

폴리(비닐 아세테이트)의 산촉매 가수분해 반응

박상수[†] · 윤희숙*

서울보건대학 의료공학과, *서울대학교 화학교육과
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Acid-Catalyzed Hydrolysis Reaction of Poly(vinyl acetate)

Sangsoo Park[†] and Hisook Yoon*

Department of Biomed. Engineering, Seoul Health College,
212 Yangji-Dong, Sujeong-Gu, Gyeonggi-Do 461-713, Korea

*Department of Chemical Education, Seoul Nat'l University,
Shinrim-dong, Gwanak-Gu, Seoul 151-742, Korea

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초록 : 산을 촉매로 한 물/초산용액에서의 폴리(비닐 아세테이트) 가수분해반응을 35 °C에서, 물과 초산의 비율을 달리한 두 용액 조성에서 연구하였다. 반응시간에 따른 비닐 아세테이트(VAc)와 비닐 알코올(VA) 단량체 몰분율을 NMR로 측정하였고, 반응이 평형에 도달한 후의 화학평형상수(K_{eq})를 화학평형상태에서의 VAc와 VA의 몰분율을 이용하여 결정하였다. 화학평형에서의 VAc 몰분율이 0.78(± 0.01)이었을 때 K_{eq} 는 0.76(± 0.01)이었고, VAc 몰분율이 0.57(± 0.02)일 때 0.69(± 0.01)이었다. 가수분해반응은 가상 1차 반응을 따랐으며, 반응속도상수는 3.4×10^{-6} /sec이었다.

Abstract: The acid-catalyzed hydrolysis reaction of poly(vinyl acetate) (PVAc) in water/acetic acid solution at 35 °C was studied at two different solvent compositions. The mole fractions of vinyl acetate (VAc) and vinyl alcohol (VA) during the course of the reaction were determined by NMR, and the equilibrium constant K_{eq} of the reaction was determined using the molar ratio of VAc to VA at the chemical equilibrium. K_{eq} was 0.75 (± 0.01) when the VAc mole fraction at the equilibrium was 0.78 (± 0.01) and it was 0.69 (± 0.01) when the VAc mole fraction was 0.57 (± 0.02). The reaction was found to be a pseudo 1-st order reaction with the rate coefficient at 3.4×10^{-6} /sec.

Keywords: poly(vinyl acetate), acid-catalyzed hydrolysis, equilibrium constant, rate constant.

1. Introduction

Poly(vinyl alcohol) (PVA) is obtained via hydrolysis of poly(vinyl acetate), with the use of either acid or base as a catalyst.¹⁻⁸ The base-catalyzed reaction has an advantage in that the reaction is faster and the process is more economical. However, it is difficult to control the vinyl acetate (VAc):vinyl alcohol (VA) ratio, and the product is ca. 88% VA in most experimental conditions, and the remaining VAc monomers are rather blocky.¹

The acid-catalyzed reaction in the presence of water, on the other hand, is much slower, because water has a larger affinity for proton than the first intermediate of the reaction, the protonated vinyl acetate.² This hydrolysis reaction, however, has an advantage in that it is easier to control the VAc: VA ratio, particularly when water-acetic acid is used as a solvent. We previously studied the equilibrium hydrolysis reaction of PVAc and reported that the equilibrium constant of the reaction at 25 °C is 0.75(± 0.06).⁸ To understand the reaction further, we studied the change of VAc concentration with respect to time by NMR for the acid-catalyzed hy-

drolysis reaction of PVAc at two different solvent compositions with varying water/acetic acid ratio. The reaction rate was calculated and compared with the one reported for the base-catalyzed reaction.⁹

2. Experimental

2.1 Chemicals and Instruments

PVAc with M_w at 90k was obtained from Polysciences, Inc. (Warrington, PA), dissolved in benzene, and freeze-dried under vacuum. Acetic acid, hydrochloric acid, methanol, iodine, boric acid, potassium iodide, and DMSO- d_6 were all reagent grade and used without further purification. NMR spectrum was obtained with an AMX-500 (Germany).

2.2 PVAc Hydrolysis

Two sets of experiment were performed. In Reaction I, PVAc 8 g(0.093 mol VAc) was dissolved in 72.06 g(1.2 mol) of acetic acid in an Erlenmeyer flask, and added to the solution were 5.4 g of deionized water and 4 mL of HCl. Including the water from 37 wt% HCl, the total amount of water in the reaction medium was 8.44 g(0.53 mol). The total volume of the solution was 88.02 mL

[†]To whom correspondence should be addressed. E-mail: spark@sh.ac.kr

and the molar concentrations of the reactants are collected in Table 1. The reaction flask was kept in an incubator at 35 °C, and 5 mL of the solution was taken at an 8 hour interval for precipitation in water. The precipitate was dried under vacuum for 3 days for NMR determination of VAc mol fraction. In Reaction II, the amount of PVAc, acetic acid, and hydrochloric acid were the same as in Reaction I, but the total amount of water in the reaction flask was increased to 23.04 g (1.44 mol).

2.3 Determination of VAc mol%

The vacuum-dried poly(VAc-co-VA) sample was dissolved in DMSO-d₆ at 3 wt% for NMR. The acquisition time was 4.0 sec, sweep width 3500 Hz, pulse delay 1.0 sec, and pulse width 9.8 microsec. The mole fraction of VAc during the hydrolysis reaction, X_{VAc}, was obtained from the following equations:

$$X_{VAc} = \frac{2I_{CH_3}}{3I_{CH_2}} \quad (1A)$$

$$X_{VAc} = \frac{2I_{CH,VAc}}{I_{CH_2}} \quad (1B)$$

where I_{CH₃}, I_{CH₂}, and I_{CH,VAc} represent the intensities of methyl peak, methylene peak, and methin peak of VAc, respectively.¹⁰

3. Results and Discussion

The NMR spectra of PVAc and partly hydrolyzed PVAc with VAc mole fraction at 0.55 are compared in Figure 1. After the hydrolysis, the methylene (CH₂) peak (1.1~1.9 ppm) as well as the methin peak (4.7~5.2 ppm) splits, and new peaks representing the -OH (4.2~4.7 ppm) and the methin (CH) of VA (3.4~3.9 ppm) shows up.

The mole fractions of VAc calculated from Eq. (1A) and (1B) are collected in Table 2. The VAc mole fraction calculated from Eq. (1A) was slightly larger than that from Eq. (1B), by 3.9(±2.0)% in Reaction I and by 4.0(±1.6)% in Reaction II. We suspect that this is because the methyl and methylene peaks are not completely resolved in the NMR spectra of poly(VAc-co-VA).

Since there is also a possibility of overlap between the methin and hydroxy peaks, we took the average of the two values obtained via Eq. (1A) and (1B), instead of using the values obtained from Eq. (1B) exclusively. The hydroxy peak at 4.2~4.7 ppm or the methin peak attached to VA at 3.4~3.9 ppm could also be used for determination of VAc or VA mol fraction by NMR. However, the

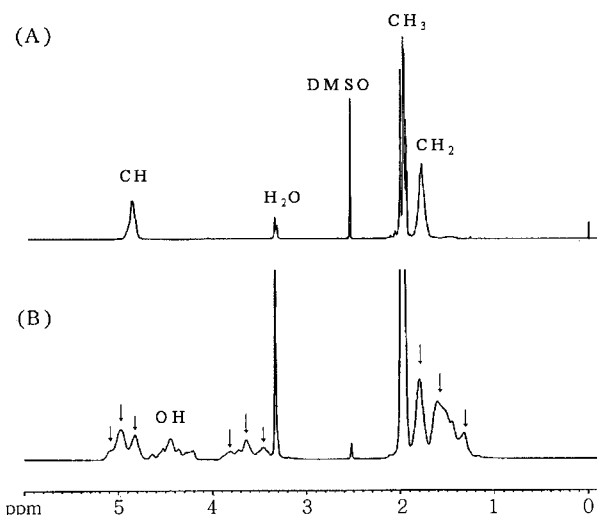


Figure 1. NMR spectra of PVAc (A) and poly(VAc-co-VA). (B) The methylene peak splits (1.1~1.9 ppm) and new hydroxide peak (4.2~4.7 ppm) shows up after hydrolysis of PVAc. Both methin peak in the VAc segment (4.7~5.2 ppm) and VA segment (3.4~3.9 ppm) splits into 3 subpeaks.

Table 2. Mole Fractions of VAc Determined by NMR during the PVAc Hydrolysis

Reaction time/hours	Reaction I			Reaction II		
	1A	1B	Avg.	1A	1B	Avg.
8	.945	.914	.929	.930	.905	.917
16	.871	.843	.857	.821	.804	.812
24	.840	.809	.824	.785	.758	.772
32	.783	.762	.773	.701	.670	.686
40	.795	.759	.777	.625	.612	.619
48	.806	.777	.791	.570	.535	.553
56	.811	.743	.777	.616	.584	.600
64	.770	.755	.762	.571	.535	.553
72				.578	.557	.568

intensities of these peaks at high VAc mole fraction employed in this study were too small for accurate determination of the monomer fraction.

The change of VAc mole fraction with respect to reaction time is shown in Figure 2. The mole fraction of VAc did not change after 32 hours in Reaction I, and 48 hours in reaction II, indicating that the reaction reached an equilibrium.

At the chemical equilibrium, the equilibrium constant *K*_{eq} of the hydrolysis reaction can be written as follows:

$$K_{eq} = [VA][HOAc] / [VAc][H_2O] \quad (3)$$

where [VA], [HOAc], [VAc], [H₂O] represent the equilibrium molar concentration of VA, acetic acid, VAc, and water, respectively. The mole number of HOAc produced by the reaction, which is the same as the mole number of VA, should be added to the original mole number of HOAc, and the mole number of H₂O used

Table 1. Initial Molar Concentrations of the Reactants

	Reaction I	Reaction II
[VAc]	1.06	0.90
[CH ₃ COOH]	13.6	11.7
[H ₂ O]	6.02	14.0

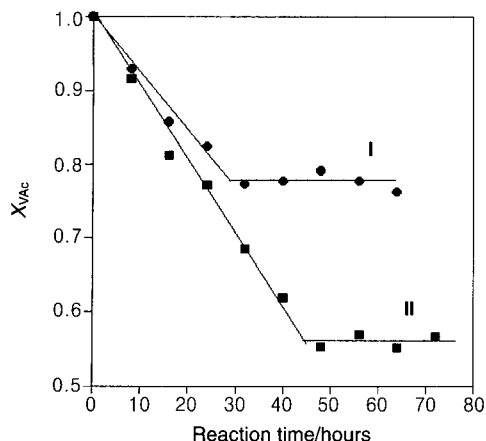


Figure 2. Change of VAc mole fraction in equilibrium hydrolysis reaction of PVAc. The mole fraction did not change after about 32 hours in reaction I and about 48 hours in Reaction II.

by the reaction should be subtracted when calculating the equilibrium HOAc and H₂O concentration. [VA]/[VAc] can be replaced with the mole fractions of VA and VAc. The equilibrium constant K_{eq} calculated this way was $0.76(\pm 0.01)$ in Reaction I and $0.69(\pm 0.01)$ in Reaction II. The slight difference between the two values can be a reflection of solvent quality difference for the poly(VAc-co-VA) at different solvent compositions, but the difference is too small to warrant further discussion. Also the values are not significantly different from the one reported previously, $0.75(\pm 0.06)$ at 25 °C for poly(VAc-co-VA) samples with VAc mole fraction range at 0.45~0.86.⁸

The hydrolysis reaction of PVAc in acetic acid/water medium can be written as a pseudo 1-st order reaction as follows:

$$\frac{dx}{dt} = k(a - x) \quad (4)$$

$$\frac{kt}{2.303} = \log \frac{a}{a - x} \quad (5)^{3,9}$$

Here a represents the initial molar concentration of VAc, and x the molar concentration of VA. The ratio of $a/(a-x)$ can be calculated from the mole fractions of VAc and VA. In Figure 3 are plotted $\log(a/(a-x))$ with respect to reaction time for Reaction II. The data for Reaction I was not included as the plot has only 3 data points before reaching the equilibrium. $\log(a/(a-x))$ was linearly proportional to the reaction time, indicating that the reaction is indeed a pseudo 1-st order, and that there is no indication of the induction period suggested by Joshi and Pritchard.⁹ In the case of methoxide catalyzed hydrolysis reaction of PVAc in methanol, the reaction was reported to be slower at 0~0.1 mole fraction of VA, pseudo 1st-order at 0.1~0.85 mole fraction of VA, and fall off from the 1-st order when VA mole fraction is larger than 0.85. These results were explained via contraction of the polymer chain at VA mole

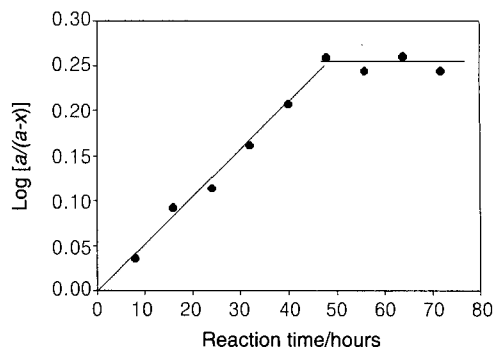


Figure 3. Kinetics of the acid-catalyzed hydrolysis reaction of PVAc in acetic acid/water medium at 35 °C. The kinetics follows a pseudo-first order rate law until the reaction reaches an equilibrium at 48 hours. The rate constant is $1.2 \times 10^{-2} \text{ hour}^{-1}$.

fractions smaller than 0.1 or larger than 0.85, where the solvent quality is not good for the polymer chain.⁹ The result in Figure 3 shows that there is no induction period for hydrolysis in the case of acid-catalyzed equilibrium hydrolysis reaction in water/ acetic acid. The absence of induction period should be a reflection of both the favorable solvent condition, 75.6 wt% aqueous acetic acid, for PVAc compared to the methanol and the smaller size of catalyst (H^+) compared to the methoxide used in the base-catalyzed hydrolysis reaction.⁹

The rate coefficient k calculated from the slope in Figure 3 was $1.2 \times 10^{-2} \text{ hour}^{-1}$ or $3.4 \times 10^{-6} / \text{sec}$. The rate coefficient in the base-catalyzed reaction by Josh and Pritchard was $2.53 \times 10^{-4} / \text{sec}$ at 30 °C. Therefore the acid-catalyzed hydrolysis reaction of PVAc is slower than the base-catalyzed reaction by two orders of magnitude, and this difference should be the reflection of the unstable first intermediate in the acid-catalyzed reaction, as suggested by Sakaguchi *et al.*²

4. Conclusions

We studied the acid-catalyzed hydrolysis reaction of PVAc at two different water/acetic acid compositions via NMR, and found out the following:

- 1) The equilibrium constant at 35 °C was $0.76(\pm 0.01)$ in Reaction I and $0.69(\pm 0.01)$ in Reaction II, which is about the same as the one obtained previously at 25 °C.
- 2) The acid-catalyzed reaction in water-acetic acid was found to follow a pseudo 1-st order reaction with a rate coefficient at $3.4 \times 10^{-6} / \text{sec}$, which is smaller than that of the base catalyzed reaction by 2 orders of magnitude, probably due to the instability of the first intermediate in the acid catalyzed reaction in the presence of water.

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