Characterization of Poly(vinyl Alcohol-co-vinyl Acetate) by the Iodine Complexation Method

TOSHIHIRO HIRAI, AKIRA OKAZAKI, and SADAO HAYASHI,
*Faculty of Textile Science and Technology, Shinshu University,
Ueda-shi 386, Japan*

Synopsis

Analysis of sequence distribution (SD) in poly(vinyl alcohol-co-vinyl acetate) (p(VA-VAc)) by the iodine complexation method (ICM) was investigated through the formation of a red complex of p(VA-VAc) with iodine-iodide. Differential thermal analysis (DTA) has been known to be a measure of SD and the ICM was also suggested to be valid for the SD analysis. ICM can be applied for samples of p(VA-VAc) rich in VAc-unit content, in which DTA could not be used. Results of SD analysis on p(VA-VAc) by ^{1}H NMR spectra were compared with those from ICM, and excellent agreement was found between data. The ICM can be applied as a convenient screening method for SD of p(VA-VAc) as far as the red-complex formation is concerned, and was shown to have much wider applicable range than the DTA method.

INTRODUCTION

Characterization of poly(vinyl alcohol-co-vinyl acetate) (p(VA-VAc)) has been carried out extensively, and it is well known that thermal analysis (DTA or DSC) and ^{1}H NMR spectroscopy can provide valuable information on the sequence distribution (SD), although DTA can only be applied for the copolymers rich in vinyl alcohol.[1,2] Characterization of p(VA-VAc) by NMR has been reported extensively,[2-4] and quantitative discussions were carried out on SD.

Poly(vinyl acetate) (PVAc) has been known to form a red complex with I_3^- under the iodide rich condition ($[I^-]/[I_2] \gg 1$) at ambient temperature in aqueous solution.[5-7] P(VA-VAc) has been also known to form the red complex with I_3^- under the absence of boric acid.[8-11] (In the presence of boric acid poly(vinyl alcohol) or vinyl alcohol rich p(VA-VAc) can form a blue complex similar to the starch-iodine complex.[12]) The red complex results from the VAc-unit block sequences in the copolymer chain,[8,10,13] and reflects SD difference. Although the red-complex formation has been used only as a qualitative measure of SD in p(VA-VAc), we have been convinced the complexation must have more than a qualitative relation with SD of VAc-unit, and have verified that the iodine complexation method (ICM) can be applied as a complementary method for SD analysis through the comparison with the results from DTA.[14] In the present article, we show that ICM can be utilized as a semiquantitative measure of SD as far as the red complex can be formed, in contrast with DTA which can only be applied for vinyl alcohol-rich p(VA-VAc).

EXPERIMENTAL

Materials

The PVA sample used was Kuralay-110, whose degree of polymerization (DP) is approximately 1000, according to Kuralay Co. Ltd. Because commercial PVA usually contains residual VAc-units, it was hydrolyzed completely in the presence of excess NaOH in a methanolic aqueous solution (methanol/water 95/5 by volume) at 50°C for 2 h. PVAc was derived by acetylation of the pure PVA in pyridine and acetic anhydride solution at 110°C for 6 h.[15] P(VA-VAc) samples were prepared by the following three methods:

Direct Saponification. Saponification of PVAc was carried out in aqueous acetone (water/acetone 20/80 by volume) solution in the presence of equivalent amount of NaOH to vinyl acetate content at 25°C. The reaction was terminated by an addition of the same amount of HCl. Degree of saponification was controlled by changing the reaction time.

Alcoholysis. Methanolysis of PVAc was carried out by using sodium methoxide as a catalyst at 25°C. The reaction was terminated by the addition of HCl. Degree of alcoholysis was controlled by the reaction time.

Reacetylation. Reacetylation of PVA was performed by acetic acid employing HCl as a catalyst. Degree of esterification was controlled by changing the water content of the reaction medium.

Copolymer compositions were determined from infrared and ^{1}H NMR spectra. Results from both methods were in good agreement.

^{1}H NMR Spectra

The 200-MHz spectra were obtained in 5-mm tubes at 70°C with a JEOL FX-200 spectrometer. Sample concentration was 5% (w/v) in perdeutrated dimethyl sulfoxide (Me_2SO-d_6, Merc). Tetramethyl silane was used as an internal standard. The sweep width of the spectrometer, operated in the FT mode, was 4000 Hz and the acquisition time was 4.09 s; a pulse delay of 5.91 s and a pulse width of 12 μs (67.5° pulse angle) were chosen. A total of 16 free induction decays were accumulated.

Iodine Complex Formation

The iodine concentration of the complex solution was varied from 0.2×10^{-5} to 10.0×10^{-5} mol/L. The concentration ratio of iodine to iodide was held at 1:100 in all cases. The complex was formed in aqueous solution containing 4% (v/v) of methanol which is needed to solubilize the copolymers rich in vinyl acetate. In the case of PVAc or vinyl acetate-rich p(VA-VAc), these polymers are hardly soluble in water. As a result, methanolic solution of the polymers were prepared as a stock solution, and to an aliquot of the solution was added a small amount of concentrated iodine-iodide solution. The concentrated complex solution was then diluted to give a 4% (v/v) methanolic aqueous solution. The UV-visible spectrum of the complex solution was measured at 20°C after standing for 2 h in the thermostatted waterbath, employing a Shimazu UV-200 spectrophotometer.
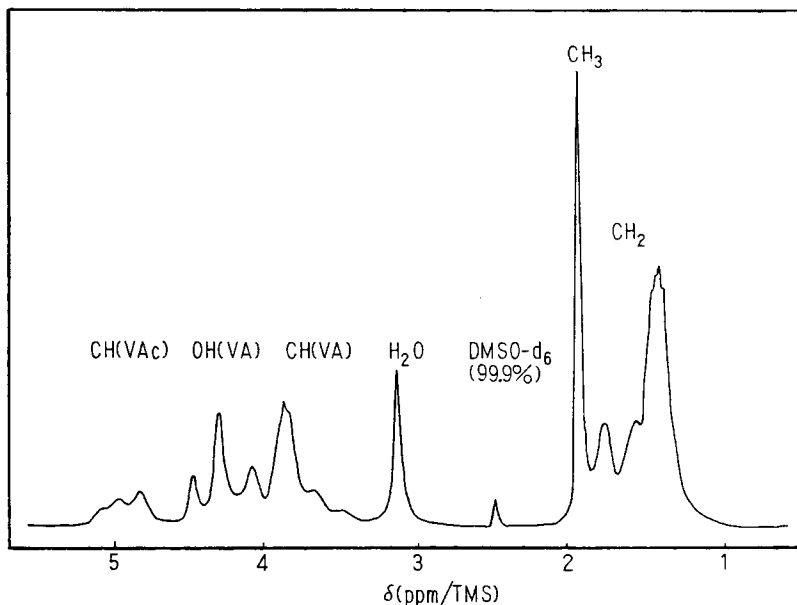
Fig. 1. ^{1}H NMR spectrum of a p(VA-VAc).

RESULTS AND DISCUSSION

SD Analysis from ^{1}H NMR

Figure 1 shows a spectrum of a p(VA-VAc). Assignments of all resonances that we mention here have been known and tabulated in Table I[2-4,16-20] In the present paper, the two kinds of monads and their mole fractions are denoted by VA and VAc, while the six kinds of triads are given by (VA,VA,VA), (VAc,VAc,VAc), (VA,VA,VAc), etc. Note the hydroxyl resonances which contain information not only on the triad composition, (VA,VA,VA), (VA,VA,VAc), and (VAc,VA,VAc), but also on the configuration. The chemical shift differences among the peaks at 4.10, 4.34, and 4.52 ppm in p(VA-VAc) were found to be in excellent agreement with the results for ethylene-VA copolymers,[20] concentrating only on the hydroxyl resonances of the (VA,VA,VA) compositional triad. It is reasonable, therefore, to assign the hydroxyl resonances to a mixed configurational-compositional triad, and the

TABLE I
^{1}H NMR Spectral Assignments for Vinyl Alcohol-Vinyl Acetate Copolymers

Chemical shift (ppm)	Protons	Triads[3]
3.47	CH(VA)	(VAc,VAc,VAc)
3.65	CH(VA)	(VAc,VA,VA)
3.85	CH(VA)	(VA,VA,VA)
4.10	OH	(mm + mr + rr)(VAc,VA,VAc) + (rr + mr/2)(VA,VA,VAc) + (rr)(VA,VA,VA)
4.34	OH	(mm + mr/2)(VA,VA,VAc) + (mr)(VA,VA,VA)
4.52	OH	(mm)(VA,VA,VA)

following set of equations is arrived at:[3]

$$I(\text{h}) = (mm + mr + rr)(\text{VAc,VA,VAc}) + (rr + 0.5\text{-}mr)(\text{VAc,VA,VA})$$

$$+ (rr)(\text{VA,VA,VA}) \tag{1}$$

$$I(\text{c}) = (mm + 0.5\text{-}mr)(\text{VAc,VA,VA}) + (mr)(\text{VA,VA,VA}) \tag{2}$$

$$I(\text{l}) = (mm)(\text{VA,VA,VA}) \tag{3}$$

where m and r denote meso and racemic, respectively. $I(\text{c})$ and $I(\text{l})$ are measured intensities of the hydroxyl resonances in the ^{1}H NMR spectrum at, respectively, high, central, and low field. The parameters mm, mr, and rr for this particular copolymer has the fractions of 0.22, 0.48 and 0.18, respectively. The values were in excellent agreement with those reported by Velden et al.,[3] irrespective of the difference in the origin of the copolymer. The number-average VA-unit sequence lengths, l_0^{VA} and l_{2+}^{VA}, the latter being the sequence length greater than two, can be estimated by

$$l_0^{\text{VA}} = \frac{(\text{VA,VA,VA}) + (\text{VA,VA,VAc}) + (\text{VAc,VA,VAc})}{(\text{VAc,VA,VAc}) + 0.5(\text{VA,VA,VAc})} \tag{4}$$

$$l_{2+}^{\text{VA}} = \frac{(\text{VA,VA,VA}) + (\text{VA,VA,VAc})}{0.5(\text{VA,VA,VAc})} \tag{5}$$

In Table II, the fractions of the hydroxyl-proton triads were tabulated with the number-average VA-unit sequence lengths l_0^{VA} and l_{2+}^{VA} estimated by Eqs. (4) and (5), respectively.

Methine resonances at 3.49, 3.66, and 3.84 ppm, which are the chemical shifts given with respect to internal tetramethyl silane, are assigned to the triads, (VAc,VA,VAc), (VA,VA,VAc), and (VA,VA,VA), respectively.[3] These triads can also be used for the SD analysis by Eqs. (4) and (5). The results are tabulated in Table III. The values of the block character η defined by Eq. (6)[2] were also estimated and listed in Table II and III.

$$\eta = \frac{(1/\text{X}_{\text{VA}})}{\left(l_0^{\text{VA}}\right)} \tag{6}$$

where X_{VA} is the mole fraction of VA-unit in the copolymer.

The value of η can range from zero to two, and $0 < \eta < 1$ suggests the blockiness, $\eta = 1$ ideal randomness, and $1 < \eta < 2$ alternativity.[2] Taking this into account, and comparing η of R101 and R102 in Tables II and III, the discrepancy from unity in Table III is unacceptable as the copolymers have been known to have almost ideally random sequence distribution.[2] The results from VA-unit methine triad resonance, therefore, should be discarded, and this seems to be mainly due to the overlap of (VA,VA,VA) to (VA,VA,VAc). In the following discussion, the results from hydroxyl proton triad (Table II) are used.

TABLE II
Fractions of Vinyl Alcohol Hydroxyl Proton Triads, Number-Average Sequence Lengths, and Block Characters of Vinyl Alcohol-Vinyl Acetate Copolymers via ^{1}H NMR

Sample	VAc mol%[a]	Triad fraction (VA,VA,VA):(VA,VA,VAc):(VAc,VA,VAc)			Number average sequence lengths l_0^{VA}	l_{2+}^{VA}	Block Character η
S102	8.6	0.932	0.038	0.030	20.5	51.4	0.54
S104	13.4	0.923	0.036	0.041	16.9	48.0	0.44
S105	29.1	0.853	0.105	0.042	10.6	18.2	0.32
S106	37.6	0.788	0.140	0.072	7.04	13.3	0.38
S108	79.7	0.544	0.360	0.096	3.62	5.02	0.35
A102	12.1	0.877	0.112	0.011	14.9	17.7	0.56
A104	25.0	0.773	0.213	0.014	8.30	9.26	0.48
A106	52.4	0.548	0.312	0.140	3.37	5.51	0.57
A108	76.1	0.277	0.505	0.218	2.13	3.10	0.62
R101	2.5	0.954	0.041	0.005	39.2	48.5	1.02
R102	5.4	0.895	0.099	0.006	18.0	20.1	1.03
R106	55.8	0.185	0.621	0.196	1.97	2.60	0.91
R107	63.0	0.165	0.627	0.208	1.91	2.53	0.83

[a] VAc-unit content in the copolymer in mol%.

TABLE III

Fractions of Vinyl Alcohol Methine Triads, Number Average Sequence Lengths, and Block Characters of Vinyl Alcohol-Vinyl Acetate Copolymers via ^{1}H NMR

Sample	Triad fraction (VA,VA,VA):(VA,VA,VAc):(VAc,VA,VAc)			Number average sequence lengths		Block characters
				l_0^{VA}	l_{2+}^{VA}	η
S102	0.886	0.076	0.038	13.2	25.3	0.88
S104	0.851	0.097	0.049	10.3	19.5	0.72
S105	0.818	0.091	0.091	7.33	20.0	0.47
S106	0.758	0.141	0.101	5.83	12.8	0.46
S108	0.317	0.270	0.413	1.82	4.35	0.69
A102	0.812	0.122	0.066	7.86	15.3	1.01
A104	0.731	0.154	0.115	5.21	11.5	0.77
A106	0.407	0.333	0.259	2.35	4.44	0.81
A108	0.221	0.307	0.472	1.60	3.44	0.82
R101	0.854	0.098	0.049	10.2	19.4	3.92
R102	0.843	0.100	0.057	9.34	18.9	1.98
R106	0.207	0.345	0.448	1.61	3.20	1.11
R107	0.178	0.311	0.511	1.50	3.14	1.06

SD Analysis by ICM

The iodine complex composed of VAc-unit block and triiodide ion is red[7-10] rather than blue that was formed under the presence of boric acid, and is supposed to have a structure similar to the iodine-starch complex.[12] The red complex has its λ_{max} at approximately 500 nm and has an extinction coefficient of 42000.[13,21] In our previous paper,[14] we defined a parameter Y which was determined through the saturation point of the absorbance-triiodide concentration curve, which is a ratio of the amount of the bound triiodide to that of VAc-unit in the reaction system, and can be used as a parameter for SD analysis. However, it is preferable to convert Y into a more direct parameter that is directly comparable with, for instance, sequence probability (p) or the number average sequence length (l_0) that can be easily converted from p by

$$l_0 = 1/(1 - p) \tag{7}$$

In the PVAc-triiodide complex, the ratio of VAc-unit to a triiodide ion has been considered to be 25,[13] and using this value and the assumption that the iodine complex of p(VA-VAc) with triiodide ion has the same structure as PVAc-triiodide complex does, Y can be related to p by[14]

$$Y = \frac{1 - \sum_{n=1}^{n_c - 1} p_{VAc}^{n_c - 1}(1 - p_{VAc})^2}{25} \tag{8}$$

where p_{VAc} and n_c are sequence probabilities of VAc-unit in the polymer chain, and critical sequence length (a minimum sequence length of VAc-unit required for the complexation), respectively. When n_c is known, p_{VAc} can be estimated using Y value experimentally determined. The n_c value[14] determined from the comparison of ICM and DTA is 8. Applying this n_c value and employing Eqs. (7) and (8), p_{VAc}, p_{VA}, l_0^{VAc}, and l_0^{VA} were estimated and tabulated in Table IV. The value of l_{2+}^{VA} was also shown in Table IV, which was estimated by

$$l_{2+}^{VA} = \frac{\text{(total number of VA-units)} - \text{(isolated VA-units)}}{\text{(total number of VA-unit blocks)} - \text{(number of isolated VA units)}}$$

$$= \frac{DP\left(X_{VA} - X_{VA}(1 - p_{VA})^2\right)}{\left(DP \cdot X_{VA}/l_0^{VA}\right) - X_{VA}(1 - p_{VA})^2 DP}$$

$$= \frac{l_0^{VA} p_{VA}(2 - p_{VA})}{1 - l_0^{VA}(1 - p_{VA})^2} \tag{9}$$

The comparison of l_0^{VA} and l_{2+}^{VA} obtained from ICM (or DTA[14]) and NMR is possible through the results shown in Figures 2 and 3. In Figures 2 and 3, l_i^{VA} ($i = 0$ or $2 +$) from either method has exactly coincided with each other for p(VA-VAc) samples from reacetylation and alcoholysis. In the case of

TABLE IV
Sequence Probabilities, Number Average Sequence Lengths, and Block Characters of
Vinyl Alcohol-Vinyl Acetate Copolymers via Iodine Complexation Method

| Sample | Sequence probabilities | | Number average sequence lengths | | | Block character |
	p_{VA}	p_{VAc}	l_0^{VA}	l_0^{VAc}	l_{2+}^{VA}	η
S102	0.981	0.802	52.6	5.05	53.6	0.22
S104	0.983	0.897	58.8	9.71	59.8	0.12
S105	0.969	0.925	32.3	13.3	33.3	0.11
S106	0.952	0.920	20.8	12.5	21.8	0.13
S108	0.768	0.941	4.31	16.9	5.31	0.29
A102[a]	0.939	0.557	16.4	2.26	17.4	0.50
A104	0.891	0.674	9.17	3.07	10.2	0.44
A106	0.835	0.846	6.06	6.49	7.06	0.32
A108	0.672	0.897	3.05	9.71	4.05	0.43
R101[a]	0.976	0.024	41.7	1.02	42.7	1.00
R102[a]	0.944	0.050	17.9	1.05	18.9	1.01
R107	0.474	0.691	1.90	3.24	2.90	0.84

[a] Results were from DTA in reference 14.
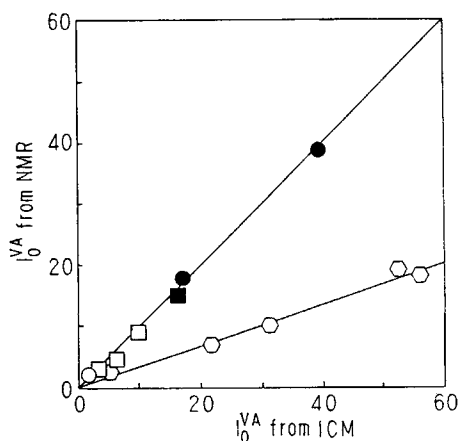
Fig. 2. Comparison of l_{0s}^{VA} from NMR and ICM. p(VA-VAc)s were from saponification (○), alcoholysis (□), and reacetylation (○). Open plots were on the comparison between NMR and ICM, while closed plots were on that between NMR and DTA (Ref. 14).

p(VA-VAc) samples from saponification, however, l_i^{VA}s from ICM and NMR differ systematically, suggesting the l_0^{VA} from NMR is underestimated or that from ICM is overestimated. In the ICM method, underestimation of n_c can cause an overestimation of l_i^{VA} although there is no reason for it. However the n_c value can even be supported by the results from reacetylation and alcoholysis or by the comparison of n_cs to other copolymers, such as poly(VAc-vinyl propionate) and poly(VAc-isopropenyl acetate).[13] With regards to NMR results, there is a possibility of a systematic error introduced by the method used to calculate the triad fractions (VA,VA,VA), (VA,VA,VAc), and (VAc,VA,VAc). This is because in Eqs. (1), (2), and (3), it is assumed that mm, mr, and rr triads are all contained statistically.[3] If the reaction proceeds selectively on m or r configuration, these equations cannot be valid any more.
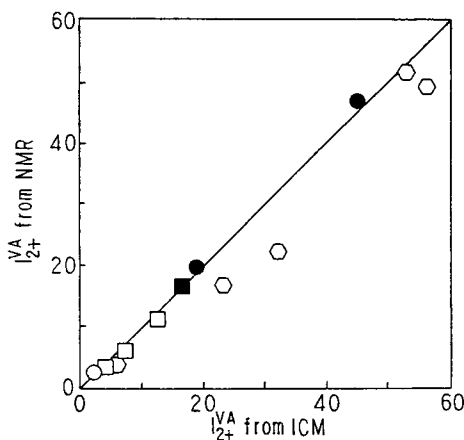
Fig. 3.   Comparison of l_{2+}^{VA}s from NMR and ICM. p(VA-VAc)s were from saponification (○), alcoholysis (□), and reacetylation (○). Open plots were on the comparison between NMR and ICM, while closed plots were on that between NMR and DTA (Ref. 14).

Computational analysis on the ^{1}H NMR data is under way, and the results will be published elsewhere.[23] From preliminary results, it has been clarified that the systematic difference of l_i^{VA} (i = 0 or 2 +) values between ICM and NMR on p(VA-VAc) samples from saponification is suggested to result from high m selectivity and low r selectivity in the saponification process.[23] Thus Eqs. (1), (2), and (3) are not very quantitative, although they are still useful for qualitative analysis of sequence distribution when compared with results of other estimations.[3] The peak at 4.10 ppm has the intensity denoted as I(h) in Eq. (1), and contains information on isolated VA-unit sequence, (VAc,VA,VAc). The possible overestimation of (VAc,VA,VAc) content can lead to the underestimation of l_0^{VA}. This complexity will be avoided in ^{13}C NMR spectra as has been shown.[3] In this paper, however, only ^{1}H NMR spectra are discussed. For the l_{2+}^{VA} value, the effect of overestimation of
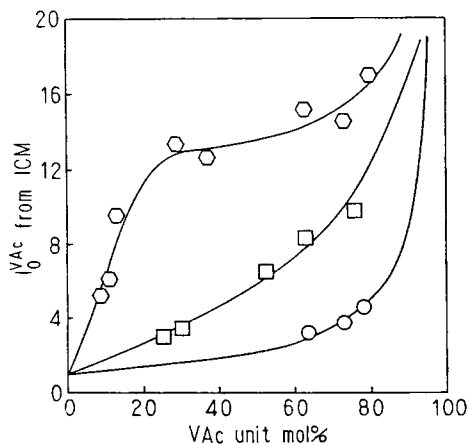

Fig. 4.   Dependence of l_0^{VAc} from ICM on VAc-unit content in p(VA-VAc). P(VA-VAc)s were from saponification (○), alcoholysis (□), and reacetylation (○).

isolated VA sequence can be expected to be small. The agreement of l_{2+}^{VA} from ICM and NMR was found to be remarkably improved in Figure 3. This improvement resulted mainly from the large discrepancy between l_0^{VA} and l_{2+}^{VA} from NMR, particularly on the saponified samples (Table II). As can be seen in Table IV ICM did not cause such a discrepancy, suggesting either l_0^{VA} or l_{2+}^{VA} can be used as a measure. We now may be able to consider the ICM as at least a semiquantitative measure of SD analysis on a p(VA-VAc), in spite of some ambiguity in the complex structure that remains unsolved.

We can then use either l_i^{VAc} or l_i^{VA} as a measure of SD and discuss the time-dependent change of SD accompanying PVAc saponification. Figure 4 shows the dependence of l_0^{VAc} obtained from ICM on VAc-unit composition. It is obvious for the saponified p(VA-VAc) samples that the blockiness was greater in the range of $X_{VAc} < 0.5$. In this range of composition ($X_{VAc} < 0.5$), the reaction medium became turbid or heterogeneous. It can be suggested the heterogeneity of the medium may lead to the "slide fastener reaction"[24] and cause an increase in blockiness of VAc-units or VA-units in the polymer chain.

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