Synthesis of the Polymer with Polar Side Groups. II. Synthesis and Dielectric Properties of the β -Cyanopropionaldehyde Acetal of Poly(vinyl alcohol)

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ABSTRACT: In order to synthesize a new polymer having flexible polar side groups, the β -cyanopropionaldehyde acetal of poly(vinyl alcohol) (hereafter abbreviated as acetal) was synthesized from poly(vinyl alcohol) and β -cyanopropionaldehyde, with sulfuric acid as a catalyst. The rate of the reaction, and the acetalization degree and dielectric properties of the acetals obtained were examined. The rate was proportional to the product of the concentration of both β -cyanopropionaldehyde and poly(vinyl alcohol) in the early stage of the reaction, but showed a deviation from the second-order kinetics later in the reaction. In order to account for the deviation, a modified second-order rate equation, $dx/dt = k(a-x)(p-2x)[1 - x/(p-x)]^2$, was proposed by considering the isolated hydroxyl groups remaining in the polymer chain which can no longer react with the aldehyde; here a , p , and x represent the initial concentrations of the aldehyde and alcohol, and the amount of the aldehyde consumed at time t . The dielectric constants (ϵ) measured at 1 kHz were 5.2 for the acetylated acetal film of acetalization degree 78.3% and 4.5 for the one of acetalization degree 75.4%.

KEY WORDS Poly(vinyl alcohol) / β -Cyanopropionaldehyde / Acetal / Acetalization Rate / Dielectric Constants /

According to Debye's "dipole theory," a polymer with a high dielectric constant should have groups with large dipole moments. In a search for new polymers with high dielectric constants, we have been investigating the syntheses and dielectric properties of new polymers having flexible polar side groups. In part I of this series we reported on the syntheses and dielectric properties of such new substances as 2-(2, 2-dicyanoethylene)-2, 3-dihydropyran, 2-(2, 2-dicarboalkoxyethylene)-2, 3-dihydropyran, and 2-(2-cyano-2-carboethoxyethylene)-2, 3-dihydropyran.¹ In the present study we took up the acetalization of poly(vinyl alcohol) with β -cyanopropionaldehyde, which is industrially available as an intermediate in the production of L-sodium glutamate. Although acetalization reactions of poly(vinyl alcohol) with various aldehydes have

been reported in the past,² the acetalization of poly(vinyl alcohol) with β -cyanopropionaldehyde is not known and this seems to be the most convenient method to introduce flexible polar side groups into the polymer chain.

This paper deals with the synthesis of the β -cyanopropionaldehyde acetal of poly(vinyl alcohol) and with the kinetics of the reaction. In addition, preliminary results of some dielectric measurements are described.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) commercially obtained (Kurare Poval 105, saponification degree 99%, average polymerization degree 300-700) was dried under reduced pressure. β -Cyanopropionaldehyde (CPA) was prepared from commercially available β -cyanopropionaldehyde dimethylacetal (CPAA) (Ajinomoto Co., Inc.) by

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refluxing with water, then dried over anhydrous sodium sulfate, and distilled under reduced pressure, bp 62–63°C/1 mmHg.³ Dioxane, acetone, methanol, and acetic acid were used after ordinary purifications.

Typical Procedure for the Acetal Synthesis

Measured amounts of PVA and CPA were dissolved in a dioxane–water binary solvent; the solution was kept at 40°C and sulfuric acid was added to the solution as a catalyst with stirring. Additional dioxane, which can dissolve the acetal formed, was successively added into the solution from a dropping funnel to keep the solution system homogeneous throughout the reaction. The total composition of the binary solvent was 65:35 (dioxane:water) at the end of the reaction. After 4 hr the reaction solution was poured into a large excess of water; the precipitated polymer was filtered, washed with water, then reprecipitated from acetone–water, and dried under reduced pressure at 60°C. The acetal was obtained as a white solid mass. Reaction conditions and results of the acetalization are listed in Table I. Characterization of the acetal was made by the IR and NMR

spectra of the acetal formed and also by acetylating the acetal. IR spectrum: ν_{CN} 2220 cm^{-1} , $\nu_{\text{C-O}}$ 1240 cm^{-1} (acetal moiety), $\nu_{\text{C-O-C}}$ 1130 cm^{-1} (acetal moiety), ν_{OH} 3450 cm^{-1} , ν_{CH} 2900 and 2840 cm^{-1} , δ_{CH} 1430 and 1380 cm^{-1} , 820 cm^{-1} (skeletal vibration of acetal ring⁴). NMR spectrum (CDCl_3): τ 5.30 (multiplet, $-\text{CH}-\text{O}-$), τ 6.10 (multiplet, $\text{O}-\text{CH}-\text{O}$), τ 7.54 (triplet, $-\text{CH}_2\text{CH}_2\text{CN}$), τ 8.05 (multiplet, $-\text{CH}_2-$), τ 8.40 (multiplet, $-\text{CH}_2-$ in acetal ring).

Acetylation of the Acetal

Since it was very difficult to dry the acetal sufficiently to determine the acetalization degree and to measure the dielectric properties, acetylation of the acetal was performed. The acetal was dissolved in acetic acid–acetic anhydride (1:1), and a catalytic amount of pyridine was added to the solution, which was then heated to 90°C. After 4 hr the reaction solution was poured into a large amount of water and the acetylated acetal precipitated was filtered, washed with water, then reprecipitated from acetone–water, and dried under reduced pressure at 60°C. The acetylated acetal was obtained as a pale–brown powder. The acetylation was confirmed

Table I. Acetalization of poly(vinyl alcohol) (PVA) with β -cyanopropionaldehyde (CPA)

No.	PVA, mol/l ^a	CPA, mol/l ^a	Acid, mol/l ^a	Solvent ^b	Reaction temp, °C	Reaction time, hr	N, % ^c	Acetalization ^d degree, %	Softening range, °C
1	0.77	0.15	H ₂ SO ₄ 0.50	Dioxane–Water (65:35)	40	4	3.06	36.1	—
2	0.76	0.40	H ₂ SO ₄ 0.50	Dioxane–Water (65:35)	40	4	6.66	75.0	130–140
3	0.81	0.42	H ₂ SO ₄ 0.50	Acetone–Water (65:35)	40	4	6.36	72.0	132–142
4	0.76	0.57	H ₂ SO ₄ 0.50	Dioxane–Water (65:35)	40	4	7.18	80.4	—
5	0.81	0.38	HCl 1.4	Dioxane–Water (65:35)	40	4	6.61	74.4	145–153
6	0.76	0.40	H ₂ SO ₄ 0.50	Methanol–Water (65:35)	40	4	3.04	35.9	—
7	2.52	1.34	H ₂ SO ₄ +pTS ^e 0.50+0.06	Water	25	4	3.63	42.5	128–137
8	2.52	1.81	0.50+0.06	Water	25	4	4.55	52.6	—
9	0.76	0.38	0.50+0.06	Dioxane–Water (65:35)	20	4	3.94	45.9	—

^a Initial concentration.

^b The figures in the parentheses denote the composition at the end of the reaction.

^c Nitrogen contents of the acetylated acetals.

^d Calculated from the equation:

Acetalization degree (A. D.) = $8600 \text{ N} / (700 + 9.5 \text{ N})$. N: % of nitrogen content.

^e *p*-Toluene sulfonic acid.

by the disappearance of the OH stretching vibration band in the IR spectrum of the acetylated acetal.

IR spectrum: ν_{CH} 2910 and 2850 cm^{-1} , ν_{CN} 2240 cm^{-1} , $\nu_{\text{C=O}}$ 1730 cm^{-1} (acetyl moiety), $\nu_{\text{C-O-C}}$ 1130 cm^{-1} (acetal moiety), δ_{CH} 1420 and 1360 cm^{-1} , $\nu_{\text{C-O}}$ 1230 cm^{-1} , 820 cm^{-1} (skeletal vibration of acetal ring).

NMR spectrum (hexadeuterio acetone): τ 5.30 (multiplet, CH—O), τ 6.15 (multiplet, O—CH—O), τ 7.46 (triplet, —CH₂—CH₂CN), τ 7.95 (singlet, —CO—CH₃), τ 8.15 (multiplet, —CH₂—), τ 8.45 (multiplet, —CH₂— in acetal ring).

Rate Measurements of the Acetalization Reaction

The reaction rate was followed in a dioxane—water (40:60) binary solvent at 40°C. The measurement of the rate was carried out by titration of the unreacted aldehyde with sodium borohydride. Details of the procedure are described in our previous paper.⁵

A 2 ml aliquot was pipetted out from the reaction system at appropriate time intervals, and added to 10 ml of 0.5 *N* sodium hydroxide aqueous solution. To this solution was added 10 ml of aqueous solution of 0.5 *N* sodium hydroxide containing 25 mg of sodium borohydride. After standing for 2 hr, 20 ml of 0.25 *N* KIO₃ aqueous solution, 2 g of KI, and then 25 ml of 4 *N* H₂SO₄ solution were added to the solution. The solution was allowed to stand for 5 min in the dark and titrated with 0.1 *N* sodium thiosulfate. Since the reaction solution usually became turbid after 30% of the equivalent amount of β -cyanopropionaldehyde was consumed, the rate measurement was limited to this range.

Measurements

The IR spectra were taken with a Hitachi EPI-G-2 infrared spectrometer. The NMR spectra were measured in deuterio chloroform or hex-

adeuterio-acetone with TMS as an internal standard with a Japan Electron Optics Laboratory JNM-3H-60 spectrometer.

Measurement of the dielectric constant and loss was carried out with a G. R. Capacitance Bridge Type 1615 A at room temperature. Disk samples of 40-mm diameter and 0.45-mm thickness were submitted for the measurement.

RESULTS AND DISCUSSION

Synthesis of the β -Cyanopropionaldehyde Acetal of Poly(vinyl alcohol)

Since it has generally been accepted that a higher degree of acetalization of poly(vinyl alcohol) (PVA) is obtained in a homogeneous system than in a heterogeneous system, the present acetalization reaction was carried out ordinarily in a dioxane—water binary solvent with sulfuric acid as a catalyst. Under the reaction conditions described in the experimental section no appreciable side reaction such as the hydrolysis of the nitrile group of β -cyanopropionaldehyde (CPA) occurred. The results are summarized in Table I. However, when the reaction was carried out in a methanol—water binary solvent, the acetal formation was accompanied by the formation of β -cyanopropionaldehyde dimethylacetal (CPAA), which was confirmed by the analysis of the reaction mixture by means of gas chromatography.

It was then expected that the acetal should also be synthesized from CPAA and PVA in a solvent containing water since the above reaction is a reversible one. This was indeed found to be

Table II. The formation of the β -cyanopropionaldehyde acetal of poly(vinyl alcohol) from Poly(vinyl alcohol) (PVA) and β -cyanopropionaldehyde dimethyl acetal (CPAA) in dioxane—water (40 : 60) at 40°C.

PVA, mol/l	CPAA, mol/l	H ₂ SO ₄ , mol/l	Reaction time, hr	Elementary ^a analyses (N, %)	Acetalization ^b degree, %
0.78	0.41	0.50	4	5.68	64.8
0.64	0.40	0.50	4	5.15	59.2

^a Nitrogen contents of the acetylated acetals.

^b Calculated from the equation: A. D.=8600 N/(700+9.5 N). N; % of nitrogen content.

Table III. Solubilities of the acetals and the acetylated acetals

Solvent	Acetal		Acetylated acetal	
	A. D., 42.5%	A. D., 74.4%	A. D., 35.9%	A. D., 74.4%
Methyl alcohol	○	●	○	○
Dioxane	◐	○	◐	◐
Pyridine	○	◐	○	◐
Acetic acid	◐	○	○	◐
Acetone	●	◐	◐	◐
Acetonitrile	◐	◐	◐	◐
Ethyl acetate	×	◐	◐	◐
Benzene	×	●	◐	●

◐, easily soluble; ○, soluble; ◐, partly soluble; ●, swollen; ×, insoluble.

true. Table II shows the results of the formation of the acetal from PVA and CPAA with sulfuric acid as a catalyst in dioxane—water (40 : 60) at 40°C. Generally, the degree of acetalization was found to increase with increasing concentration of the aldehyde. When the acetalization was carried out in water, the degree of acetalization of the acetal obtained was lower, probably because the reaction system became heterogeneous. When the acetalization was carried out in methanol—water (65 : 35) the degree of acetalization was also lower, probably due to the occurrence of a side reaction as described above. Although the degree of acetalization varied greatly depending upon the reaction conditions, it could reach 81% under certain reaction conditions, a value which is close to the theoretical maximum value 86.46% reported by Flory, based on a statistic calculation.⁶

The acetals and acetylated acetals obtained were white masses and pale-brown powders,

Figure 1. Time—conversion curves of the acetalization reaction of PVA with CPA under varying initial concentrations of the reactants: ●, [PVA], 0.15 mol/l, [CPA], 0.15 mol/l, [H₂SO₄], 0.5 mol/l; ◐, [PVA], 0.15 mol/l, [CPA], 0.075 mol/l, [H₂SO₄], 0.5 mol/l; ◐, [PVA], 0.10 mol/l, [CPA], 0.075 mol/l, [H₂SO₄], 0.5 mol/l; ○, [PVA], 0.15 mol/l, [CPA], 0.038 mol/l, [H₂SO₄], 0.5 mol/l; where [PVA] was obtained on the basis of the monomer units.

respectively. Solubilities of the acetals and the acetylated acetals were somewhat different depending upon the degree of acetalization; examples are given in Table III.

Kinetics of the Acetalization Reaction

The effect of the initial concentration of the reactants on the reaction rate was examined. Figure 1 shows examples of the time—conversion curves obtained under varying initial concentrations of the reactants. It was found that the early stage of the reaction followed the second-order rate equation:⁷

$$K = 1/t(p-2a) \ln [a(p-2x)/p(a-x)] \quad (p \neq 2a) \quad (1)$$

Table IV. The rate constants of the acetalization of poly(vinyl alcohol) (PVA) with β -cyanopropionaldehyde (CPA) in dioxane—water (40 : 60)

No.	PVA, mol/l	CPA, mol/l	H ₂ SO ₄ mol/l	pH	Reaction temp, °C	$k \times 10^4$ l/mol sec ⁻¹
1	0.10	0.075	0.50	1.10	40	7.24
2	0.15	0.075	0.50	1.10	40	7.16
3	0.15	0.038	0.50	1.10	40	7.25
4	0.15	0.15	0.50	1.10	40	6.84
5	0.15	0.075	0.50	1.10	60	24.2
6	0.15	0.075	0.50	1.10	20	1.56

$$k = [1/(a-x) - 1/a]/2t$$

$$= [1/(p-2x) - 1/p]/t \quad (p=2a) \quad (2)$$

where p and a represent the initial residue concentrations of PVA and CPA, respectively, and x stands for the amount of CPA consumed at time t . As listed in Table IV the rate constants calculated from the above equations for varying initial concentrations of the reactants were almost the same at the same pH within experimental errors, although the rate constant was dependent upon the acidity of the reaction media. Thus the present acetalization reaction of PVA with CPA may likewise be understood by the mechanism presented by Ogata, *et al.*⁷, for the formalization of PVA.

It should be noted, however, that the reaction rate deviated appreciably from the above second-order rate equations as the reaction proceeded beyond about 15% conversion. Since the reaction medium became turbid in the later stage of the reaction, it was suspected that the decrease in the concentration of hydroxyl groups in the reaction system might be responsible for the observed deviation. To check this point the rate measurement of the reacetalization reaction was carried out in dioxane—water (70:30) on the acetal obtained in exptl No. 2 (acetalization degree; A. D. 36%) of Table IV, other reaction conditions being kept the same as those in exptl No. 2 of Table IV. The reaction system did not turn turbid before 60 min in this solvent composition, but the deviation of the experimental results from the second-order rate equation was still observed to occur after 40 min, when the degree of acetalization had reached 45.3%, as shown in Figure 2. In fact, a deviation of the observed reaction rate from the ordinary second-order rate equation appears to be more or less a general tendency for the formalization or acetalization reaction of PVA. The following two factors are considered as causes for this deviation: (a) different reactivities of hydroxyl groups due to different tacticities; it is known that the rate of the acetalization of the isotactic hydroxyl groups is three times larger than that of the syndiotactic hydroxyl groups in PVA,⁸ while the ratio of isotactic to syndiotactic hydroxyl groups in PVA used in the present study is 55/45; (b) the effect of isolated hydroxyl groups

Figure 2. Plots of the second-order rate equation for the reacetalization of the acetal (A. D. 36%) with CPA in dioxane—water (70:30) at 60°C: [OH in the acetal], 0.096 mol/l; [CPA], 0.075 mol/l; [H₂SO₄], 0.5 mol/l. Plots of kt vs. time t , where k value at each time t were calculated from eq 1. If the second-order kinetics eq 1 is correct, the plots should be linear, as shown by the solid line.

which can no longer react with aldehyde; in the early stage of the reaction the number of the isolated hydroxyl groups is very small, and the ordinary second-order rate eq 1 or 2 can be applied to the reaction; however, as the reaction proceeds, accumulation of the isolated hydroxyl groups becomes appreciable and its effect on the reaction can no longer be negligible, resulting in a deviation from the ordinary second-order rate equation.

Modified rate equations which taken into account the isolated hydroxyl groups have been derived separately by Boucher⁹ and by Vlodavets.¹⁰ As the Boucher's modified rate equation is derived under the condition of the pseudo-first-order reaction, this equation could not be applied to our present second-order kinetics. Contrary to this, the Vlodavets' equation represents the second-order kinetics. But, when we wish to apply this modified rate equation to the practical rate measurements to obtain the rate constant k at time t , we meet the difficulty that the rate equation cannot be integrated analytically. However, this equation can still be integrated numerically. By inserting our experimental data, the curve (a) in Figure 3 is obtained, which shows

Figure 3. Examination of the ordinary second-order rate equation and the modified one: (a), kt value was obtained from Vlodavets' equation; (b), kt value was obtained from our eq 4; (c), kt value was obtained from the usual eq 2. If the rate constants k are obtained from the correct rate equation, they should be independent of time t , and the plots of kt vs. t should be linear, as shown by the straight line. When the k values are calculated from the ordinary second-order eq 2, the plots of kt vs. t deviated from a straight line at times $t > 20$ min, as seen in the curve (c). The plots are made in the case of $p = 2a$. When the k values are obtained from our modified eq 4 and Vlodavets' equation, considering the effect of the isolated hydroxyl groups, the plots showed less deviation, as seen in the curves (a) and (b).

the second-order rate constant k multiplied by t vs. t under the assumption that the Vlodavets' equation is applicable in our case.

In what follows, we will derive another modified second-order rate equation which takes account of the accumulation of the isolated hydroxyl groups and can be applied conveniently to practical rate measurements, although it will be correct only in the early stages of the reaction.

The total concentration of the hydroxyl groups at time t can be expressed as $(p - 2x)$, where p represents the initial concentration of the hydroxyl groups in PVA and x is the amount of the aldehyde formed after time t . If any unreacted hydroxyl group accompanies a pair of hydroxyl groups already reacted on both sides,

that free hydroxyl group must be an isolated one which can no longer react with aldehyde. This case will occur with the probability of $[x/(p-x)]^{*1}$. Therefore, the concentration of the hydroxyl groups available for the acetalization reaction at time t is represented by $(p - 2x)[1 - [x/(p-x)]^2]$. Thus, the ordinary second-order rate equation, $dx/dt = k(a-x)(p-2x)$, will be modified into eq 3

$$dx/dt = k(a-x)(p-2x)[1 - [x/(p-x)]^2] \quad (3)$$

In the case of $p = 2a$, integration of eq 3 affords eq 4

$$kt = x/p(p-2x) + x(p-x)/2p(p-2x)^2 + (1/4p) \ln [p/(p-2x)] \quad (4)$$

Equation 4 will be replaced by eq 4' by substituting X for $2x/p$.

$$pkt = 1/(1-X) - 1 - 1/4(1-X) + X/4(1-X) - 3X^2/8(1-X) \quad (4')$$

Equation 2 is likewise replaced by eq 2'

$$pkt = 1/(1-X) - 1 \quad (2')$$

When eq 4' and eq 2' are compared, it can be seen that the higher-order terms in eq 4' represent the correction due to the accumulation of the isolated hydroxyl groups. Figure 3 shows the plot of kt against t where k is the second-order rate constant. The kt value in curve (c) was derived from eq 2, whereas the kt values in curves (a) and (b) were obtained from Vlodavets' equation and our eq 4, respectively. The curves (a) and (b) show less deviation from the straight line than does the curve (c). With respect to the curves (a) and (b), the curve (a) is closer to a straight line than the curve (b). A comparison between Vlodavets' equation and ours is given in Appendix II.

As can be seen in Figure 3, all three curves show a deviation from an ideal straight line at the later stage of the reaction even though the effect of the isolated hydroxyl groups is taken into consideration. This may be mainly due to the factor (a) mentioned before, that different reactivities of the hydroxyl groups in PVA are due to the difference in tacticities.

*1 See Appendix I.

Dielectric Properties

Dielectric constants at 1 kHz were 5.2 for the acetylated acetal film of the acetalization degree 78.3% (Sample 1) and 4.5 for that of the acetalization degree 75.4% (Sample 2). Frequency dependences of the dielectric constant (ϵ') and dielectric loss (ϵ'') are shown in Table V.

Table V. Frequency dependences of the dielectric constant and dielectric loss at room temperature

Frequency	Sample 1		Sample 2	
	ϵ'	$\epsilon'' \times 10^2$	ϵ'	$\epsilon'' \times 10^2$
30 Hz	5.3	7.95	4.6	3.7
1 kHz	5.2	4.2	4.5	3.6
100 kHz	4.9	22.0	4.3	10.7
1 MHz	Below 4.8	Above 48.0	4.1	22.3

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APPENDIX I

We assumed that PVA has a closed infinite long chain, and that the acetalization reaction occurs at random at any pair of adjacent unreacted hydroxyl groups. If the number of the acetal groups formed at time t is represented as

Total p OH groups.

Number of acetal groups; x ,
unreacted OH groups; $p-2x$.

Sum of the number of the unreacted OH groups and that of acetal groups; $p-x$.

x , then the number of the unreacted hydroxyl groups is $p-2x$. At this time, the probability that the group adjacent to any unreacted hydroxyl groups is also an unreacted hydroxyl group is given by $(p-2x)/(p-x)$, where $(p-x)$ denotes the sum of the numbers of the unreacted hydroxyl groups and those of the acetals. The probability that the group adjacent to any unre-

acted hydroxyl group is the acetal is given by $x/(p-x)$. Therefore, the probability that any unreacted hydroxyl group has unreacted hydroxyl groups on both side is $(p-2x)^2/(p-x)^2$, and the probability that any unreacted hydroxyl group has an unreacted hydroxyl group on one side and an acetal group on the other side is $2x(p-2x)/(p-x)^2$; the probability that both are

acetals, that is, the unreacted hydroxyl group is the isolated one, is $x^2/(p-x)^2$. Since the isolated hydroxyl groups are not available for the reaction, the number of unreacted hydroxyl groups available for the reaction at time t will be

$$(p-2x)[1-[x/(p-x)]^2].$$

APPENDIX II

Expansions of Vlodavets' equation with application of our notation, *i.e.*, $\alpha_p=2x/p$, $C_p^0=p$, $C_p=p-2x$, $C_a^0=a$, $C_a=a-x$, and $b=2a/p$, and of our eq 3 yield eq 5 and 6.

Vlodavets':

$$\begin{aligned} dx/dt &= k(a-x)(p-2x)[1-(1/4)\ln^2(1-2x/p)] \\ &= k(a-x)(p-2x)[1-(1/4) \\ &\quad \times [2x/p + 4x^2/2p^2 + 8x^3/3p^3 + \dots \\ &\quad + (1/n)(2x/p)^n]^2] \end{aligned} \quad (5)$$

Ours:

$$\begin{aligned} dx/dt &= k(a-x)(p-2x)[1-[x/(p-x)]^2] \\ &= k(a-x)(p-2x)[1-(1/4) \\ &\quad \times [2x/p + 4x^2/2p^2 + 6x^3/3p^3 + \dots \\ &\quad + 2(x/p)^n]^2] \end{aligned} \quad (6)$$

In the early stage of the reaction, $x \ll p$, both equations reduce to the same eq 7:

$$dx/dt = k(a-x)(p-2x)[1-(1/4)[2x/p + 4x^2/2p^2]^2] \quad (7)$$

Thus, our equation is a simple and clear one which can sufficiently evaluate the concentration of the isolated hydroxyl groups in the early stage of the reaction. However, later in the reaction, this equation gives a smaller value of the concentration of the isolated hydroxyl groups than the actual one, since its derivation is based on some approximations. Therefore, it leads to an underestimation of the rate constants, as shown in Figure 3.