Effect of Sequence Distribution of Poly(vinyl Alcohol-vinyl Acetate) on the Coloring Reaction with Iodine

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Synopsis

Red complex formation between poly(vinyl alcohol-vinyl acetate) with iodine was investigated from the standpoint of its application as a measure of sequence distribution in the copolymer. Defining a parameter Y which means a ratio of the bound triiodide ion to the VAc unit in a copolymer, we could relate the Y value to the sequence probabilities. Sequence probabilities have also been evaluated by differential thermal analysis. Comparing the probabilities obtained from both methods, the iodine complexation method is concluded to be a complementary method with thermal analysis, that is, the iodine complexation method is applicable to the VAc unit-rich copolymers, in which the melting point cannot be measured by the thermal analysis.

Poly(vinyl alcohol-vinyl acetate) (p(VA-VAc)) has been prepared by several methods. Differences in the preparation method such as saponification, alcoholysis, and reacetylation have been shown to cause a remarkable difference in the sequence distribution of the copolymer.[1] Investigation of the sequence distribution in p(VA-VAc) has been carried out by several methods.[2-13] From thermal analysis, a quantitative method on the estimation of the sequence probabilities was established by applying Flory's theory.[2,3] Baur's equation[4] was also applied for the analysis of sequence distribution of p(VA-VAc), and was found to yield excellent agreement with the results from Flory's equation, in spite of the big difference in the heat of fusion.[5] Thermal analysis is applicable, however, to the p(VA-VAc) whose VAc unit content is small enough, while nuclear magnetic resonance (NMR) is advantageous[6] as having no restriction on the copolymer composition.

Both poly(vinyl acetate) and p(VA-VAc) have been shown to form a red complex with iodine-iodide in aqueous solution.[3,5,9,14-17] It is also known that the red complex formation is very sensitive to the sequence distribution of the p(VA-VAc) copolymer,[3,5,9] with the effect of the sequence distribution of the VAc unit on the complexation investigated on poly(VAc-vinyl propionate).[18,19] However, application of the iodine complexation method has been reported to be only qualitative and not necessarily useful as a quantitative measure of the sequence distribution of p(VA-VAc).[3,5] In this paper, the iodine complexation method (ICM) was investigated in detail and it will be shown that the method is a complementary one with the thermal analysis technique.

EXPERIMENTAL

Materials and Sample Preparations

Poly(vinyl alcohol)s p(PVAs) were GL-05(DP = 500) from Nipon Gosei Co. Ltd. and Kuralay-110 and -117 (DP = 1000 and 1700, respectively) from Kuralay Co. Ltd. PVAcs whose DPs are 1000 and 1700 were prepared by esterification of the corresponding PVAs in pyridine and acetic anhydride solution at 110°C for 6 h.[20] Commercial PVA usually contains residual VAc units to some extent.[21, 22] In order to obtain pure PVA, hydrolysis was carried out completely in the presence of excess sodium hydroxide in methanol/water (95/5 by volume) solution at 50° for 2 h. P(VA-VAc)s were prepared by one of three methods, that is, saponification, alcoholysis from PVAc, and reacetylation of PVA. Saponification was carried out in aqueous acetone (water/acetone = 20/80) solution in the presence of a certain amount of sodium hydroxide at 25°C for a prescribed period of time. The reaction was terminated by addition of a certain amount of hydrochloric acid. Degree of saponification was determined by the titration of an aliquot of the reaction solution, or by the analysis of the infrared (IR) spectrum of the copolymer film. The agreement between these two analytical results was usually excellent as long as the conversion did not exceed ca. 60%. The results employed were mainly from IR analysis. Alcoholysis was carried out in anhydrous methanol by using sodium methylate as a catalyst at 25°C for a prescribed period of time. The reaction was terminated by the addition of hydrochloric acid. Reacetylation of PVA was performed by acetic acid employing hydrochloric acid as a catalyst. Degree of esterification was controlled by changing the water content of the reaction media.[23] High degree of esterification was realized by reaction of solid PVA in anhydrous acetic acid at 95°C for 48 h.

TABLE I
Copolymer Compositions

Sample no.	VAc content (mol %)	Sample no.	VAc content (mol %)	Sample no.	VAc content (mol %)
S-52	6.6	A-51	1.7	R-101	2.5
S-53	10.2	A-52	3.2	R-102	5.4
S-54	16.2	A-53	4.4	R-103	5.8
S-55	23.3	A-54	8.0	R-104	63.0
S-56	63.3	A-55	29.8	R-108	72.7
S-57	77.8	A-56	36.0	R-109	78.0
S-101	3.4	A-57	54.2		
S-102	8.6	A-58	57.1		
S-103	11.1	A-59	76.4		
S-104	13.4	A-102	12.1		
S-105	29.1	A-103	18.0		
S-106	37.6	A-104	25.0		
S-107	73.1	A-105	30.1		
S-108	79.7	A-106	52.4		
		A-107	63.2		
		A-108	76.1		

S: Direct saponification, A: Alcoholysis, R: Reacetylation, 5x: DP = 500, lxx: DP = 1000.

The reaction media became homogeneous at the end of the reacetylation. Copolymer compositions prepared were tabulated in Table I.

Thermal Analysis

Differential thermal analysis (DTA) was carried out under the nitrogen gas flow using a Rigaku thermal analysis instrument (Rigaku Co. Ltd.). Rate of heating was 20°C/min. Thermal gravimetry (TG) was also carried out, and it was suggested that under the conditions used, degradation of p(VA-VAc) does not proceed until the temperature exceeds the melting point of the copolymer.

Complexation of p(VA-VAc) with Iodine

The iodine concentration of the complex solution was varied from 0.2×10^{-5} to 10.0×10^{-5} mol/L. The complexation was performed in aqueous solution containing 4%(v/v) of methanol, which is needed to solubilize the copolymers rich in VAc unit content. The aqueous complex solution was kept at 20°C for 2 h, and then the spectrum was measured, employing Shimazu UV-200 spectrophotometer (Shimazu Co. Ltd.). Resonance Raman spectra were recorded for the iodine complex solutions at ambient temperature employing a JOEL JRD-400D Raman spectrophotometer. An argon ion laser was used for excitation.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of some iodine complexes. The iodine complex or the bound iodine has the maximum absorption wavelength (λ_{max}) at around
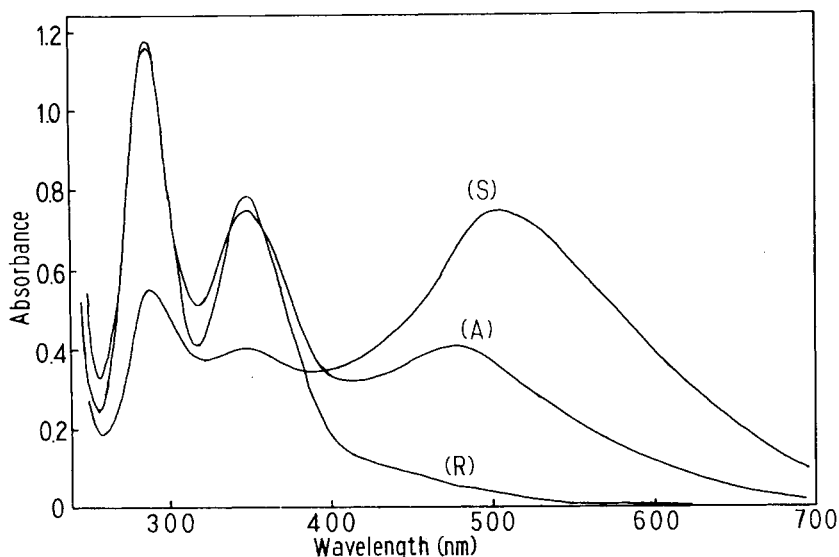

Fig. 1.   UV-VIS spectra of iodine complexes at 25°C. $[I_2]$ = 5×10^{-5} mol/L, $[I^-]$ = 5×10^{-4} mol/L. (S) direct saponification: [copolymer] = 0.127 g/L, VAc content = 23.5 mol%; (A) alcoholysis: [copolymer] = 0.124 g/L, VAc content = 25 mol%; (R) reacetylation: [copolymer] = 0.483 g/L, VAc content = 24.4 mol%
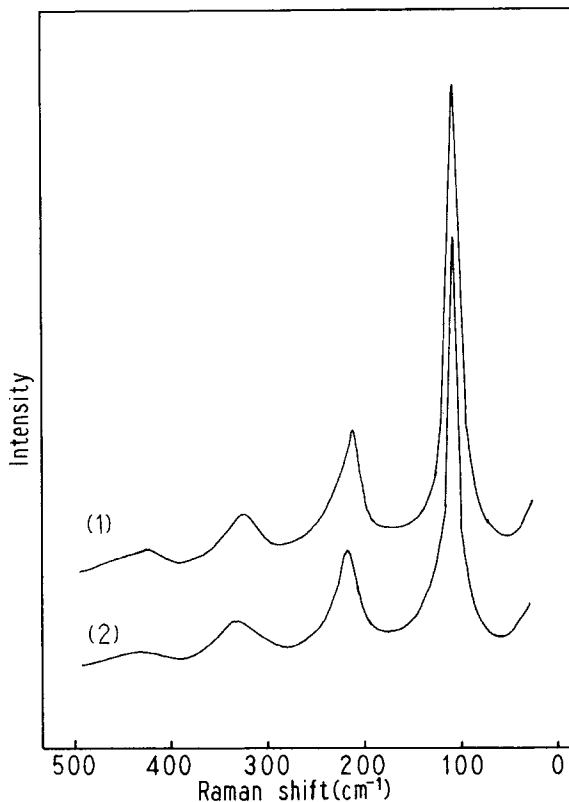
Fig. 2.   Resonance Raman spectra of the iodine complexes of (1) PVAc and (2) p(VA-VAc) at 20°C. $[I_2] = 2 \times 10^{-5}$, $[I^-] = 2.04 \times 10^{-3}$.

500 nm. The λ_{max}s at 290 and 350 nm are assigned to I_3, which is free from complexation.[9,16,18] The difference in the spectra were distinct, reflecting the difference in the copolymer structure. Taking the difference in the copolymer composition and the concentration into account, the effect of the preparation procedure of the copolymers on the colored complex formation is remarkable. According to the resonance Raman spectral study, the red complex of PVAc with iodine-iodide is known to be composed of the polyiodide in the form of $(I_3^-)_n$.[14,16] In Figure 2, the resonance Raman spectra of the iodine complex of p(VA-VAc) is shown in comparison with that of PVAc. As can be seen in Figure 2, Raman shifts observed were exactly the same as that of the PVAc complex, suggesting that polyiodide in the p(VA-VAc) complex is in the form of $(I_3^-)_n$. Therefore, it can reasonably be accepted that the red complex mentioned in this paper has the same polyiodide structure irrespective of p(VA-VAc) structure. Then, the difference in the absorbance at 500 nm in Figure 1 can be attributed to the difference in the amount of the polyiodide formed in the complex, allowing one to compare the complex formability of p(VA-VAc)s through the comparison of the absorbance at 500 nm.

   In Figure 3, the dependence of absorption at 500 nm on the iodine concentration was shown. Saturation in absorbance at 500 nm was observed with the increase of iodine concentration. When the saturation point was de-
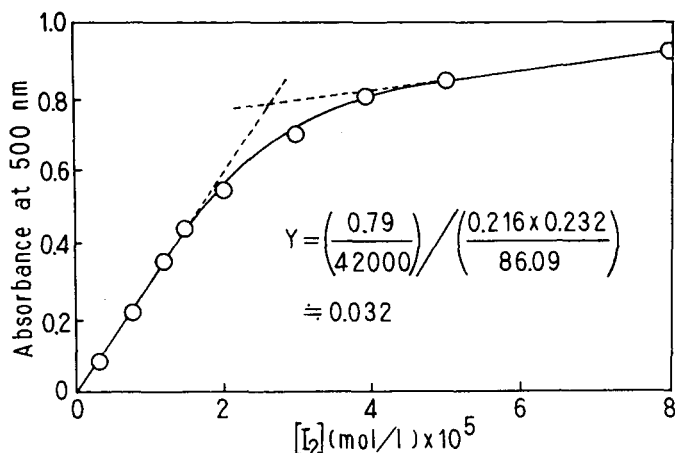
Fig. 3. Dependence of absorbance at 500 nm on iodine concentration, and an example of Y-value estimation. [copolymer] = 0.216 g/l, VAc content ≈ 13.4 mol% (or 0.232 wt%), $[I_2]/[I^-]$ = 10^{-2}, at 20°C, and the molar absorption coefficient of the red complex employed is 4.2×10^4.[18]

termined as shown in Figure 3, the iodine affinity (Y) can be defined as the ratio of the bound I_3^- to the VAc unit concentration at saturation point. The molar absorption coefficient of the bound I_3^- has been estimated to be 4.2×10^4.[18] The value of Y can be considered to be a characteristic parameter of the polymer under the experimental conditions. In Figure 4, the dependence of Y value on the copolymer composition was shown together with the melting points from DTA thermograms. It is obvious that thermal analysis is very restricted in its applicable region, since detection of the melting point becomes very difficult with the increase of the VAc unit content of the
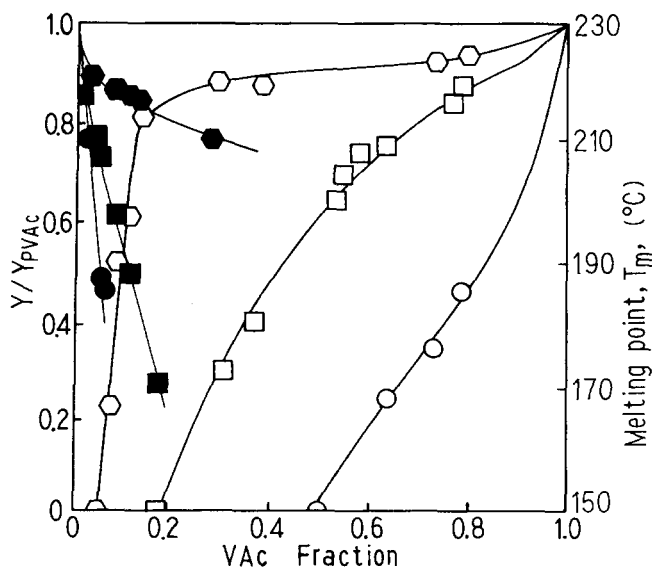

Fig. 4. Dependence of Y/Y_{PVAc} value(open plot) and melting point(close point) on the copolymer composition. ⬡ ⬣: saponification, □■: alcoholysis, ○●: reacetylation.

copolymer. On the other hand, the iodine complexation method (ICM) is insensitive for p(VA-VAc) of small VAc unit content, particularly less than 5% in a unit mole. However, ICM has a much wider applicable region than the thermal analysis. In a sense, both the thermal analysis and ICM are complementary with each other. The extreme dependence of the Y value on the preparation method or the sequence distribution of the copolymer suggests that ICM can be employed as a measure for the sequence distribution in p(VA-VAc).

For the quantitative discussion of the sequence distribution, it is preferable to set some common parameter for the comparison, which can be obtained independently from DTA or ICM. For this purpose, we mentioned the sequence probability (p) which was defined by Tubbs,[2] and can be estimated from Equation (1). Equation (2) which was derived by Baur[4] is also used for the estimation of the sequence probability.

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \frac{R}{\Delta H_u} ln P_{VA} \tag{1}$$

$$= -\frac{R}{\Delta H_u}(ln P_{VA} - 2(1 - P_{VA})x_{VA}) \tag{2}$$

where T_m and T_m^o are the melting points of the copolymer and that of PVA, respectively, R is gas constant, ΔH_u is heat of fusion of PVA, P_{VA} is the sequence probability of VA unit which means the VA unit is followed by another VA unit, and X_{VA} is the mole fraction of VA unit in the copolymer.

By applying Baur's relation [Eq. (2)] for the results from the random p(VA-VAc), prepared by reacetylation in acetic acid, the value of ΔH_u was estimated to be 1.9 kcal/mol. This value agrees well with those reported in other papers.[5] While 0.56 kcal/mol was obtained from Eq. (1), which agrees with that by Tubbs from copolymer method.[24] The difference between these results were discussed by Tubbs, and concluded 1.9 kcal/mol is more reasonable as ΔH_u value.[25] In the following discussion, we employed Baur's Eq. (2) in order to estimate the sequence probability p_{VA} which means a VA unit is followed by another VA unit, and it is assumed to be independent of the number of preceding VA units, that is, the "terminal model" is applied. According to the Tubbs treatment,[2] p_{VAc}, which means the sequence probability of VAc unit can also be estimated by the following Eq. (3),

$$X_{VA}(1 - p_{VA}) = X_{VAc}(1 - p_{VAc}) \tag{3}$$

where X_{VAc} is the mole fraction of a VAc unit and is equal to $(1 - X_{VA})$.

On the other hand, the Y value is defined as the number of I_3^- bound to p(VA-VAc) per VAc-unit in the copolymer. Therefore, it is a characteristic value for the copolymer as long as the iodine-iodide concentration used for the complexation and the reaction temperature are kept constant. Under the experimental conditions employed, the complexation has been clarified from resonance Raman spectral study[16] to proceed between the sequence of VAc unit and I_3^-. Also the sequence length required for the complexation has been

estimated to be 25 per a bound I_3^-.[18] Dependence of degree of polymerization on the coloring reaction was investigated, and it was found that the complexation needs more than 12 VAc units in successive form.[17] The sequence length, 25 in VAc unit, is, therefore, considered to be reasonable, and Y can be defined by the following equation,

$$Y = \frac{(\text{number of } I_3^- \text{ participating in the red complex formation})}{(\text{number of VAc-units})}$$

$$= \frac{\left(x_{VAc} - \sum_{n=1}^{n_c-1} n(1 - p_{VAc})^2 p_{VAc}^{n-1} \right) M/25}{M x_{VAc}}$$

$$= \frac{1 - \sum_{n=1}^{n_c-1} n(1 - p_{VAc})^2 p_{VAc}^{n-1}}{25} \tag{4}$$

where M is the total amount of monomer units in the reaction solution, and $\left(\sum_{n=1}^{n_c-1} n(1 - p_{VAc})^2 p_{VAc}^{n-1} \right) M$ is the amount of VAc units not involved in the complexation, and n_c is the minimum sequence length which is required for the complexation. Here we assumed that the complexation proceeds in the same manner as in the case of PVAc,[18] so the sequence of 25 VAc units is employed in order to convert the VAc unit amount involved in the complexation into the amount of I_3^- in the complex. Now we can estimate the value of p_{VAc} from Eq. (4). For the purpose of n_c determination, we compared the results from DTA on p(VA-VAc) prepared from partial saponification of PVAc with those from complexation method, since the series contains more comparable data than other series of copolymers. In Figure 5(a), the plots were from DTA and the curves were from complexation method calculated by Eq. (4) at $n_c = 4$, 8, and 12 as examples, and the excellent agreement is found at $n_c = 8$. Square of the difference (D) of the two p_{VAc}s (one from DTA and the other from ICM), that is, $D = ((\Sigma(p_{VAc, DTA} - p_{VAc, ICM})^2)/4)^{1/2}$ were plotted against n_c in Figure 5(b). D showed the minimum at $n_c = 8$ as shown in Figure 5(b), so we employed 8 as n_c value, which is smaller than 25. This might suggest the involvement of some VA units in the complex formation and lowered the n_c value in appearance. Similar phenomena were observed in the cases of the iodine complexes of poly(VAc-vinyl propionate) and poly(VAc-isopropenyl acetate).[19] In Figure 6(a), the relationship between p_{VAc} and x_{VAc} is shown for the series of p(VA-VAc) from not only saponification but also alcoholysis and reacetylation, adopting $n_c = 8$. In Figure 6(a), the closed plots were from DTA and the open plots were from the complexation method, and the excellent agreement and the continuation of plots between the p_{VAc}s from both methods were shown. The dependences of the two p_{VA}s on the copolymer composition were plotted in Figure 6(b). For p(VA-VAc)s from reacetylation which have been suggested to have an almost ideally random sequence distribution,[2,5,6] all plots were on one line of the gradient
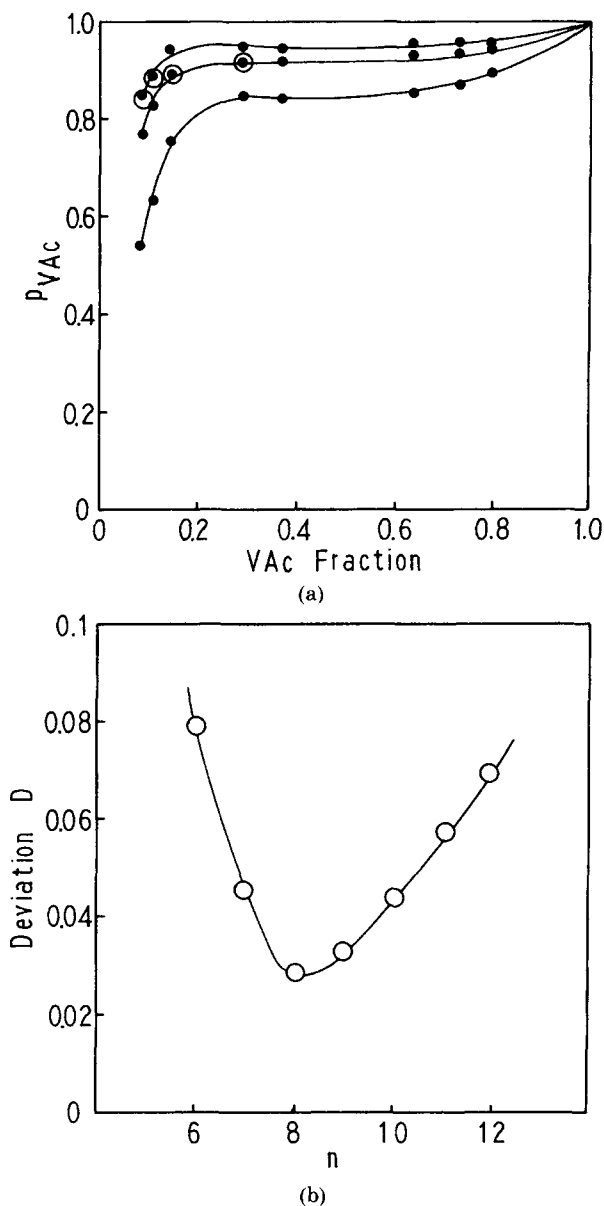
(a)

(b)

Fig. 5. Determination of n_c in Eq. (4). (a) Comparison of the values p_{VAc} obtained from DTA(open plots) with those from ICM(solid curves) at various n_c values. (b) Dependence of deviation (D) between p_{VAc} values estimated from DTA($p_{VAc,DTA}$) and those from ICM($p_{VAc,ICM}$) on n_c value.

one, suggesting the p_{VAc}s obtained by ICM showed reasonable values. Now one can say that the iodine complexation method can be a measure for the sequence distribution analysis of p(VA-Vac). The effect of the preparation method of the p(VA-VAc) can therefore be discussed by comparing the p_{VAc} values. Then the remarkable differences in p_{VAc} found among the series of p(VA-VAc) give the following information, that is, the reacetylation leads the
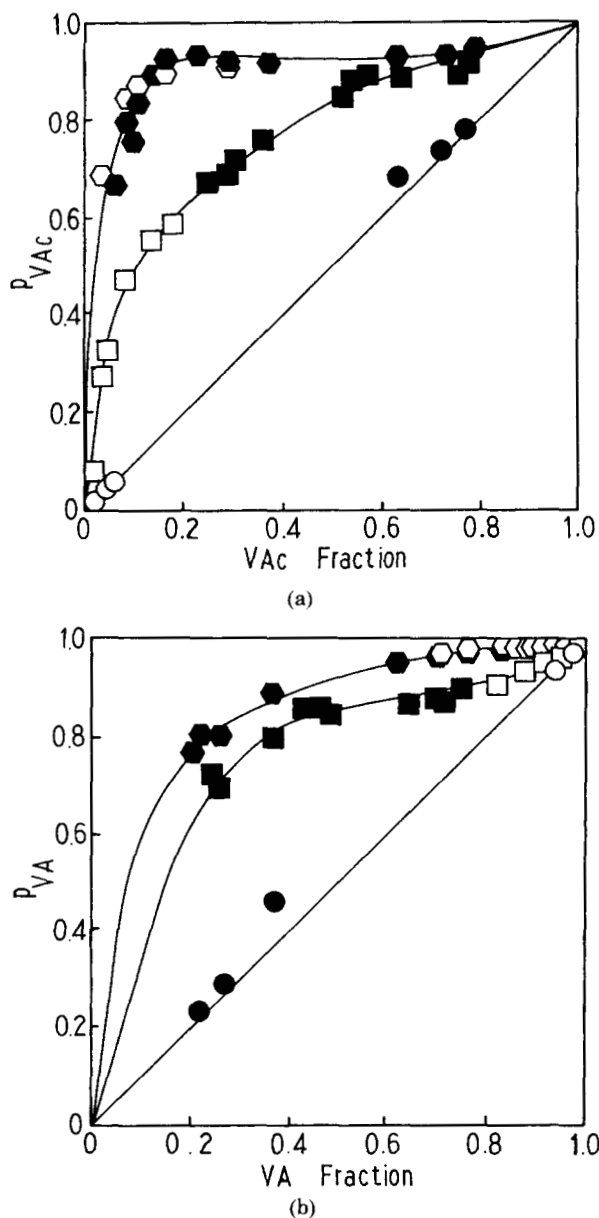
Fig. 6. Sequence probabilities (a)p_{VAc} and (b)p_{VA} from DTA(open plot) and ICM(closed plot), and the dependence on the copolymer composition. ◯·◗ : Saponification, ☐ ■: alcoholysis, ◯ ●: reacetylation.

ideal random copolymer, the saponification the most blocky one, and the alcoholysis lead to the intermediate one as has been known.[2,5,6] Finally, we can conclude that the ICM is applicable as a measure of the sequence distribution of the p(VA-VAc)s enriched in VAc-unit content, which is difficult by the melting-point measurement method. For the confirmation of the quantitativity of the ICM, it must be compared with the NMR analysis which

has been known as the most powerful method for the sequence distribution analysis, and the investigation is under way.

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