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A novel approach to hydrolyzable polyvinylketal from poly(vinyl alcohol) and acetone under phase transfer catalyst conditions

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Abstract

Ketalization reaction of poly(vinyl alcohol) (PVA) by acetone under acidic-catalyst/phase-transfer-catalyst was carried out easily and the structure of the product both swelled and dissolved in dimethyl sulfoxide-d_6 (DMSO-d_6) was confirmed, which then indicated the structural change in the product polyvinylketal (PVKT) due to its hydrolysis in water, by NMR measurements. The effect of catalysts on reaction was probed from experimental viewpoint, compared with the theoretical calculation applicable to the previous classical method. It was observed that high ketalization degree PVKT was obtained with the presence of water and the effect of water on reaction was also probed in the present method, which may result in further application in the total syntheses of complex macromolecules from polyols and ketones. The behavior of PVKT in water under different conditions, which is very similar to that described in previous report, was also studied, as well as the specific viscosity (η_{sp}) of PVKT solution, and proper explanation is proposed. And the present study may lead to a further investigate of attractive intrinsic properties of PVKT.

Keywords: Poly(vinyl alcohol); Polyvinylketal; Ketalization

1. Introduction

Poly(vinyl alcohol) (PVA), a water-soluble and degradable polyhydroxy polymer, is produced on the order of several hundred kton/yr all over the world, making it the largest volume synthetic resin produced today. The excellent chemical resistance, physical properties, and complete biodegradability of PVA resins have led to their broad practical applications like biomedicine, adhesives, paintings, packaging, and others. [1–5] In addition to its attractive intrinsic properties for these applications it also confers a high functionality, allowing the potential for modification of the polymer via chemical transformations. PVA is usually functionalized by two methods. One is the copolymerization of vinyl monomer having a functional group with vinyl acetate followed by the hydrolysis of acetyl groups, [6–9] and the other is chemical modification of hydroxyl groups of PVA by the reaction with appropriate reagents. [10–13] Esterification and acetalization are occasionally used in the latter case. But few reports on ketalization reaction by ketones are known.

I.G. Farben AG [14] reported successful results with ring ketones such as cyclohexanone for the first time. Then further reports [15,16] reacting ketones as ketal of alcohol are known. Recently, Nakamura et al. [17] reacted PVA with various ketones to prepare polyvinylketal (PVKT). Their results indicated that PVKT is easier hydrolyzed in water than PVA, and the hydrolyzation time is controlled by both ketalization degree and pH value of water. However, in such methods, PVKT was obtained in homogenous reaction system maintained from the beginning to the end. It is confirmed that the presence of water lowers the degree of ketalization significantly because the equilibrium constants of ketalization is very small. Consequently, in despite of attractive intrinsic properties of PVKT, few studies were made since then.

The recent tendency toward 'green and sustainable chemistry' has again attracted attention to the technique of phase transfer catalyst using quaternary salts as catalyst. In this technique, the catalyst has the function of transferring

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one of the chemicals from the aqueous phase to the organic one in which the reaction takes place. [18,19] Its significance for organic micro-molecule syntheses has been acceleration of heterogeneous reaction. [20–23] Phase transfer catalysis has also been a widely used tool in macromolecules synthesis [24–27]. However, noteworthy is that no report has been published up to the present on such a ketalization reaction of macromolecules under phase transfer catalyst conditions.

In a recent study of ketalization reaction, we succeeded in synthesizing PVKT through ketalizing PVA with acetone, as a representative ketone, by a novel approach under phase transfer catalyst conditions. From the methodical point of view, the structure of the product PVKT, as well as the changed structure due to the hydrolysis of ketal rings in DMSO-d_6 (contain a amount of water both from itself and the sample) was confirmed by the measurements of ^{1}H NMR spectrum, ^{13}C NMR spectrum and two-dimensional (2D) correlation spectroscopy (COSY). The possible hydrolization mechanism has also been proposed. Furthermore, the effect of the catalyst and that of the presence of water on the reaction were also probed. This is the first time, to our best knowledge, to synthesize PVKT easily under phase transfer catalyst conditions through ketalization reaction, which is difficult to proceed by previous classical methods.

The behavior of the product in water was studied, and our results indicate that the PVKT obtained by the present method may have the same property as the PVKT obtained by previous classical method. The specific viscosity (η_{sp}) of PVKT solution was also studied. And the present study may lead to a further investigate of attractive intrinsic properties of PVKT.

2. Experimental section

2.1. Materials

PVA (degree of polymeration 1750±50, saponification value >98%) was saponified ulteriorly by 0.5 mol/L NaOH at 60 °C in a flask with a condenser for 2 h, then was washed with $NaHCO_3$ and distilled water until the filtrate had a neutral pH value. After that, PVA was purified in an extraction apparatus with methyl alcohol as extracting solvent for 8 h, and then purified by acetone. Finally, after dried at 50 °C for more then 3 days and at 102 °C for another 2 h, PVA was kept in a desiccator.

All other chemicals: dimethyl sulfoxide (DMSO, A.R.), p-toluene sulfonic acid (PTS, A.R.), acetone (A.R.), tetrabutylammonium bromide (TBAB, A.R.), Triton^R X-100 and cetyltrimethyl ammonium bromide (CTAB, A.R.) were used as received without further purification.

2.2. Synthesis of PVKT in DMSO

PVA was reacted with acetone in DMSO, and with PTS/TBAB as catalyst, or other catalyst, to prepare PVKT.

Details of a typical experiment are as follows: PVA was dissolved in DMSO in a round bottom flask immersed in an oil-bath at 70 °C. When PVA was completely dissolved, the solution cooled down to 30 °C. Then PTS/TBAB (or other catalyst) were added in. Acetone was added in at last, which was followed by the reaction at 30±1 °C for 21 h. Then the solution was neutralized by 0.5 mol/L NaOH. The product was then purified for several times: dissolving in ethanol solution of specifically concentration [17a] and precipitation with either acetone or ethyl acetate (10-fold volume). With the pH value kept around 7, the hydrolysis of PVKT was not observed at all during purification. And then superfluous solvent was removed by a vacuum pump and the product was dried at 50 °C in vacuo for 3 days.

Suppose,

a mol/L PVA initial concentration (value obtained against 2 basic PVA mol)
b mol/L acetone initial concentration
c mol/L water initial concentration
x mol/L PVKT concentration
$X = x/a$ ketalization degree
$E = b/a$ acetone equivalent (mol ratio acetone against 2 basic PVA mol)

And the appropriate experimental value was as follows: $a = 0.2$ mol/L, $E = 4$ (mol/mol). And the amount of PTS engaged in the reaction, the same as TBAB (or CTAB, Triton^R X-100), is in the range of 10 g/L.

2.3. Synthesis of PVKT in DMSO/H_2O

Based on the experiments above, pre-counted amount of H_2O was added in after PVA was completely dissolved at 70 °C. Here, a value, E value, the amount of PTS and that of TBAB kept the same as described previous.

2.4. NMR analysis

NMR analysis was performed with an Avance AV 400 Bruker solution-state spectrometer for the ^{1}H NMR spectrum, ^{13}C NMR spectrum and 2D COSY spectrum. The study and characterization of PVKT were made with DMSO-d_6 as solvent. Water content in PTS, acetone and TBAB was also measured, respectively, with DMSO-d_6 as solvent, whereas water content in DMSO was analyzed in acetone-d_6.

Conditions in the ^{13}C NMR measurement were as follows: pulse width P_1 $\pi/4$, pulse interval D_1 2.0 s, number of scan 20k. And relaxation time, as well as nuclear Overhauser effect, was taken into account. And for ^{1}H NMR: pulse width P_1 $\pi/2$, pulse interval D_1 2.0 s.

All the NMR experiments were conducted at 300±0.05 K and with tetramethyl silane (TMS) as the standard.

2.5. Hydrolysis behavior of PVKT of different ketalization degrees in acidic water

PVKT samples of different ketalization degrees, purified by ethyl acetate, were soaked in water of various pH values at different temperatures, and the deketalization degree was determined in iodoform method [17a]. The iodine consumed by PVA itself has to be deduced from the results. The analysis was done by ultraviolet (UV) absorbance analysis, and UV-365 (Shimadzu, Japan) was used. The pH value was measured with PHS-25 pH meter (Shanghai Precision & Scientific Instrument Co. Ltd, China).

2.6. Solubility of PVKT of different ketalization degrees in distilled water

PVKT samples of different ketalization degrees were soaked in distilled water whose pH value is neutral. The experiments were carried out at room temperature.

When the sample was dissolved in water completely, the film was prepared using the solution immediately. And then the ketalization degree was determined by ^{1}H NMR spectrum again.

2.7. Viscosity measurement

A dilution-type Ubbelohde viscometer with capillary diameter 0.55 mm was used. All viscosity measurements were carried out at 25±0.05 °C.

To investigate the viscosity of PVKT solution, the following experimental procedures were performed. [28,29] The flow time of PVKT solution (1.000 g/L) in the clean untreated viscometer was first measured. Afterwards, a known volume of pure DMSO solvent was added successively into the viscometer, in order to decrease the solution concentration in the viscometer. The flow times for each solution with different concentrations in the viscometer were measured. After finishing the solution viscosity measurements, the PVKT solution was poured out and the viscometer was cleaned immediately using the pure DMSO solvent for 3–5 times. Next, having reset the viscometer in the bath, the flow time of pure DMSO solvent was measured. Specific viscosities of PVKT solutions were computed neglecting the density difference between solution and solvent.

The viscosity of PVA (degree of polymeration 1750±50) solution was also measured.

3. Results and discussion

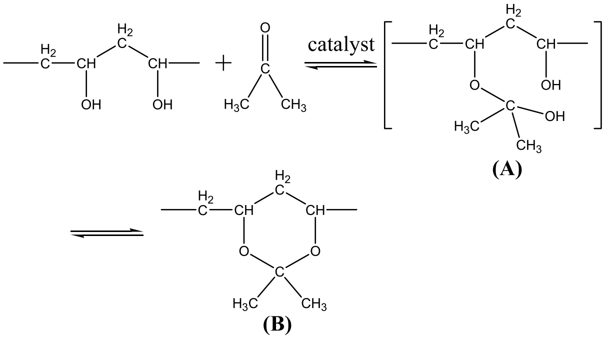
3.1. Synthesis of PVKT in DMSO and structural analysis

PVA was reacted with acetone in DMSO, and PTS/TBAB as catalyst to prepare PVKT. The reaction is considered to proceed as the one shown in Scheme 1.

Fig. 1 shows the representative 1D NMR spectra of PVKT, where A and B were acquired by the sample purified by ethyl acetate, and C was acquired by the same sample purified by acetone specially to avoid the signals from ethyl acetate. The ^{1}H NMR spectrum of PVKT swelled in DMSO-d$_6$ (Fig. 1A) is nearly identical to the spectrum of PVKT reported previously, [17a] and Fig. 1B was the spectrum of PVKT dissolved in DMSO-d$_6$ completely. For both of Fig. 1A and 1B: signals attributed to –OH groups at 4.7, 4.5, and 4.3 ppm (isotactic, heterotactic, and syndiotactic structures, respectively) decreased, instead methyl groups of PVKT (H^b) were clearly visible at around 1.2 ppm and thus the structure (B) (Scheme 1) of the product is confirmed. And there was no signal of either TBAB or PTS. The signals at 2.0, 2.5 and 3.3 ppm were due to ethyl acetate, DMSO and water, respectively.

The expectative strong signals 97 ppm (C^e), 30 ppm (equatorial-C^b) and 20 ppm (axial-C^b) shown in Fig. 1C indicated that the ketalization reaction of PVA with acetone is the intramolecular reaction, not intermolecular reaction. Since the formation of the rigid six-membered ketal ring, the methyl carbons from the grafted acetone are in different local environments, which result in different signals due to the sensitivity of the NMR signals to geometry. However, if the reaction was an intermolecular reaction, the methyl carbons from the acetone may have the same chemical shift because of the rapid rotation of these mobility methyl groups, particularly on the NMR time scale. The well dissolution of the product in DMSO, with nothing swelled or insoluble at last, could also indicate no formation of network.

Moreover, as shown in Fig. 1C, small signals 98, 26, 25, 24 ppm, etc., which appear in our results in addition to the expectative signals, are possibly due to C^g (98 ppm) and C^h in structure III, as well as to quaternary carbon atoms and methyl groups of ketals produced with non-neighboring OH groups. All these signals, which will be assigned in detail by theoretical calculation in our later report, are greatly effected by the configurations of main chain backbone,



Scheme 1. The ketalization reaction of PVA with acetone.

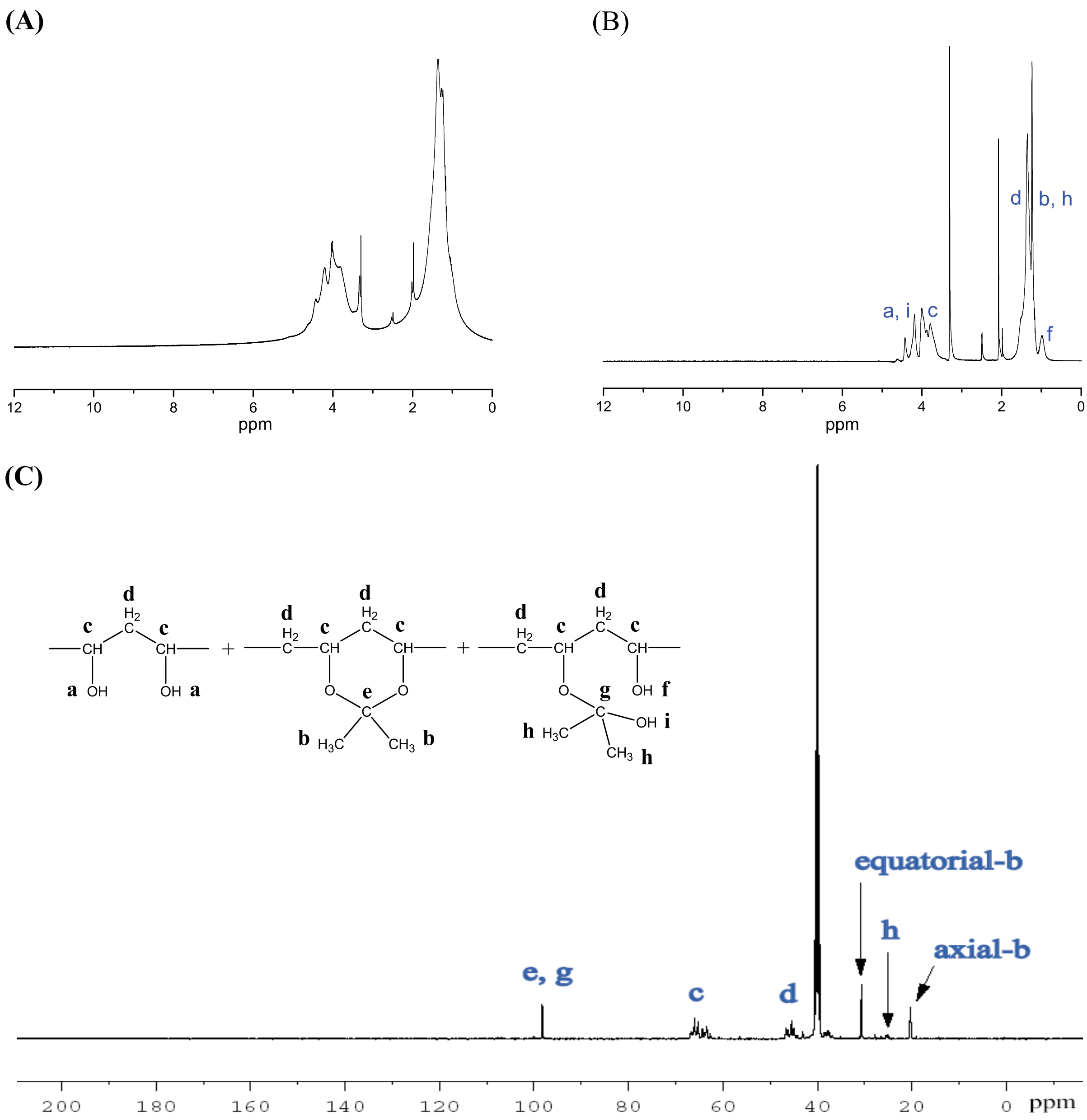


Fig. 1. 400 MHz solution-state ^1H NMR spectra of PVKT (purified by ethyl acetate) in DMSO-d_6 solvent swelled (A) and then dissolved (B) completely, number of scan 64, (C) is the ^{13}C NMR spectrum of PVKT (the same sample purified by acetone specially) dissolved in DMSO-d_6, number of scan 20k. All spectra were acquired at 300 K.

especially in the interval 18–32 ppm due to methyl groups and 61–69 ppm due to methine groups.

Ulteriorly, at about δ $^1H \approx 1.00$ ppm, a signal appeared in Fig. 1B and there was no obvious peak in Fig. 1A. But there was no signal at 2.2 ppm due to acetone, which indicated that no acetone was produced. Although a new signal's appearance at 1.00 ppm after dissolution is difficult to interpret, it clear reflects changes in the polymer conformation and/or microstructure induced by the dissolution.

Note, in particular, the new signal (1.00 ppm) only appeared after dissolution. The ^1H NMR spectra were tested over a 18 h period, the time from mixed the product into DMSO-d_6 in NMR tube to the completely dissolution of the product. During this time the sample was kept at 300 K in capped NMR tubes. The spectrum slowly changed, and no signal appeared at 1.00 ppm at all in the first 30 min, then the new signal at 1.00 ppm grew up slowly and ultimately yielded the spectrum as shown in Fig. 1B. And one of the spectra of the swelled PVKT was as the one shown in Fig. 1A.

To make it clear the signal at 1.00 ppm due to which proton, more information was obtained by employing ^{13}C–^1H 2D COSY measurement of the PVKT (purified by acetone specially) shown in Fig. 2. No cross peak in the area where δ $^1H \approx 1.00$ ppm indicated that the proton (1.00 ppm) is not from C–H bond. In other words, δ $^1H \approx 1.00$ ppm was due to –OH group. On the basis of ^1H–^1H 2D COSY data, the signal (δ $^1H \approx 1.00$ ppm) is assigned, together with the result that no signal around 1.00 ppm appeared in the ^1H spectrum of PVA which indicated that it was foreign to the –OH groups unmodified in the ketalization reaction, to the H^f. And one of the possible reasons for the its signal shifted to so high a field is mainly related to O–H–O hydrogen bond.

The structural change in PVKT indicated by the solution-state NMR spectrum was the formation of a hemiketal-containing chain due to the hydrolysis of ketal rings. That is, the dissolution of PVKT in DMSO-d_6 solvent (contains a amount of water both from itself and the sample), whose pH value is almost neutral, is a two-way process: one is the physical dissolution of PVKT itself and another is by hydrolization of PVKT [17(a)], which was confirmed by our experiment directly. Compared with PVA, the great decrease of –OH groups makes PVKT more hydrophobic. And the formation of the structure III (Scheme 2) may be a great help to the dissolution in almost neutral DMSO-d_6 solvent.

Although not fully understood, it seems that ketal decomposition proceeds though a concerted mechanism via intermediate II in the above mechanism, according to the decomposition mechanism for acetal ring. [17h, 30] Despite its preliminary character, further investigation of the mechanism of ketal decay in almost neutral DMSO-d_6 solvent (contains water itself) is needed to confirm this hypothesis.

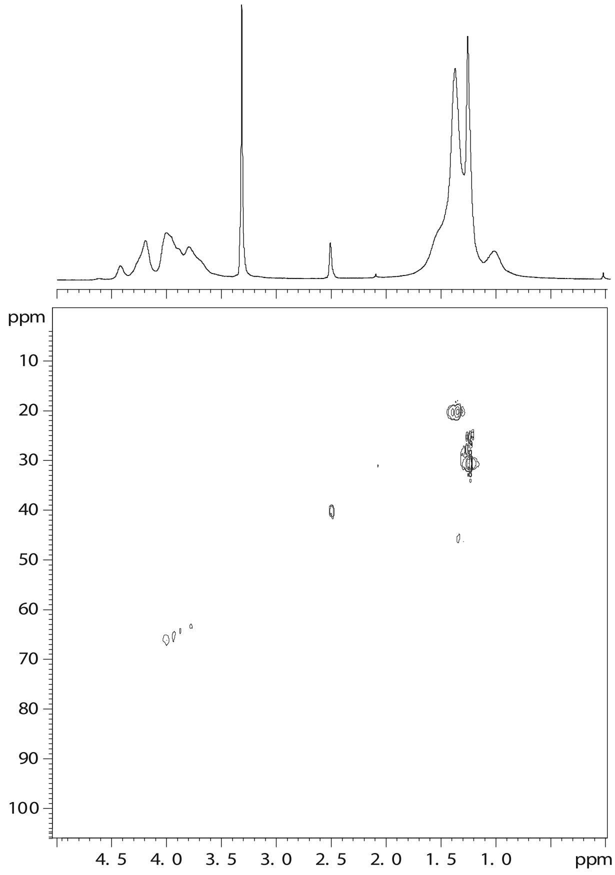


Fig. 2. 400 MHz solution-state 2D COSY spectrum of PVKT (purified by acetone specially) dissolved in DMSO-d_6 completely. The measurement condition was as follows: spectral width 3205.128×15093.035 Hz, data points TD 1024×256, temperature 300 K.

3.2. Determination of ketalization degree by ^1H NMR spectrum

According to the analysis above, I_1, the integrated intensity of the given polymer line in the interval 4.1–4.7 ppm, was due to both H^a and H^i, so the following relation (Formula (1)) was established to calculate the ketalization degree D_H (mol/mol) on the PVA hydroxyl functions:

$$\text{ketalization degree } D_H = 1 - \frac{I_1 - I_4}{I_2} \qquad (1)$$

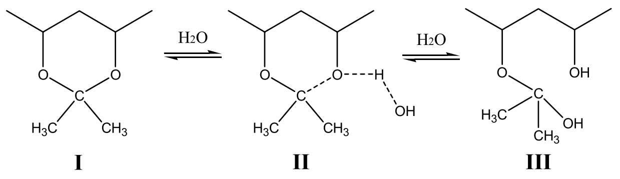
Where I_2 is the integrated intensity of the given polymer line due to H^c (3.5–4.1 ppm), and I_4 due to H^f (0.7–1.1 ppm). Note that for the sample purified by acetone, I_2 can be used to calculate the ketalization degree D_H directly, whereas for the sample purified by ethyl acetate, the contribution of the ethyl acetate protons should deduct from the I_2 value before calculates D_H. Actually, except in part 3.5 in the present study, the ketalization degree D_H was always obtained from the ^1H NMR spectrum of the sample purified by acetone.

Certainly, we can also determine the ketalization degree in iosoform method, but it takes long time to do the job properly. So the iosoform method is only used in part 3.5 the present study, in which experiment it may be easier to prepare the solutions of various pH values and much cheaper than by ^1H NMR spectrum.

We can thus determine the ketalization degree D_H for the product PVKT. The value for the sample shown above is about 0.88. Though taking account of the experimental errors, it is a high ketalization degree. Then, what on earth is the amount of water contained in chemicals engaged? Water content in chemicals engaged listed in Table 1 was determined by ^1H NMR spectrum. So we can obtain $c \approx 0.4707$ mol/L, and then $c/a \approx 2.35$.

3.3. Catalytic efficiency of different catalysts

Previous publication [17a] indicated that a little water exist in the reaction system would hinder the progress of the ketalization reaction. Now, a high ketalization degree



Scheme 2. The structural change in PVKT in DMSO-d_6 (contain a amount of water both from itself and the sample).

Table 1
The amount of water contained in chemicals engaged

Chemical engaged	Solvent-d	Water in chemicals engaged $n(H_2O)$
DMSO	Acetone-d_6	1.185×10^{-4} mol/(ml DMSO)
PVA	DMSO-d_6	8.061×10^{-3} mol/(g PVA)
Acetone	DMSO-d_6	1.633×10^{-4} mol/(ml acetone)
PTS	DMSO-d_6	1.438×10^{-2} mol/(g PTS)
TBAB	DMSO-d_6	4.967×10^{-3} mol/(g TBAB)

Table 2
Formation of PVKT using different catalysts at different temperatures

Catalyst	Temperature (°C)	Ketalization degree D_H (mol/mol)
TBAB	30	0
CTAB	30	0
PTS/TBAB	22	0.93
	30	0.88
	42	0.81
		0.76
	52	0.73
		0.78
PTS/CTAB	24	0.81
	32	0.79
	42	0.79
PTS/Triton^R X-100	28	0.83
		0.83
	38	0.80
		0.79
	45	0.66
		0.65
		0.67
		0.67

product was obtained by the use of TBAB as additional catalyst besides PTS with $c/a\approx2.35$ in the reaction system, even taking account of the experimental errors. While the theoretical ketalization degree $D_{\text{theor.}}$ (mol/mol) calculated from the formula as follows (Formula (2)), which is applicable to the homogenous reaction system, $Q= c/a+K(E+1)$, $K=0.07$ [17a], is only 0.10:

$$D_{\text{theor}} = \frac{-Q+\sqrt{Q^2+0.2604E}}{1.86} \tag{2}$$

The result indicates that TBAB must play an important role in our experiment. So the effect of catalyst using TBAB, CTAB, PTS/TBAB, PTS/CTAB and PTS/Triton^R X-100 in the present reaction was studied, respectively, at different temperatures as shown in Table 2.

Noteworthy is that the ketalization reaction did not proceed at all in the absence of PTS under otherwise identical conditions as included in Table 2; however, using PTS as reaction catalyst, by adding TBAB, CTAB or Triton^R X-100, the product with a great higher ketalization degree compared with the theoretic calculation was achieved. Further, the fact that the employment of TBAB as the phase transfer catalyst resulted in higher ketalization degree of the PVKT than that owing to CTAB, under otherwise identical conditions, was emphasized by the profound effect of the structurally well-defined catalyst on the reactivity as well as the selectivity. It should be added that although the expected product was certainly achieved with PTS/Triton^R X-100 in the present reaction, the reactivity was far less than that of TBAB/PTS or CTAB/PTS. Obviously, the application of TBAB or CTAB can, on the one hand, solubilize the reactant PVA which did not dissolved in either acetone or water at the experimental temperatures, and form the catalytic intermediate which was then transferred into the organic phase to conduct the subsequent reaction on the other hand. While Triton^R X-100 maybe only play the role as emulsification. Further studies be expounded later that the reaction system becomes emulsion as the amount of water increases reveals the feasibility of this hypothesis.

3.4. *Effect of water in reaction system*

Phase transfer catalysis offers further advantages because it typically involves mild conditions just as the expatiation above. In the present study, the effect of water addition was also explored. The experimental results are shown in Table 3. The product of highest ketalization degree was obtained in the condition without adding water and the ketalization degree D_H became as high as 0.88, while only 0.10 by theoretical calculation. The ketalization degree decreased with increasing the content of water used, and each ketalization degree was greatly higher than that of theoretical calculation applicable to the homogenous reaction system with the only catalyst PTS. This demonstrates that the phase transfer catalyst plays an important role in our experiment.

The case of $C(H_2O)=0.200$ (L/L), even though the viscosity of reaction system and emulsion was obviously observed, it was confirmed that the reaction proceeds smoothly. And except the beginning about 1 h, the reaction system looked as if two immiscible homogenous phases when holded still, when $C(H_2O)<0.200$ (L/L); but hemi-transparence colloid was formed when $C(H_2O)>0.400$ (L/L). Hence, PVKT is synthesized from the reaction of two immiscible reactants existing in different phase.

Thus, using of solvent DMSO/H_2O under phase transfer catalyst conditions makes the reaction condition more easily than previous classical methods, and the most important that the former is more friendly to the environment. This represents a distinct advantage of our approach for the elaboration of effective synthesis of PVKT under phase transfer catalyst conditions, which should play a crucial role in the development of still unexplored phase-transfer catalyzed macromolecule ketalization reactions. And the present study may lead to a further investigate of attractive intrinsic properties of PVKT.

Table 3
The effect of water in the reaction system

Concentration of water in the reaction system $C(H_2O)$ (L/L)	C/a[a]	Ketalization degree (mol/mol)	
		Experimental D_H	Theoretical[b] D_{theor}
0.050	13.888	0.533	0.0196
0.111	30.833	0.284	0.0090
0.143	39.722	0.253	0.0070
0.147	40.833	0.248	0.0068
0.200	55.556	0.217	0.0050
0.211	58.611	0.178	0.0048
0.286	79.444	0.143	0.0035
0.400	111.111	0.108	0.0025
0.500	138.889	0.137 0.104	0.0020
0.650	180.556	0.114 0.044	0.0016
0.667	185.278	0.038	0.0015
0.800	222.222	0.041 0.020	0.0013

[a] The values were calculated from the corresponding $C(H_2O)$ in the reaction system.

[b] The values were calculated from Formula (2).

3.5. Hydrolysis of PVKT of different ketalization degrees in acidic water

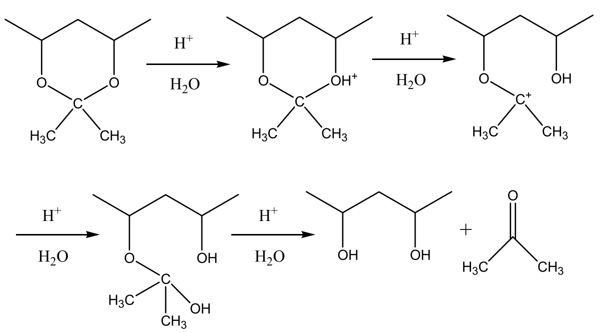
To confirm that the PVKT obtained by the present method has the same property as the PVKT obtained by previous classical method, hydrolysis of the product in acidic water was studied.

As high ketalization degree PVKT is insoluble in water, it is considered that as hydrolysis proceeds, it gradually becomes water soluble [17b]. It become clear that the dissolution of PVKT in acidic water is the dissolution by hydrolization of PVKT as shown in Scheme 3. As was expected, the ketalization degree of PVKT 1 $D_{io}=0.549$ determined in iodoform method after acidic decomposition shows the satisfactory coincidence with $D_H=0.533$ obtained from ^1H NMR spectrum within the experimental error, and for PVKT 2, $D_{io}=0.418$ from iodoform method, $D_H=0.406$ from ^1H NMR spectrum.

After the hydrolysis reaction, acetone existing in water is quantitatively determined in iodoform method and deketalization degree was determined, and deketalization ratio is given as (Formula (3)):

$$\text{Deketalization ratio}(\%) = \frac{\text{deketalization degree}}{\text{initial ketalization degree}} \times 100 \qquad (3)$$

As is clear from Figs. 3 and 4, the product is hydrolyzed with water and the rate of hydrolysis largely depends on pH values of water and varies also appreciably with different ketalization degrees. And the behavior is very similar to that described in previous report [17b].



Scheme 3. The hydrolysis reaction of PVKT in acidic water.

It can be observed that in such reactions, the lower the initial ketalization degree, the easier the daketalization proceeds, and the closer of the pH value to neutral, the lower the hydrolysis rate. At 25 °C, PVKT 1 ($D_{io}=0.549$) is deketalized perfectly in less than 7 h after soaking in water of pH=2.50, and the time needed for the complete deketalization of PVKT 2 ($D_{io}=0.418$) is about 4 h. However, in water of pH=3.50, deketalization rate is very slow, and it takes PVKT 1 about 42 h to completely deketalize, and about 32 h for PVKT 2.

An increase in temperature leads to an increase in deketalization rate [17b], on the one hand. At 37 °C, the hydrolysis of both PVKT 1 and PVKT 2 in water whose pH=3.50 are easier than at 25 °C. On the other hand, in our opinion, for this polymer, inter and intra hydrogen bonding in the PVKT mainly due to the fractions of the hydroxyl groups is disrupted by thermal energy, thus increasing solubility of the PVKT. And the intramolecular and intermolecular interactions between chains gradually increase the viscosity of the PVKT solution, depending on the polymer concentration and the ketalization degree of the PVKT.

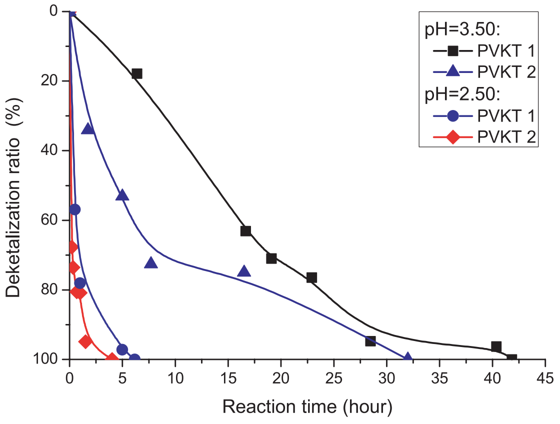


Fig. 3. Hydrolysis of PVKT 1 ($D_{io}=0.549$) and PVKT 2 ($D_{io}=0.418$) in water of various pH values at 25 °C.

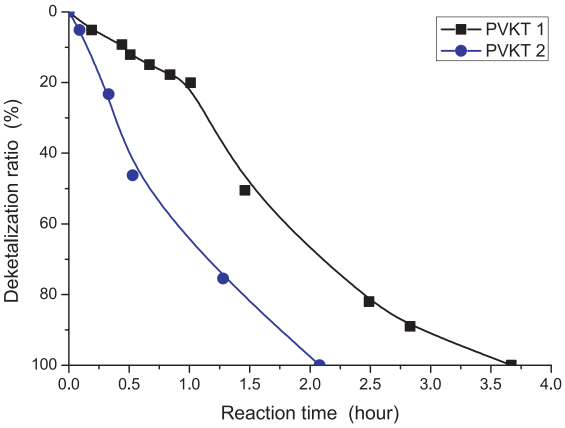


Fig. 4. Hydrolysis of PVKT 1 ($D_{io}=0.549$) and PVKT 2 ($D_{io}=0.418$) in acidic water (pH=3.50) at 37 °C.

3.6. Solubility of PVKT of different ketalization degrees in distilled water

Both conformed by our experimental results and [17b], the hydrolysis rate of high ketalization degree PVKT ($D_H=0.886$) in water whose pH value is kept close to neutral is very low, and it must be noted that hydrolysis does not proceed to 100%. Furthermore, as shown in Fig. 1, the significant strong signals due to equatorial-C^b and axial-C^b indicated that only a few ketal rings hydrolyzed in DMSO-d_6 (contains a amount of water both from itself and the sample). The dissolution of PVKT in water whose pH value is kept close to neutral is mainly the physical dissolution of PVKT itself.

The solubility of PVKT in water is primarily determined by the degree of ketalization. The PVKT of medial ketalization degree may be considered to be amphiphilic, and PVKT of low ketalization degree becomes water-soluble. It is believed that the interactions between solute and solvent will increase with a further increase of the hydroxyl group fraction in the PVKT chains due to the increasingly hydrophilic influence of the additional hydroxyl groups. High ketalization degree PVKT ($D_H=0.886$) is very stable in water without swelling for more than 3 weeks at room temperature. However, it only takes PVKT of ketalization degree $D_H=0.533$ about one weeks to swell completely, and about another 3 days to dissolution completely. The ketalization degree of the film prepared using the solution is about $D_H=0.496$, which is nearly the same as the initial ketalization degree $D_H=0.533$.

However, because it may take a long time to dissolve completely in water, the quantitative analysis of dissolution property of PVKT in water is difficult.

3.7. Viscosity of PVKT solutions

Considering that high ketalization degree PVKT is insoluble in water and the hydrolysis of PVKT of a low ketalization degree may affect the experimental result, DMSO was used as solvent.

A PVKT of a low ketalization degree dissolves in DMSO much more readily at room temperature than one of a higher ketalization degree. As was discussed before, the decrease in number of hydrophilic hydroxyl groups, i.e. increase of ketalization degree, decreases the interactions between solute and solvent, and consequently decreases the solubility of the PVKT.

The decrease of associations between polymer chains, due to the decrease in number of hydrophilic hydroxyl groups, reduces the viscosity of the PVKT solution. Fig. 5 shows this effect upon the specific viscosity (η_{sp}) of two PVKT solutions with different ketalization degrees and a PVA solution. It is noticed that the PVKT solutions show significantly lower viscosity than the PVA solution, although the molecular weight of the former solution was higher than that of the second solution. The PVKT solution of ketalization degree $D_H=0.533$ also shows a higher viscosity than the solution of ketalization degree $D_H=0.886$.

It is also seen from the figure that the specific viscosity decreases significantly when the polymer concentration decreases. This decrease of viscosity, for the lower concentration, is most certainly due to the gradual decrease of the extents of inter and intra chain hydrogen bonding and hence the decrease in interactions and entanglements between the polymer chains.

4. Conclusion

In the present study, the synthesis of PVKT from the mass-production synthetic resin PVA and acetone under phase transfer catalyst was investigated. The initial structure of the product PVKT and the formation of a hemiketal-containing chain due to the hydrolysis of ketal rings in

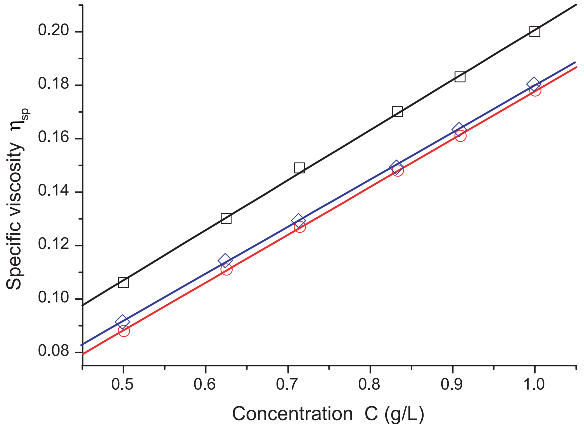


Fig. 5. Variation of the specific viscosity with the polymer concentration at 25±0.05 °C: □, PVA (degree of polymeration 1750±50); ◇, PVKT of ketalization degree $D_H=0.533$; ○, PVKT of ketalization degree $D_H=0.886$.

DMSO-d_6 (contain a amount of water both from itself and the sample) were confirmed from the experimental results. Different catalysts PTS/phase-transfer-catalyst (or emulsifier) were employed to compare their catalytic efficiency: PTS/TBAB > PTS/CTAB > PTS/Triton^R X-100 >> PTS, herein, the efficiency of using PTS in previous classical method came from theoretical calculation. The ketalization degree decreased and kept grate higher than that from theoretical calculation applicable to the homogenous reaction system with the only catalyst PTS, as the concentration of water increased.

The PVKT obtained by the present method may have the same property as the PVKT obtained by previous classical method that the behavior in water is nearly the same between them. The lower the initial ketalization degree, the easier the daketalization proceeds in acidic water, and the closer of the pH value to neutral, the lower the hydrolysis rate. An increase in temperature leads to an increase in deketalization rate. It become clear that the dissolution of PVKT in acidic water is the dissolution by hydrolization of PVKT, whereas the dissolution of PVKT in water whose pH value is kept close to neutral is mainly the physical dissolution of PVKT itself. The solubility of PVKT in distilled water or DMSO at room temperature is primarily determined by the ketalization degree. The decrease in number of hydrophilic hydroxyl groups, i.e. increase of ketalization degree, decreases the interactions between solute and solvent, and consequently decreases the solubility of the PVKT. And the decrease of associations between polymer chains reduces the viscosity of the PVKT solution.

In conclusion, the present synthesis method has been found to be useful for ketal formation in aqueous media. In addition to previous classical method, this is an excellent alternative method because of high ketalization degree and use of non-toxic inexpensive solvent. This area will continue its rapid growth in importance as the methodology finds further application in the total syntheses of complex macromolecules from polyols and ketones. And the present study may lead to a further investigate of attractive intrinsic properties of PVKT.

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