Self-Association through Hydrogen Bonding and Sequence Distribution in Poly(vinyl acetate-*co*-vinyl alcohol) Copolymers

BAIJAYANTIMALA GARNAIK, SUNITA M. THOMBRE

National Chemical Laboratory, Pune 411008, India

Received 17 July 1998; accepted 12 September 1998

ABSTRACT: Correlation between hydrogen-bonding self-association and sequence distribution in poly(vinyl acetate-*co*-vinyl alcohol) copolymers (ACA) with different degrees of basic hydrolysis and sequence distributions has been studied by thermal analysis and NMR spectroscopy. ¹³C NMR spectroscopy has also been used to elucidate the blocky nature, branching, and tacticity of the copolymers. Thermal analytical studies indicate that hydrogen bonding distribution in block alcohol and vinyl acetate copolymers strongly depend on the sequence distribution wherein hydroxyl-hydroxyl self-association is preferred. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 123–133, 1999

Key words: poly(vinyl acetate-*co*-vinyl alcohol) copolymers; sequence distribution; blocky nature; branching; tacticity; hydroxyl–hydroxyl self-association

INTRODUCTION

Poly(vinyl alcohol) (PVA) has a very large number of industrial applications and is used as a protective colloid in emulsion and suspension polymerizations. The most common application is as surfactants for the production of poly(vinyl chloride). Copolymers of vinyl alcohol and vinyl acetate (ACA copolymers) can be prepared by hydrolysis or saponification of poly(vinyl acetate) (PVAC) and by reacetylation of PVA.^{1,2} The total degree of hydrolysis and sequence distribution of monomer units in the distribution of monomer units in the copolymer regulate several properties of these copolymers, such as degree of crystallinity, melting point, solubility, viscosity, and surface tension of aqueous solution.

Classical methods (such as calorimetry,³ infrared spectroscopy,⁴ and iodine color adsorption⁵) have been used to give some qualitative indication of the sequence distribution. The ¹³C NMR technique is a

powerful tool for quantitative characterization of sequence distribution and chemical composition of ACA copolymers obtained by saponification.⁶ Although some techniques show the occurrence of blocky distribution due to alcoholysis in a basic medium, to our knowledge, a systematic ¹³C NMR study of the sequence distribution of such copolymers has not accomplished so far.

Thermal analytical techniques have been widely used to characterize the comonomer sequence distribution in ACA copolymers. We have also used this technique to determine copolymer composition, sequence length, and block character of residual vinyl acetate units, and to compare the results with those obtained from NMR. Micelle formation in ACA copolymers was observed by thermogravimetric analysis and X-ray analysis.

EXPERIMENTAL

Materials

Three commercial PVA acetate samples A, B, and C were obtained from Polychem., India. These

Correspondence to: B. Garnaik.

Journal of Applied Polymer Science, Vol. 72, 123-133 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/010123-11

Sample	${ar M_n \ imes 10^{-4}}$	% of Hydrolysis by Titration	$ar{M}_w imes 10^{-4}$	P.D	
A B C	$1.95 \\ 0.81 \\ 0.40$	97–99 87–89 71–73	$4.20 \\ 1.90 \\ 0.57$	2.16 2.37 1.41	

Table ICharacteristics of the Studied PVASamples

samples correspond to three different hydrolysis (e.g., A = 97-99%, B = 87-89%, and C = 71-73%, respectively) whose characteristics are shown in Table I.

Analyses

The ¹³C NMR spectra were obtained by using a Brucker MSL-300 spectrometer at 65 MHz, with proton noise decoupling and D_2O as the internal locking agent. Spectra were obtained after accumulating ~ 800 scans of 20% w/v D₂O solutions. Samples were run at 18°C, with a relaxation delay of 5.0 s, a 30,000 Hz bandwidth, radiofrequency pulses of 30 μ s, and 10 mm o.d. tubes. All carbon chemical shifts are reported relative to tetramethylsilane via external reference. The solvent D₂O was used because the resonances of these solvents do not overlap the methylene carbon lines in ACA copolymers. Differential scanning calorimetry (DSC) data were obtained using a Perkin-Elmer DSC-7, equipped with a thermal analysis data station. Polymer samples were run in aluminum pans with 8–10 mg sample weights under a nitrogen atmosphere. Instrument calibration was obtained by use of an indium standard. The effect of heating rate on T_m was observed for one sample, and then all samples were run at 20°C min⁻¹. Melting points and heats of fusion were calculated using the appropriate software provided by the DSC manufacturer.

X-ray diffraction patterns were obtained using nickel-filtered CuK α radiation on a Philips X-ray (Philips PW 1730 generator).

RESULTS AND DISCUSSION

¹³C NMR Analysis

The main features of the ¹³C NMR spectra for ACA copolymer have been described elsewhere.^{7–11} The most interesting region of the sequence distribution is that of the methylene region. Figure 1 shows the ¹³C NMR spectra of the methylene region (38–46 ppm) for three ACA copolymers (A, B, and C) with different degrees of hydrolysis by saponification, but the starting materials PVAC prepared by solution polymerization. The three well-resolved lines of the methylene region have been assigned, taking into account the chemical shifts for the homopolymers PVA and PVAC to the three diad sequences (OH,OH), (OH,OAC), and (OAC,OAC) with increasing field strength.⁷ Stereochemical configuration of ACA copolymers was determined from methine carbon resonances.

As described earlier in the literature,⁷⁻¹⁰ the mole fractions of the diad sequences can be calculated from integrated intensities of the three methylene lines. The vinyl alcohol content (OH) for the copolymers can be derived from the diad data by means of

$$(OH) = (OH, OH) + (OH, OAC/2)$$
 (1)

The block character of the copolymers is obtained by the expression:

$$\eta = OH, OAC/2(OH)(OAC)$$
(2)

where η is a measure of departure from random character. It takes $0 \le \eta < 1$ for blockier distributions, $\eta = 0$ for block copolymers, $\eta = 1$ for completely random cases, and $1 < \eta \le 2$ for alternative-like cases. Results of this analysis are shown in Table II for all three samples studied in this work. In the case of (OH) mole fractions calculated from diad data, they agree with those obtained from chemical titration within $\pm 1\%$ is absolute value. Table II agrees with data from other studies: $0.2 < \eta < 0.5$. Autocatalytic effects are important in the cases of saponification or basic hydrolysis.⁷

Tacticity

Stereochemical configuration has been assessed by ¹³C NMR spectroscopy. In this investigation, the triad tacticities have been determined from methine carbon resonances. The methine carbon is split into three well-resolved resonance lines that have been assigned to the isotactic, heterotactic, and syndiotactic triads, with increasing field strength. These triads are represented according to Bovey's notation as mm, mr, and rr, respectively. The tacticity results of the polymers were summarized in Table III, considering the relative areas of the methine carbon.



Figure 1 ^{13}C NMR spectrum of ACA copolymers in D_2O at 18°C. (OH) mol %: (a) 98.21; (b) 86.90; and (c) 75.98.

Sample	(OH) (mol %)	(OAC) (mol %)	$L_{ m OH}$	$L_{ m OAC}$	η
A	98.21 (99.00 ^b)	1.79	62.0	2.0	0.23
В	86.90 (87.00 ^b)	13.10	15.02	2.6	0.45
С	75.98 (74.00 ^b)	24.02	8.9	2.8	0.44

Table II Chemical Compositions, Mole Fractions of Diads, and Values of η ACA Copolymers Obtained by Different Degree of Hydrolysis^a

^a PVAC was dissolved in a 3 : 1 (v/v) solution of methanol-water (≈ 6 g dl⁻¹). The degree of hydrolysis is stochiometrically controlled by the amount of concentrated solution of NaOH in water (40% w/v) added with stirring. The reaction was added to go to completion in the gel state at room temperature. Reaction products with a low degree of dissolution in methanol were reprecipitated in water. Reaction products with a higher degree of hydrolysis were precipitated in methanol and purified by Soxhlet extraction with methanol for at least 4 h.

^b Data were obtained from chemical titration.

The PVA derived from radical polymerized PVAc obeys Bernoullian statistics. Thus, a single parameter, P_m , can be used to describe the stereochemical configurational sequence of the polymer. P_m is defined as the probability that growing polymer chain will form a sequence with the same configuration (i.e., the *m* sequence). The value of P_m was obtained from the expression of $P_m = (\text{mm})^{1/2}$, where mm is the fraction of the isotactic triads (the square root dependency arises from the fact that two successive meso placements are needed to produce an mm triad). P_m values of 1, 0, and 0.5 represent isotactic, syndiotactic, and atactic polymers, respectively. Table III lists the P_m values of the three polymers. These values suggest that these polymers do not vary significantly in their stereochemical configuration and are essentially atactic.

The methylene carbon spectral region is split into three copolymer diad sequences. Each of these diads shows additional configurational splittings. Figure 1 shows the alcohol–alcohol diad region. These splittings are assigned in terms of tetrads. They have been assigned as rrr, rrm+mrm, mmr+rmr, and mmm with increasing field strength according to similar absorption peaks reported by Wu and coworkers.^{11,12} The methine carbon resonances pre-

Table IIITriad Tacticities of PartiallyHydrolyzed PVA

Sample	mm	\mathbf{mr}	rr	P_m	
А	0.392	0.266	0.340	0.626	
В	0.324	0.292	0.383	0.569	
С	0.317	0.330	0.352	0.563	

viously described were preferred for tacticity estimations, because they are gradually better separated from each other.

Branching

Branching in ACA copolymers has been considered quantitatively by Dunn and Naravane¹³ and by Inoue and colleagues.¹⁴ Both groups of workers used NMR spectroscopic analyses, and branching in ACA copolymers was examined by using their method. Table IV lists the methine/methylene ratios and branching frequencies for the three ACA copolymer samples. Branching decreases with a decreasing degree of hydrolysis that is attributed to the extent of nonhydrolyzable branching increases with a decreasing degree of hydrolysis.

DSC Analysis

The mean concentration and sequence distribution of the residual vinyl acetate groups in partially hydrolyzed PVA is considered to be a very important structural feature affecting the rate of dissolution of the polymer in water,¹ surface activity of aqueous solutions,¹⁵ and a stabilizing influence on hydrophobic materials.¹⁶

Table IVBranching Distribution per 1000Main Chain Carbons of PVA

Sample	$\Sigma CH / \Sigma CH_2$	No. of Branches/1000 Main Chain Carbons
A B	$0.858 \\ 0.917$	70.7 41.0
С	0.944	28.0

Copolymer composition, sequence length, and block character of residual vinyl acetate units that mainly affect the structure–property relationship can be quantitatively measured by $^{13}\mathrm{C}$ NMR spectroscopy, as shown in the preceding sections of this article. Thermal analysis is a more convenient tool experimentally and can provide accurate results, provided the melting temperature (T_m) is consistent after annealing.

Melting temperatures (T'_m) provided by DSC analyses were used to estimate blockiness of ACA copolymers using the theory of Flory¹⁷ or Baur.¹⁸ Flory relates the melting point, T_m , of a copolymer to the homopolymer of the crystallizable monomer T°_m by:

$$(1/T_m) - (1/T_m^\circ) = -(R/\Delta H_u) \ln P_{\rm OH,OH}$$
 (3)

where *R* is the gas constant, ΔH_u is the molar enthalpy of fusion per crystallizable monomer unit, and $P_{\rm OH,OH}$ is the probability that a crystallizable group here (vinyl alcohol) joined to another like group. For a random copolymer, $P_{\rm OH,OH}$ = the mole fraction of crystallizable units = (OH), alternating copolymers of $P_{\rm OH,OH} <$ (OH). Baur's theory yields the expression¹⁸:

$$(1/T_m) - (1/T_m^{\circ}) = -(R/\Delta H_u)$$

 $\times [\ln P_{\rm OH,OH} - 2[1 - P_{\rm OH,OH}](\rm OH)] \quad (4)$

Flory assumes that longer sequences of crystallizable monomer residues crystallize at higher temperatures than shorter sequences. Baur's model postulates that every sequence length can be found in the amorphous, as well as in the crystalline, regions of the solid polymer.

The sequence probability of noncrystallizable units, $P_{\text{OAC,OAC}}$, can be defined analogously to $P_{\text{OH,OH}}$. It has been shown³ that

$$P_{\text{OAC,OAC}} = 1 - [(\text{OH})(1 - P_{\text{OH,OH}})/(\text{OAC})]$$
 (5)

Note that (OH) + (OAC) = 1, but $P_{\text{OH,OH}}$ + $P_{\text{OAC,OAC}}$ is not necessarily = 1.) It is also possible to determine the number-average sequence length L_{OH} defined as¹⁹:

$$L_{\rm OH} = (1 - P_{\rm OH,OH})^{-1}$$
(6)

Similarly, the definition of the blockiness factor, η , is¹⁹:

$$\eta = (1 - P_{\text{OH,OH}}) + (1 - P_{\text{OAC,OAC}})$$
 (7)

Equations (5)–(7) hold for both theories. In this part of our studies, constant crystallization temperatures of polymer samples were determined by DSC. Subsequently, DSC results were analyzed by Flory's and Baur's theories and then compared with NMR data.

Thermogravimetric curves of different ACA copolymers show that, at low temperatures, $\sim 100^{\circ}$ C, the loss of physically retained water takes place. Its peak is moved toward the lower temperatures, with decreasing degrees of hydrolysis and a decrease in the number of hydrogen bonds takes place. Thermogravimetric curves of all copolymers show that they all are thermally stable up to 240°C at the rate of heating 12.4°C min⁻¹, as shown in Figure 2. The polymers-A, B, and C-were heated up to 235°, 210°, and 195°C, respectively, at the rate of 10°C min^{-1} and cooled to 50°C at the same rate. The process was repeated three times, and the results obtained are shown in Table V and depicted in Figure 3. Figure 3 (a_1-a_5) shows T_m^{-1} and T_m^{-3} at 225.48° and 223.81°C, respectively. The melting temperature T_m has little effect, but changes in enthalpy decrease fivefold. Figure 3 (b_1-b_5) and (c_1-b_5) $c_{\rm 5})$ shows there is consistent decrease in T_m as well as change in enthalpy after repeated heating and cooling treatments. Figure 4 also shows similar trends in X-ray diffraction analyses of these samples after the same repeated heating and cooling treatment under a nitrogen atmosphere. The decrease in crystallinity and changes in enthalpy are attributed to the arrangement of the OH group due to hydrogen bonding. At the outset, the OH groups in a blocky ACA copolymer assemble themselves through hydrogen bonding. The polymer was heated up to 235°C at the rate of 10°C min⁻¹ and held at 235°C for 2 min and subsequently cooled down to 50°C. Then, again, it was heated at the same rate and held there for 10 min and cooled. The final T_m was obtained at the same heating rate.

These observations indicate that, once the hydrogen bond breaks by heat treatment, it becomes very difficult to attain the same arrangement in the polymer samples. Some hydrogen bonds occur among the OH groups and some remain free. Such a fact is clearly reflected in terms of melting temperature and changes in enthalpy. X-ray data show that a larger number of crystallites that were present at the beginning may be due to the self-assembly nature of the OH group through hydrogen bonding at the molecular level (intramolecular hydrogen bonding) and intermolec-



Figure 2 Thermogravimetric curves of different ACA copolymers. (OH) mol %: (a) 98.21; (b) 86.90; and (c) 75.98.

ular hydrogen bonding between two polymer chains. During the course of heat treatment, the intramolecular hydrogen bonds disappear and intermolecular hydrogen bonds reappear. Gel permeation chromatograms of all the three samples in solution at room temperature also show two peaks. The peak due to micelle appears at the lower retention time followed by the peak due to the free chain. An equilibrium exits between the free chain and the micellar aggregate. To gather

Sample	T_m^1 (°C)	$\Delta H \ ({ m J~g}^{-1})$	$\begin{array}{c} T_c^1 \\ (^{\circ}\mathrm{C}) \end{array}$	$\Delta H \ ({ m J~g}^{-1})$	T_m^2 (°C)	$\Delta H \ ({ m J~g}^{-1})$	$\begin{array}{c} T_c^2 \\ (^{\circ}\mathrm{C}) \end{array}$	$\Delta H \ ({ m J~g}^{-1})$	T_m^3 (°C)	$\Delta H \ ({ m J~g}^{-1})$
А	225.48	$82.26 \\ 52.5\%^{\mathrm{a}} \\ 34.0\%^{\mathrm{b}}$	201.89	-63.67	223.63	52.83	194.57	-16.32	223.81	15.72 27.0% ^b
В	189.70	44.40 28.4% ^a 17.0% ^b	118.97	-5.47	174.31	5.38	103.56	-4.38	152.70	10.20
C	181.87	21.77 13.9% ^a 11.0% ^b	123.30	-0.70	168.78	6.13	_	_	160.03	5.04

Table V Comparison of % Crystallinity Between DSC and X-ray Analysis

^a % crystallinity from DSC data.

^b % crystallinity from X-ray data.



 $\label{eq:Figure 3} \begin{array}{l} \textbf{DSC curves of different ACA copolymers.} (OH) \ mol \ \%: (a_1-a_5) \ 98.21; (b_1-b_5) \ 86.90; \ and \ (c_1-c_5) \ 75.98. \end{array}$



Figure 4 X-ray diffraction patterns of virgin ACA copolymers. (OH) mol %: (a) 98.21; (b) 86.90; and (c) 75.98. a', b', and c' are the X-ray diffraction patterns of the same polymers after consecutive heating and cooling treatments.



Figure 5 DSC curves of three different ACA copolymers after annealing at 120°C for 10 min. (OH) mol % (a) 98.21; (b) 86.90; and (c) 75.98.

more evidence, these polymers were heated up to 235° C at the rate of 20° C min⁻¹ and then cooled up to 120° C at the cooling rate of 350° C min⁻¹. The three copolymers were then annealed at 120° C for 10 min, and the crystalline melting temperature was recorded. To obtain constant crystallization temperatures, the same procedure was repeated thrice. In each case, the constant crystallization temperature was obtained. As reported previously, hydrogen bonding could lead to a more ordered liquid state in PVA.

Tubbs²⁰ has illustrated a dependency of T_m on heating rate. It was also observed that there is a strong influence of the DSC heating rate on both T_m and T_g of one of the polymer samples. Both T_m and T_g increase with heating rate to maximum values at $\sim 30^{\circ}$ C min⁻¹. To eliminate this effect, all samples were run at a standard (20°C min⁻¹) heating rate. A second more important factor that can affect T_m is the thermal history of the polymer. To eliminate this phenomenon, a known thermal history had to be established for the polymer samples before the consistent ${\cal T}_m$ value was determined. This was achieved by first heating the original polymer samples \sim 20°C above the initial T_m at a heating rate of 20°C min⁻¹. The polymer was then rapidly cooled at 320°C to a predetermined annealing temperature at 120°C, where the polymer was isothermally annealed for 10 min. The thermogram of these copolymers is shown in Figure 5, characterized by broad and sharp endotherms. Figure 5(a) shows a broad endotherm at 215°C and a much sharper endotherm with a maximum at 228.40°C. The broad endotherm that appears at 215°C is due to shorter sequences of OH groups and intermolecular hydrogen bonds between the hydroxyl group of PVA. The endotherm at 228.40°C is undoubtedly melting, because it is accompanied by softening of the polymer particles and fusion of the powder into a more transparent mass. No increase in the melting point of the homopolymer was observed upon



Figure 6 Determination of ΔH_u and T_m° using copolymer samples and eq. (8). $\Delta H_u = 33.25 \text{ kJ mol}^{-1} T_m^{\circ} = 230^{\circ}\text{C}.$

cooling and reheating. Figure 5(b) shows two broader endotherms at 137°C and 160°C, respectively, and sharp endotherm at 221°C. The low temperature transition at 137°C is not interpreted as a true endotherm, but as the result of a second-order transition in the crystalline phase followed by further crystallization. It has been demonstrated that the PVA crystallite undergoes a transition at $\sim 130^{\circ} C.^{21}$ The transition involves a change in the temperature coefficient of specific heat as well as a change in the crystal lattice expansion coefficients. The endotherm at 160°C is due to the shorter sequences of the OH group and also the intermolecular hydrogen bonds between the hydroxyl groups of ACA copolymers. Figure 5(c) shows two broader endotherms at 137°C and 158°C, respectively, and a sharper endotherm at 211.0°C. These endotherms were interpreted as previously described. Equilibrium values of T_m

were achieved in this work and have not been cited anywhere in the earlier literature.

DSC Measurement of Chemical Composition

As previously described, the Flory equation for random copolymer eq. (8) becomes

$$1/T_m - 1/T_m^{\circ} = -(R/\Delta H_u)\ln(OH)$$
 (8)

where (OH) is the mole fraction of vinyl alcohol units. Equation (8) should not apply to the samples studied, because these materials all had significant blocky character. However, this equation was used with values of $T_m^{\circ} = 228^{\circ}$ C and $\Delta H_u = 6.86 \text{ kJ mol}^{-1}$ and T_m equilibrium temperatures with established thermal history, the (OH) values derived did not agree well with NMR measurements of copolymer composition. Because the values $T_m^{\circ} = 228^{\circ}$ C and $\Delta H_u = 6.86 \text{ kJ mol}^{-1} \text{ had}$ been obtained from PVA-glycerol mixtures by plotting T_m° versus volume percentage of glycerol. The intercept $(T_m^{\circ} C)$ and slope $\Delta H_u = 6.86 \text{ kJ}$ mol^{-1} were obtained from the plot simultaneously. The random copolymers of vinyl alcohol and vinyl acetate had been prepared by equilibrium reacetylation of PVA (DP-1500) in mixtures of acetic acid and water at 100°C.

The T_m data for ACA copolymers plotted according to eq. (8) and a linear regression analysis yielded $T_m^{\circ} = 230^{\circ}$ C and $\Delta H = 33.25$ kJ mol⁻¹, and the experimental plot is shown in Figure 6. Using the obtained results, $T_m^{\circ} = 230^{\circ}$ C and ΔH_u = 33.25 kJ mol⁻¹, the blockiness, sequence lengths, probability of a crystallizable vinyl alco-

Sample	(OH) (mol %)	OAC (mol %)	$P_{\rm OH,OH}$	$P_{\rm OAC,OAC}$	$L_{ m OH}$	$L_{ m OAC}$	η
А	0.990^{a}	0.010			_	_	
	0.982^{b}	0.018	_	_	128.0	2.6	0.23
	0.976°	0.024	0.325	0.674	125.0	3.0	0.33
В	0.870^{a}	0.130	_	—	_	_	
	0.869^{b}	0.131	_	_	15.0	2.6	0.45
	0.862°	0.138	0.946	0.662	18.5	2.6	0.40
С	0.740^{a}	0.260	_	_	_	_	_
	$0.759^{ m b}$	0.241	_	_	8.9	2.8	0.44
	0.743°	0.257	0.881	0.655	8.4	2.8	0.46

 Table VI
 Chemical Composition, Mean Run Lengths, and Block Character of Partially Hydrolyzed

 PVAs from DSC Studies

^a Titration value.

^b NMR value.

^c DSC value.



Figure 7 Chemical composition as determined by ${}^{13}C$ NMR and DSC melting temperature measurements. Numbers on the axis refer to mol % vinyl alcohol units. (\triangle) Sample A. (\bigcirc) Sample B. and (\bigcirc) Sample C.

hol group, $P_{\rm OH,OH}$, and the noncrystallizable vinyl acetate group, $P_{\rm OAC,OAC}$, were calculated and these values match very well with those measured by ¹³C NMR as shown in Table VI and Figure 7. Compositional data obtained through DSC are more consistent with titration, as well as the NMR value shown in Figure 7. The values $T_m^{\circ} = 228^{\circ}$ C and $\Delta H_u = 6.86 \text{ kJ mol}^{-1}$ could be used from 58.0 to 78.0 mol percentage of (OH) group of ACA copolymers, where the values $T_m^{\circ} = 230^{\circ}$ C and $\Delta H_u = 33.25 \text{ kJ mol}^{-1}$ can be used from 58 to 99.0 mol % of the (OH) group of ACA copolymers for calculating chemical compositions, probability factors ($P_{\rm OH,OH}$ and $P_{\rm OAC,OAC}$) sequence lengths and blockiness.

Recently, it has been observed by Fourier transform infrared spectroscopy that hydrogen bonding distribution in ACA copolymers strongly depends on sequence distribution for block copolymers; hydroxyl–hydroxyl self-association is preferred.²²

CONCLUSIONS

The sequence lengths of alcohol and acetate residues, degree of hydrolysis of PVA, tacticity, and branching can be determined using high-field ¹³C NMR spectroscopy. The equilibrium crystal melting points of commercial samples of PVA vary greatly with thermal history. After a standardized and accurate thermal history, the melting temperature of a given sample can be used to estimate the degree of hydrolysis, blockiness of the polymer, and sequence probability of crystallizable and noncrystallizable units—depending on a particular theory that is applied to these data. It has been confirmed that basic hydrolysis permits the synthesis of ACA copolymers with a blocky nature of sequence distribution. Thermal analyses show that block copolymers exhibit an association behavior close to PVA, where hydroxyl-hydroxyl self-association is preferred.

The authors thank Dr. S. Sivaram for his valuable comments. The authors also thank Drs. S. Ganapathy and P. R. Rajmohan for many useful discussions and NMR measurements.

REFERENCES

- Finch, C. A., Ed. Polyvinyl Alcohol; Wiley: New York, 1973.
- Pritchard, J. G. Poly(vinyl alcohol), Basic Properties and Uses; Polymer Monographs, Vol 4; Garden and Breach: London, 1970.
- 3. Tubbs, R. K. J Polym Sci 1966, A4, 623.
- Nagai, E.; Sagane, N. Kobunshi Kagaku 1955, 12, 195.
- 5. Hayashi, S.; Nakano, C.; Motoyama, T. Kobunshi Kogaku 1963, 20, 303.
- Isasi, J. R.; Cesteros, L. C.; Katime, I. Macromolecules 1994, 27, 2200.
- Moritani, T.; Fujiwara, Y. Macromolecules 1977, 10, 532.
- Toppet, S.; Lemmstra, P. J.; Van der Velden, G. Polymer 1983, 24, 507.
- 9. Bugada, D. C.; Rudin, A. Polymer 1984, 25, 1759.
- Sanchez-Chaves, M.; Arranz, F.; Saenz, J. C. An Quim 1989, 85, 236.
- 11. Wu, T. K.; Ovenall, D. W. Macromolecules 1973, 6, 582.
- 12. Wu, T. K.; Sheer, M. L. Macromolecules 1977, 10, 529.
- 13. Dunn, A. S.; Naravane, S. R. Br Polym J 1980, 12, 75.
- Inoue, Y.; Chujo, R.; Nishioka, A.; Nozakura, S.; Iimuro, H. Polym J 1973, 4, 244.
- Hayashi, S.; Nakaro, C.; Motoyama, T. Kubunshi Kagaku 1964, 21, 300; 1964, 21, 304.
- 16. Shiraishi, M. Br Polym J 1970, 2, 135.
- 17. Flory, P. J. Trans Faraday Soc 1955, 51, 848.
- Baur, H. Z Kolloid 1966, 97, 212; Makromol Chem 1966, 98, 297.
- Ito, K.; Yamashita, Y. J Polym Sci, Part A 1965, 3, 2165.
- 20. Tubbs, R. K. J Poly Sci 1965, A3, 4181.
- Ishikawa, K.; Miyasaka, K. Repts Progr, Polym Phys Jpn 1964, 7, 93.
- Tabb, D. L.; Koenig, J. L. Macromolecules 1975, 8, 929.