CHAPTER 4

SEQUENCE DISTRIBUTION OF ACETYL GROUP IN PARTIALLY HYDROLYZED PVAL (PVAL-AC)

In the ^{13}C-NMR spectra of vinyl alcohol-vinyl-acetate copolymers prepared by the partial hydrolysis of PVAC and by the partial reacetylation of PVAL, three well-resolved methylene carbon lines are observed, which can be assigned to three dyad sequences, (OH, OH), (OH, OAc), and (OAc, OAc), with increasing field strength. From their relative intensities, the quantitative determination of sequence distribution in the copolymers has become possible. Some applications to various samples are reported. The hydrolyzed PVAC is blockier with the block character of 0.4-0.6, where the blockiness depends upon the method of hydrolysis, while the reacetylated PVAL is close to random with the block character of 0.8-1.1. The blockiness increases with increasing degree of hydrolysis. The results can be explained by the mechanism of successive hydrolysis along the polymer chain. The ^{1}H-NMR spectra are also studied.

4.1 INTRODUCTION

Copolymers of vinyl alcohol and vinyl-acetate (they will be abbreviated to PVAL-AC below) are prepared by hydrolysis of PVAC and by reacetylation of PVAL.[1] It has been known that the physical properties of PVAL-AC, such as melting point,[2] solubility, viscosity, and surface tension of the aqueous solution, are not a simple function of the copolymer composition, but depend on the method of preparation of the copolymers, and that this can mainly be attributable to sequence distribution in PVAL-AC. The PVAL-AC prepared by hydrolysis is regarded as being in a blockier fashion because the marked-acceleration was observed in the rate of hydrolysis of PVAC,[3-5] whereas this phenomenon could be reasonably explained by the assumption that alkali or-acid as

catalyst is adsorbed on the hydroxyl groups in the hydrolyzed sites of the chains and increases the rate of hydrolysis of directly neighboring-acetyl groups successively, and hence hydrolysis proceeds mainly along the chain.[5]

Various PVAL-AC copolymers are commonly produced and used for industrial purposes such as an emulsifier-stabilizer in emulsion polymerization. In this field, the importance of the sequence distribution PVAL-AC has been recognized, and then various methods and conditions to control the distribution have been investigated in order to get PVAL-AC of better properties.[1,6] Hence, the quantitative determination of the sequence distribution is significant for the characterization of copolymers as well as for the investigation on the mechanism of hydrolysis (and reacetylation) as one of the basic and typical high-polymer reactions.

Previously, several methods to evaluate the sequence distribution in PVAL-AC have been presented, infrared spectroscopy,[7] melting point,[2] and iodine color reaction.[8] Although they are useful and practical for certain purposes at present, they seem to be indirect and qualitative for the characterization.

In the present investigation on the ^{13}C- and ^{1}H-NMR spectra of PVAL-AC, it has been found that the methylene carbon resonance shows three well-resolved lines assigned to the three different copolymer sequences. Few ^{13}C-NMR studies have been published on the sequence distribution in vinyl copolymers such as PVAL-AC, although successful applications of ^{13}C-NMR to vinyl homopolymers,[9] ethylene-vinyl monomer copolymers,[10,11] and others[9,12] have been known.

In the following sections, the mole fractions of vinyl alcohol and vinyl-acetate units will be denoted by (OH) and (OAc), respectively, while the three kinds of dyad sequences and their mole fractions will be denoted by (OH, OH), (OH, OAc) (including (OAc, OH)), and (OAc, OAc).

4.2 EXPERIMENTAL

Materials PVAL-AC copolymers with various copolymer compositions were prepared in each of the following three ways. As starting materials, the commercially produced PVAC (Kuraray Co.) by free-radical polymerization and PVAL ($\overline{P}_n$=1700) prepared by the hydrolysis of the PVAC were used.

(A) Direct Saponification.

$$PV{\cdot}OAc + NaOH \rightarrow PV{\cdot}OH + NaOAc$$

PVAC was dissolved in a mixed solvent of acetone and water at 0.13 mol/L concentration and saponificated by adding a solution of NaOH in water with stirring to bring the solvent composition to 8:2 by volume. The degree of hydrolysis was controlled by the amount of NaOH.

(B) Alcoholysis.

$$PV \cdot OAc + CH_3OH \xrightarrow{(CH_3ONa)} PV \cdot OH + CH_3OAc$$

PVAC was dissolved in absolute methanol at 0.05 mol/L concentration and alcoholyzed at 30°C by sodium methylate (0.00638 mol/L) as catalyst. The reaction was stopped by adding excess-acetic-acid to neutralize the basic catalyst. The degree of hydrolysis was controlled by the total reaction time.

(C) Reacetylation.

$$PV{\cdot}OH + AcOH \rightarrow PV{\cdot}OAc + H_2O$$

PVAL was dissolved and acetylated in the mixture of acetic acid and water. The degree of acetylation was controlled by the relative amounts of the acetic acid and water.

All the samples of PVAL-AC were purified by means of dialysis and reprecipitation.

Method Acetone, water, and mixtures of them were used as solvents for the samples in the ^{13}C-NMR experiment according to their solubility. Dimethyl sulfoxide, a good solvent for all the PVAL-AC, is not suitable for the present purpose because the resonance line of the solvent overlaps with the methylene carbon lines in PVAL-AC. The samples of approximately 25% (w/v) in 8 mm o.d. tubes were observed at 25.144 MHz with a Varian HA-100 spectrometer, which has been modified for pulse-Fourier transform spectroscopy and interfaced with a Varian DATA 620/I computer. The free-induction decays of about 25 000 times were stored in 4K computer locations using a pulse width of 70 μs, an acquisition time of 1 s, a repetition time of 2.5 s, and a spectral width of 2000 Hz. The ^{13}C-enriched methyl iodide in a capillary was used as an external homonuclear lock signal.

^1H-NMR spectra were obtained at 50°C with the Varian HA-100 Spectrometer at 100 MHz using dimethyl sulfoxide-d_6 (DMSO-d_6) as a solvent.

4.3 RESULTS

4.3.1 ^{13}C-NMR of PVAL-AC

Figure 22 shows the ^{13}C-NMR spectra of the methine and methylene region in the two samples of PVAL-AC which were prepared by the direct saponification of PVAC and by the reacetylation of PVAL, as well as in the PVAL and PVAC homopolymer samples. The (OH) is 53.0% in the former PVAL-AC while it is 50.0% in the latter. The resonances of the-acetate methyl and carbonyl carbons are not indicated in the figure because they show simple singlet peaks.

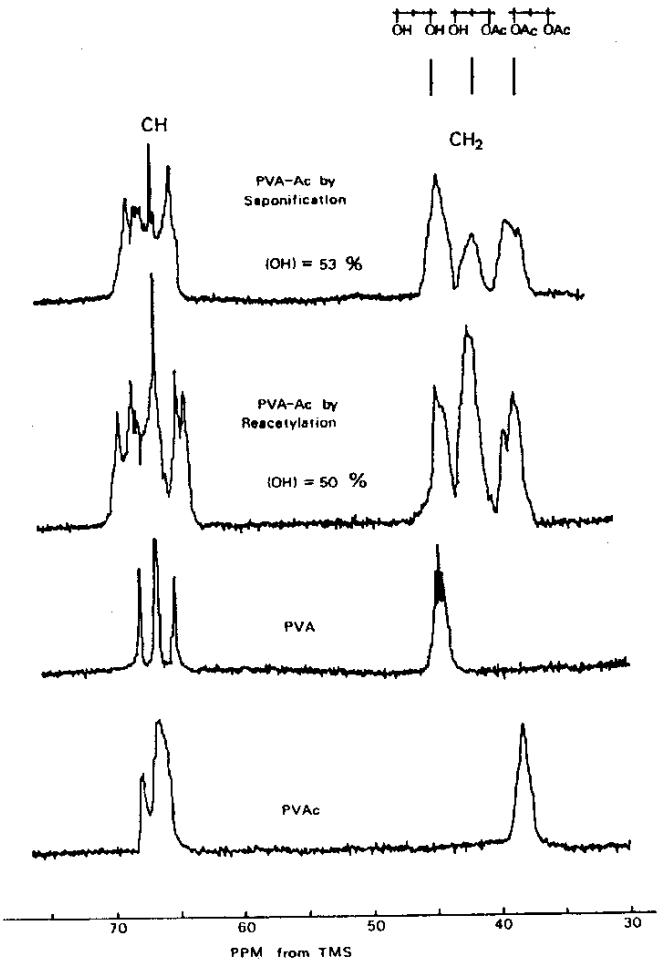


Figure 22 The 25.144-MHz 13C-FT-NMR spectra of the two samples of PVAL-AC prepared by direct saponification and by reacetylation and of PVAL and PVAC homopolymers. The stick spectrum represents the 13C chemical shift values calculated for the three difference sentences.

Three well-resolved lines are observed in the methylene carbon resonance in PVAL-AC, whereas the chemical shifts of the lines at the lowest and highest fields agree with those of the methylene carbon lines in PVAL and PVAC, respectively. Therefore, the three methylene lines in PVAL-AC can be assigned to the three dyads, (OH, OH), (OH, OAc), and (OAc, OAc), with increasing field strength. There is no possibility of unexpected overlaps of lines arising from stereochemical configuration because the splittings due to stereochemical configuration are essentially not resolved in the methylene carbon resonances in PVAL and PVAC, and because the observed mole fractions of the dyads according to the above assignment are consistent with the copolymer compositions determined independently from ^{1}H-NMR. The ^{13}C-NMR of PVAL and PVAC homopolymers has already been reported elsewhere.[13-15]

The above assignment is also ascertained by the chemical-shift estimation. The chemical shifts of the methylene carbons in the three different dyads in PVAL-AC were calculated using the empirical additivity rule about ^{13}C chemical shift,[16-18] and they are illustrated as a stick spectrum in the upper portion of the figure. On the assumption of the essentially equal enhancement due to the nuclear Overhauser effect among the three methylene carbon lines[19] the mole fractions of the three dyads can be accurately determined from the intensities of the lines.

A striking contrast is shown between the two methylene carbon spectra of PVAL-AC, with a copolymer composition of about 50% in both samples, prepared by direct saponification and by reacetylation. A small content of the (OH, OAc) lines reveals a blockier sequence distribution in the former, while in the latter the sequence is regarded as almost randomly distributed because the ratio of the intensities of the three lines are approximately 1:2:1. A quantitative discussion will be given in later sections.

The methine carbon resonance, on the other hand, appears as a complicated spectrum containing a number of lines overlapping one another. This complication may arise from the sensitiveness of the methine carbons to both copolymer sequence and stereochemical configuration. These lines have not yet been assigned since there are as many as 20 kinds of triads to be considered.

4.3.2 ^{1}H-NMR of PVAL-AC

Figure 23 shows the ^{1}H-NMR spectra of the two samples of PVAL-AC, identical with the

samples in Figure 22, dissolved in DMSO-d_6. Apparently there are some differences in the shapes of the methylene proton resonances between the two spectra. Two lines with approximately equal intensities can be observed in the upper spectrum for the hydrolyzed PVAC, while a broad band with shoulders is observed in the lower spectrum for the reacetylated PVAL. The two methylene lines in the former can probably be assigned to the (OAc, OAc) and (OH,OH) dyads because their chemical shifts agree with those of PVAC and PVAL, although the weaker line due to the (OH, OAc) dyad, which is not observed apparently, must be hidden in the two lines. In the reacetylated PVAL, on the other hand, the stronger line located between the (OAc, OAc) and (OH, OH) lines may be assigned to the (OH, OAc) dyad. From the methylene proton spectrum as well, therefore, the sequence distribution in PVAL-AC can be estimated although it can merely be done in a qualitative manner because of the severe overlapping of the lines at a 100-MHz experiment.

The methine proton resonance is observed as two well-resolved absorption bands, which can unequivocally be assigned to the two kinds of methine protons adjacent to the acetyl groups and adjacent to the hydroxyl groups with increasing field strength. From the intensities of the two methine lines the copolymer composition can be determined, although a careful analysis is required because the hydroxyl and water proton resonances are present in this region.[20] (Water remains as an impurity in the samples and solvent.) There are some indications that the positions and shapes of the methine proton bands are different between the two samples. This may be attributable to the effects of different copolymer sequences in them, but no clear peaks can be resolved in the 100-MHz measurements.

4.3.3 Intensity Analysis

The copolymer compositions and the mole fractions of dyads were determined from the methine proton resonance and from the methylene carbon resonance, respectively, for the various samples of PVAL-AC prepared by the three different ways, direct saponification, alcoholysis, and reacetylation, and with different copolymer compositions. The results are shown in Table 3, where the (OH) values derived from the dyad data are also shown for comparison.

$$(OH) = (OH, OH) + (OH, OAc)/2 \qquad (1)$$

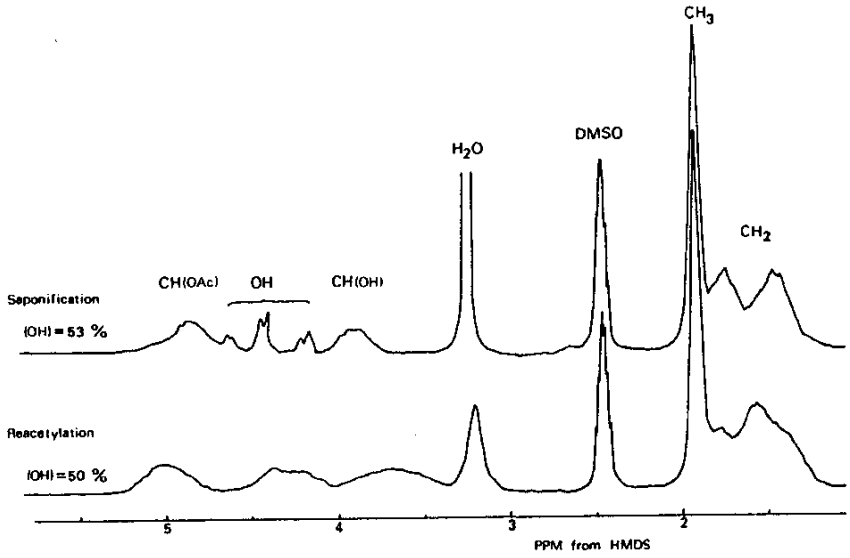


Figure 23 The 100-MHz ^{1}H-NMR spectra of the two samples of PVAL-AC prepared by direct saponification and by reacetylation.

They agree with the (OH) determined from methine proton resonance within ±2% in absolute value. Table 3 also shows the block characters, η, and the mean run lengths of vinyl alcohol and of vinyl-acetate units, l_{OH} and l_{OAc}, calculated from the following formulas.[21,22]

$$\eta = (OH, OAc)/2\cdot(OH)(OAc) \tag{2}$$

$$l_{OH} = 2(OH)/(OH, OAc), \qquad l_{OAc} = 2(OAc)/(OH, OAc) \tag{3}$$

The η value is a convenient guide to characterize a sequence distribution in binary copolymers, it takes $0 \leq \eta < 1$ for blockier distributions, $\eta = 1$ for completely random, and $1 < \eta \leq 2$ for alternate-like cases.

4.4 DISCUSSION

4.4.1 A Diagram of Sequence Distribution

The sequence distribution in binary copolymers can be plainly expressed by the use of a diagram as shown in Figure 24, where, in the present case, the mole fraction of the (OH, OAc) dyad and the mole fraction of (OH) are taken as ordinate and abscissa, respectively. The other quantities, (OAc), (OAc, OAc), and (OH, OH), can easily be obtained from (OH, OAc) and (OH).

When the sequence distribution is completely random, the following relation should hold.[21-23]

Table 3 The compositions, the mole fractions of dyads, the block characters, η and the mean run lengths, l_{OH} and l_{OAc}, in PVAL-AC copolymers

Method of preparation	Sample No.	Composition, %		Dyad, %			(OH)[a] %	η	Mean run length	
		(OH)	(OAc)	(OH, OH)	(OH, OAc)	(OAc, OAc)			l_{OH}	l_{OAc}
Direct saponification	A-I	8.5	91.5	4.2	8.3	87.5	8.4	0.53	2.05	22.0
	A-II	24.2	75.8	16.1	18.1	65.8	25.1	0.49	2.67	8.38
	A-III	53.0	47.0	41.0	23.0	36.0	52.5	0.46	4.61	4.09
	A-IV	87.6	12.4	81.0	10.9	8.1	86.5	0.50	16.1	2.28
	A-V	97.9	2.1	94.6	3.0	4.4	96.1	0.40	65.3	1.4
Alcoholysis	B-I	50.3	49.7	34.2	31.8	34.0	50.1	0.64	3.16	3.13
	B-II	60.6	39.4	44.8	29.9	25.3	59.8	0.63	4.06	2.64
	B-III	74.0	26.0	63.4	21.5	15.1	74.2	0.56	6.88	2.42
	B-IV	87.1	12.9	81.0	10.9	8.1	86.5	0.49	16.0	2.37
Reacetylation	C-I	21.5	78.5	4.2	37.0	58.8	22.7	1.10	1.16	4.24
	C-II	50.5	50.0	25.4	48.3	26.3	49.6	0.97	2.07	2.07
	C-III	66.3	33.7	45.4	39.5	15.1	65.2	0.88	3.36	1.71
	C-IV	79.0	21.0	64.4	27.4	8.2	78.1	0.83	5.77	1.53

[a] The values derived from the dyad data, for comparison.

$$(OH, OAc) = 2(OH)(OAc) \quad (4)$$

This relation is drawn by the curve in Figure 24. The (OH, OAc) value decreases as the sequence distribution becomes blockier, and (OH, OAc) = 0 for completely block copolymers. In contrast, (OH, OAc) increases as the sequence distribution becomes alternate-like, and the maximum is realized when one kind of monomer of lower content never adjoin each other and necessarily lie between another kind of monomer. For this type of distribution, which may be called a "pseudo-alternate" case, a relation

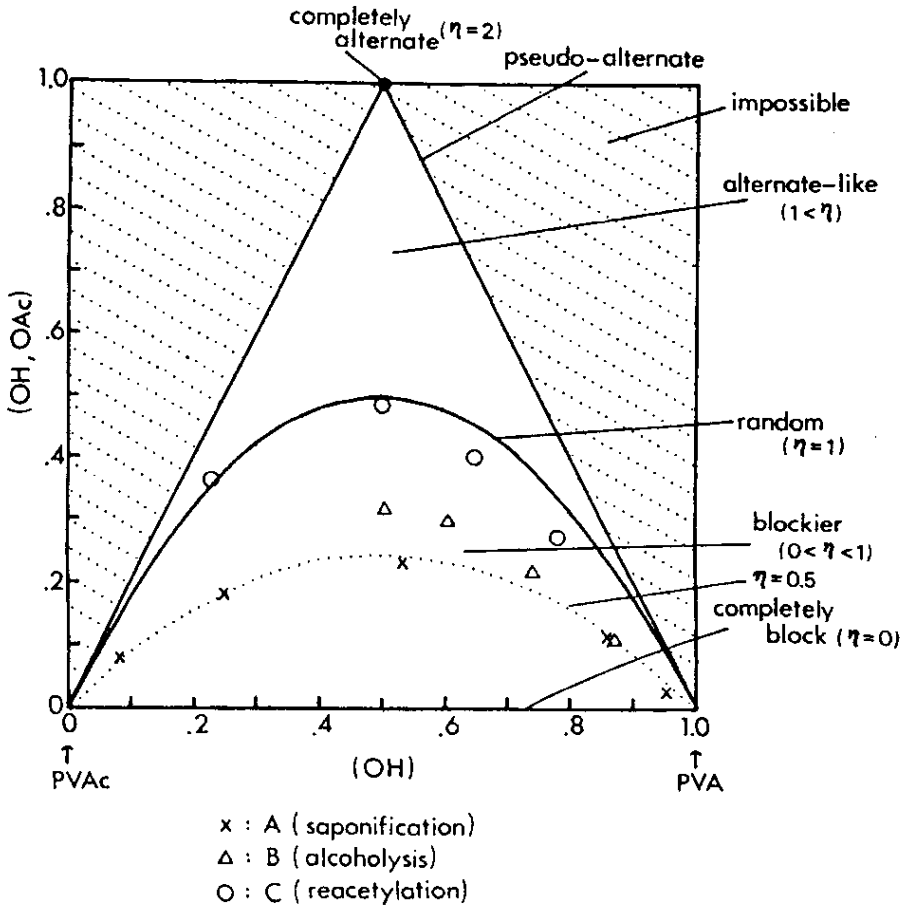


Figure 24 The diagram of the (OH,OAc) dyad proportion vs. the content of hydroxyl group

$$(OH, OAc) = 2 \cdot Min\{(OH), (OAc)\} \quad (5)$$

holds. This relation is expressed by the two straight lines. Apparently there exists no sequence distribution corresponding to any point in the outside of the triangle formed by these two straight lines and the abscissa. The completely alternate sequence, of course, is possible when (OH) = (OAc) = 50% and (OH, OAc) = 100%.

The block character, η, of a given point in the diagram can be schematically read off, from its definition, as a specific ordinate when the curve of the random distribution is taken as unity.

4.4.2 Sequence Distribution in PVAL-AC

The (OH, OAc) and (OH) for various samples of PVAL-AC copolymers are plotted in Figure 24. The following conclusions can be derived from this figure and from Table 3.

1) In the samples prepared by direct saponification, the sequence distributions are highly blocky with η = 0.4-0.5.

2) In contrast, the samples by reacetylation are close to random in distribution with η = 0.8-1.1.

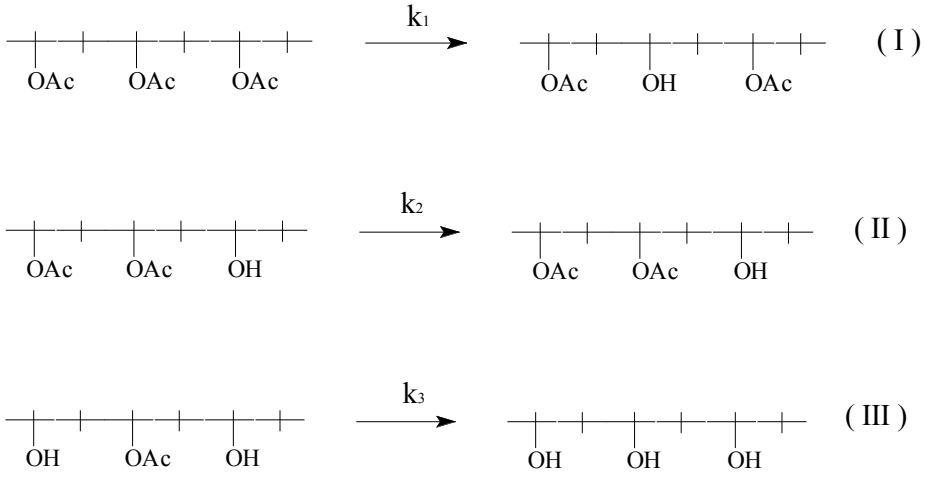
3) In the samples by alcoholysis, the sequence distributions are blockier, but their randomness increases in comparison with the PVAL-AC by direct saponification, η = 0.5-0.6.

4) The block character decreases, namely the blockiness increases with increasing the (OH) content, that is, with increasing the degree of hydrolysis or with decreasing the degree of reacetylation.

Conclusions (1)-(3) are consistent qualitatively with published presentations. Tubbs[2] has shown that the melting point of PVAL-AC is not a simple function of the composition but depends markedly upon the method of preparation. His interpretation in terms of sequence length distribution may be supported by the present results, where the sequence distributions have been determined more directly and quantitatively. Hayashi, Nakano, and Motoyama[8] have reported that the iodine color reaction is another sensitive method to estimate the sequence distribution in partially hydrolyzed PVAC although the coloration is known to be complicatedly influenced by other structural factors.[24] Minsk et al.,[3] Sakurada and Osugi,[4] and Sakurada and Sakaguchi[5] have shown that the rate of saponification reaction of PVAC by alkali or acid catalyst increases with increasing the degree of

hydrolysis and explained this phenomenon using a model, where the catalyst is adsorbed on the free hydroxyl groups and this induced successive hydrolyses in the acetyl groups of the direct neighbors. Blockier distribution of sequence in the partially hydrolyzed PVAC has been concluded from this mechanism. Sakurada and Sakaguchi have also judged well that direct saponification necessarily produces the PVAL-AC in a blockier distribution than alcoholysis does, because the former acceleration constant (m = 41.9) was found larger than the latter (m = 13.7). This conclusion was supported by Tubbs's melting point date and has been confirmed by the present ^{13}C-NMR study, where the degree of blockiness in distribution has quantitatively been characterized by the use of the η values.

Theoretical calculations on the kinetics of hydrolysis of PVAC and on the sequence distribution in PVAL-AC have been presented by Sakurada and Sakaguchi[5] on the basis of the above-mentioned model. In their calculations, the following three rate constants were taken into account,



and the mean run length l_{OH}, as a measure of sequence distribution, was deduced for the various k_2/k_1 values (the third reaction was approximately neglected) and for the various degrees of hydrolysis. Their l_{OH} can be compared with the experimentally determined l_{OH} in this work. The comparison has led to the estimation of k_2/k_1 values, approximately 20 and 8, for the present experiments by direct saponification and by alcoholysis, respectively.

Conclusion (4) has first been pointed out here from the precise determination of sequence distribution. However, this phenomenon might be expected by the reaction mechanism of hydrolysis presented above. With increasing hydrolysis, the above-mentioned second

reaction should become dominant in comparison with the first because of the increase of the increase of hydroxyl groups in polymer chains, whereas the blockier character should be generated by the second and third reaction while the first should essentially cause a random character.

More quantitative explanation is possible from the calculation by Sakurada and Sakaguchi. Their l_{OH} can easily be converted to the block character η from eq 2 and 3.

$$\eta = \{(OAc) \cdot l_{OH}\}^{-1}$$

The l_{OH} values, 2.4, 3.3, 4.0, and 4.8 calculated from $k_2/k_1 = 30$, for example, give the η of 0.46, 0.38, 0.36, and 0.35 for the degrees of hydrolysis, 10, 20, 30, and 40%, respectively, η decreases with increasing the degree of hydrolysis in this model calculation. Consequently, the present observation has afforded another support for the mechanism of hydrolysis and for the kinetics presented by Sakurada and Sakaguchi. For the highly hydrolyzed state of reaction, however, some of their assumptions should fail and laborious calculation should be necessary.

The tendency that η decreases with increasing (OH) has also been found in the PVAL-AC prepared by reacetylation of PVAL. In this case also there must be some weak effects of neighboring groups to generate a blocky character at the initial stage of reacetylation.

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