is below $c/a = 0.1$, it can be assumed that the effect of the existence of water on equilibrium ketalization degree is within experimental errors and can be neglected. In order to lessen the effect of water in

TABLE VI
The Effects of Water in Reagents on Equilibrium Ketalization Degree[a]

PVA	Water in DMSO		Water in PTS	Total amount of water		Ketalization[b]	
g	g	%	g	g	c/a	36.0 eq.	6.00 eq.
4.0	0	0	0	0	0	76.4	45.8
	0	0	0.0285	0.0285	0.035	75.7	44.7
	0.01	0.01	0.0285	0.0385	0.047	75.5	44.3
	0.05	0.05	0.0285	0.0785	0.096	74.6	42.7
	0.10	0.10	0.0285	0.1285	0.157	73.5	40.9
10.0	0.10	0.10	0.0285	0.1285	0.063	75.2	43.8

[a] At 40°C; in 100 ml of DMSO; $c/a \leq 0.1$.
[b] Equilibrium ketalization degree.

DMSO, apparently increasing initial PVA concentration, a, is one of the effective means. The case of $a = 1.11$ mol/L means ca. 10 wt% PVA solution in DMSO, and even though the viscosity of reaction system increases, it was confirmed that the reaction proceeds smoothly. Therefore, even though it was preferable to engage reagents with as little water content as possible, with reagents of water content comparable to those in guaranteed-grade reagents, polyvinylketal of prescribed ketalization degree can be obtained. However, when acetone equivalent is high, the equilibrium constant, K, becomes low, the reaction conditions have to be decided, keeping this point in mind.

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