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

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ABSTRACT: The correlation between hydrogen-bonding self-association and sequence distribution in different poly(vinyl acetate-*co*-vinyl alcohol) copolymers (ACA) of different degrees of hydrolysis and sequence distributions has been studied by infrared and NMR spectroscopy. For ACA copolymers, quasi-random distributions are obtained by acid alcoholysis, blockier distributions by saponification, and intermediate distributions by a combined method, as shown by ^{13}C NMR. FTIR spectroscopy has pointed out that hydrogen-bonding distribution in ACA copolymers strongly depends on sequence distribution. For block copolymers, hydroxyl–hydroxyl self-association is preferred. However, in random copolymers, a strong competition between hydroxyl–hydroxyl and hydroxyl–carbonyl association is observed. Hydroxyl–carbonyl association seems to occur between adjacent repeat units, leading to cyclic structures with a high thermal stability.

Introduction

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 poly(vinyl alcohol) (PVA).[1,2] Several properties of these copolymers, such as degree of crystallinity, melting point, solubility, viscosity, and surface tension of aqueous solutions, depend on the total degree of hydrolysis, but they are also a strong function of the sequence distribution of monomer units in the copolymer. It is well-known that, in the case of ACA copolymers, the reacetylation method produces a random distribution of segments, but ACA copolymers obtained by hydrolysis (or alcoholysis) are blockier.[1-3] These results can be explained by taking into account the adsorption of the catalyst of the hydrolysis or saponification processes on the hydroxyl groups in the hydrolyzed sites, so the rate of hydrolysis of neighboring acetyl groups increases.

Classic methods as infrared spectroscopy,[4] iodine color adsorption,[5] and calorimetry[3] have been employed to give some qualitative indication of the sequence distribution. However, the ^{13}C-NMR technique[6-9] has been proved to be an appropriate tool for quantitative determinations and has been used to characterize the sequence distributions of ACA copolymers obtained by different methods. Nevertheless, although some qualitative techniques show that acid alcoholysis does not produce blocky distribution as does hydrolysis or alcoholysis in a basic medium, to our knowledge a ^{13}C-NMR study of the sequence distribution in such samples has not been accomplished. In the present work, ^{13}C-NMR spectra of ACA copolymers obtained through saponification, acid alcoholysis, and a combination of both have been compared.

As is known, infrared spectra of random copolymers show a strong shoulder in the carbonyl peak or, sometimes, a double peak attributed to carbonyl groups hydrogen bonded to neighboring hydroxyl groups, but the carbonyl region of blockier copolymers is nearly identical to that of poly(vinyl acetate).[3,4] Fourier transform infrared spectroscopy (FTIR) allows, in many cases, a quantitative analysis of hydrogen-bonding distributions in homopolymers, copolymers, and polymer blends.[10] Curve-fitting methods can be applied to determine the distribution of free and hydrogen-bonded carbonyls of vinyl acetate units. Nevertheless, hydrogen-bonding distributions in ACA copolymers remain unstudied. This paper reports on the relationship between the sequence distributions of these copolymers and their hydrogen-bonding distribution.

Experimental Section

Materials. ACA copolymers studied in this work have been prepared, by different routes, from the same parent poly(vinyl acetate) (PVAc) sample. PVAc (B-1000 Erquimia S.A.) was previously purified by dissolution in acetone and precipitation into petroleum ether, followed by dissolution in methanol and reprecipitation into water. Molar mass was determined at room temperature by GPC using THF as the mobile phase. The molar mass and polydispersity were calculated using the viscometric equation for PVAc in THF:[11] $[\eta] = 3.5 \times 10^{-2} M^{0.63}$ for calibration. The results were 255 000 g/mol and 2.1 for molar mass and polydispersity, respectively.

(A) Acid Alcoholysis. ACA copolymers were obtained by hydrolysis–alcoholysis of PVAc, at 50 °C, in acidic medium. PVAc was dissolved in a stirred 9:1 (v/v) solution of methanol–water (≈5–6 g/dL). Then, 1.7 mL of concentrated hydrochloric acid was added to get an acid concentration of 0.2 M in the solution. The degree of hydrolysis was controlled by varying the time of reaction, and it was determined for some samples by titration of residual acetate groups.[1,12] Reaction products with a low degree of hydrolysis (up to 60%) were precipitated in water followed by dissolution in methanol and reprecipitation 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) Saponification. PVAc was dissolved in a 3:1 (v/v) solution of methanol–water (≈6 g/dL). The degree of hydrolysis is stequiometrically controlled by the amount of a concentrated solution of NaOH in water (40% w/v) added with stirring. The reaction was allowed to go to completion in the gel state at room temperature for several hours, and the products were purified as in the previous case.

(C) Combined Method. Other samples were prepared by combination of the previous methods: samples with less than 30% degree of hydrolysis obtained by method A were solved in a methanol–water mixture and saponified with low amounts of NaOH as in method B.

NMR Characterization. According to their solubility, acetone, water, and mixtures of them were used as solvents for the samples in the ^{13}C-NMR experiments because the resonance lines of these solvents do not overlap the methylene carbon lines in ACA. Carbon-13 NMR spectra of 20% w/v solutions were obtained at 62.89 MHz using a Bruker AC-250 NMR spectrometer in 5-mm-o.d. tubes. Approximately 1400 free induction decays

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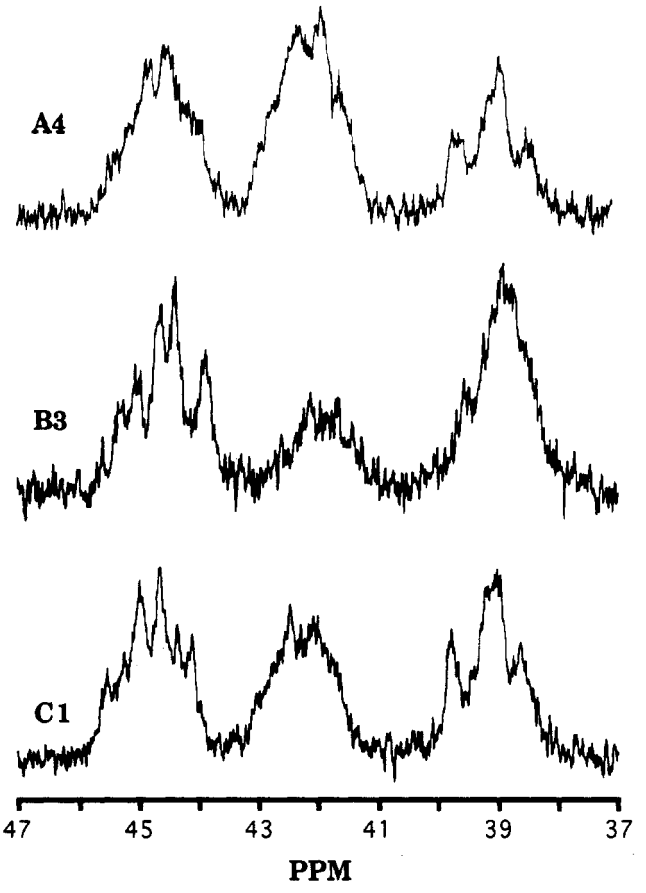

Figure 1. 62.89-MHz ^{13}C-NMR spectra of the methylene region (38–46 ppm) for three ACA copolymers with a similar degree of hydrolysis but prepared by different methods.

were accumulated using a pulse width of 5 μs and acquisition time of 2.23 s at a relaxation delay of 5 s and a spectral width of 14 700 Hz (234 ppm). The digital resolution amounted to 0.449 Hz/pt. The "Inverse gated.Au" method of Bruker library was employed (^{1}H-decoupled spectrum without NOE).

FTIR Analysis. The infrared spectra for the copolymers were recorded on a Nicolet-520 Fourier transform infrared (FTIR) spectrometer with a resolution of 2 cm^{-1}, and 100 scans were averaged. Films for FTIR measurements were cast from solutions (0.02 g/mL). Depending on the solubility, samples were dissolved in methanol or DMF and were cast directly on KBr pellets. All films were vacuum-dried and were thin enough to be within the absorbance range where the Beer–Lambert law is obeyed.

The influence of temperature on the spectral features of the ACA copolymers was studied by using a Specac variable-temperature cell P/N 21/5000. The temperature was controlled with a Eurotherm 847 unit.

Least-squares curve fittings of the spectra were performed using Nicolet FOCAS curve analysis software installed in a Nicolet 620 station. This software permits a preliminary determination of the number of peaks to be analyzed and of their position by a Fourier self-deconvolution method. After selection of the number of peaks and their tentative location, curve analysis simulates the location, peak width, and peak shape of each peak that forms the pattern of overlapping bands found in the sample spectrum.

Results and Discussion

^{13}C-NMR Analysis. The main features of the ^{13}C-NMR spectra for ACA copolymers have been described elsewhere.[6-9] The most interesting region for the study of sequence distribution is that of the methylene region. Figure 1 shows the ^{13}C-NMR spectra of the methylene region (38–46 ppm) for three ACA copolymers with a similar degree of hydrolysis but prepared by different methods. 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), (OAc,OAc) with increasing field strength.[6] The stereochemical configuration of ACA copolymers can be determined from methine carbon resonances if the vinyl acetate content is not too high, but this is not a relevant fact for our samples since all of them have been obtained from the same atactic PVAc sample.

Table 1. Compositions, Mole Fractions of Diads, and Values of η of ACA Copolymers Obtained by Different Methods[a]

sample	(OH,OH)	(OH,OAc)	(OAc,OAc)	(OH)	η
A1	0.0789	0.3079	0.6132	0.233 (0.243[b])	0.861
A2	0.1456	0.3916	0.4628	0.341 (0.350[b])	0.871
A3	0.1871	0.4139	0.3990	0.394 (0.394[b])	0.867
A4	0.3240	0.4172	0.2587	0.533 (0.546[b])	0.838
A5	0.8771	0.1063	0.0166	0.930 (0.880[b])	0.816
B1	0.1433	0.1713	0.6854	0.229	0.485
B2	0.2878	0.1985	0.5136	0.387	0.418
B3	0.3837	0.1851	0.4312	0.476	0.371
B4	0.8214	0.1012	0.0774	0.872	0.445
C1	0.3508	0.3167	0.3325	0.509	0.634
C2	0.1924	0.2618	0.5457	0.323	0.599
C3	0.2829	0.3976	0.3195	0.482	0.796

[a] A1–A5, acid alcoholysis; B1–B4, saponification; C1–C3, combined method. [b] Data obtained from chemical titration.

As is well-stated,[6-9] the mole fractions of the diad sequences can be calculated from the 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

$$(OH) = (OH,OH) + \frac{(OH,OAc)}{2} \quad (1)$$

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

$$\eta = \frac{(OH,OAc)}{2(OH)(OAc)} \quad (2)$$

where η is a measure of departure from random character.[13] It takes $0 \leq \eta < 1$ for blockier distributions; $\eta = 0$ for block copolymers; $\eta = 1$ for completely random cases; and $1 < \eta \leq 2$ for alternate-like cases. The results of this analysis are shown in Table 1 for all the 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 ±3% in absolute value, except for the highest hydrolysis degrees (A5 and B4 samples, 88% and 82% according to titrations, respectively). Since their spectra present two methylene lines of very low intensity, higher errors can be expected for these cases.

The diagram of Figure 2, in which mole fractions of (OH,OAc) diads are plotted as a function of (OH) content, permits a comparison of different extents of blockiness. The blocky character for the samples prepared by saponification (B samples) is high, and this agrees with data from other studies:[6,9] $0.4 < \eta < 0.5$.

On the other hand, although the samples obtained by acid alcoholysis (A samples) are not completely random, they are close to it, with $0.8 < \eta < 0.9$. These results confirm the qualitative idea of randomness for these copolymers given by nonquantitative techniques, such as calorimetry,[3] iodine adsorption,[5] or thermogravimetry.[14] If they are compared with those obtained from reacetylated samples (in which $0.8 < \eta < 1.1$), we can conclude that acid alcoholysis is also an adequate method for obtaining quasi-

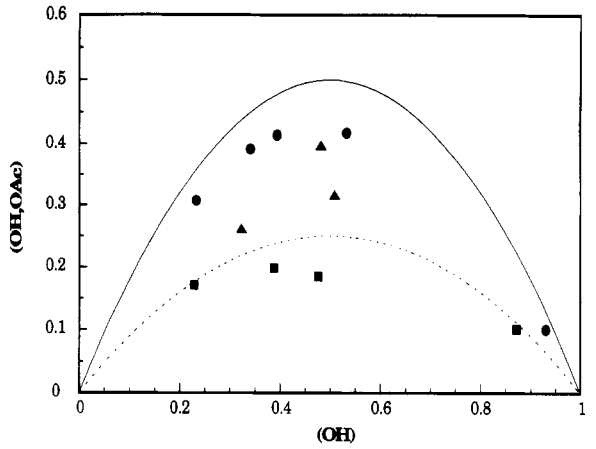

Figure 2. Plot of (OH,OAc) diad fraction as a function of the degree of hydrolysis: (—) random distribution and (- - -) $\eta = 0.5$. (●) A samples, (■) B samples, and (▲) C samples.

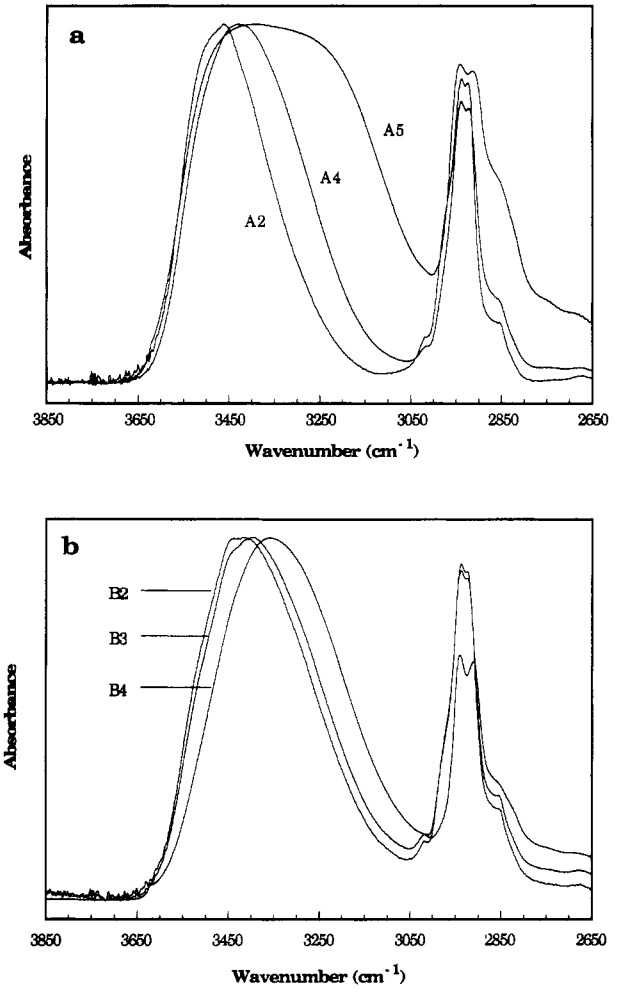

Figure 3. Autoscaled spectra in the 2650–3850-cm^{-1} region for (a) A samples and (b) B samples.

random distributions. Thus, autocatalytic effects are not as important in the acid alcoholysis mechanism as they are in the cases of saponification or basic hydrolysis.[2]

Finally, the samples prepared by the combined method (C samples) exhibit, as expected, intermediate values of block character, so it is possible to obtain ACA copolymers within a wide range of sequence distributions.

FTIR Analysis. Several regions of the infrared spectra of ACA copolymers are influenced by hydrogen-bonding self-association. Parts a and b of Figure 3 show the FTIR spectra in the 2650–3850-cm^{-1} range for different ACA copolymers prepared according to methods A and B described in the Experimental Section.

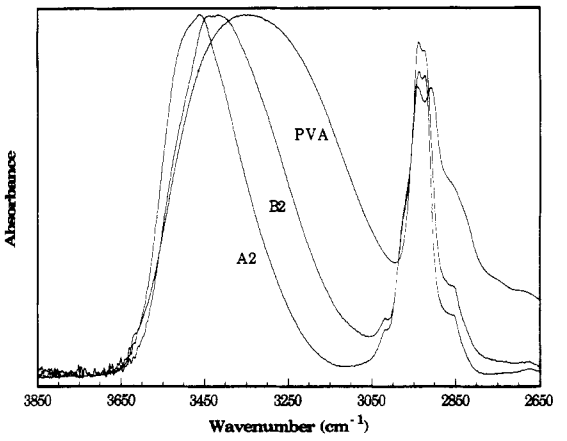

Figure 4. Autoscaled spectra in the 2650–3850-cm^{-1} region for A2, B2, and PVA samples.

First of all, it is obvious that hydrogen bonding clearly affects the hydroxyl stretching band. This broad band, overlapping the C–H stretching band, can be considered to be composed of narrow contributions corresponding to hydroxyl groups surrounded by different environments. When the spectra of random ACA copolymers are compared (Figure 3a), a shift of the peak maximum toward higher wavenumbers is observed as the vinyl acetate content in ACA increases. At the same time, the O–H band becomes narrower. These data suggest that there are different types of hydroxyl groups in ACA copolymers: free (corresponding to the highest wavenumbers), hydrogen bonded to carbonyl groups, and self-associated hydroxyl groups in the form of dimers, trimers, etc. (at low wavenumbers). Thus, carbonyl groups of vinyl acetate units compete with self-associated hydroxyl groups for hydrogen bonding causing the shift of the O–H band toward higher wavenumbers as the content of vinyl acetate units increases in the copolymer. In the case of blockier ACA copolymers (Figure 3b), this shift is less pronounced. In Figure 4, the spectra in the hydroxyl stretching region for PVA and two different ACA copolymers are displayed. Samples cast at room temperature were annealed above their glass transition temperatures to avoid nonequilibrium effects. There is a clear difference between the spectra of two samples of similar (OH) content but different sequence distribution: the block copolymer (B2) shows an O–H stretching band closer to PVA; on the contrary, this band shifts toward higher wavenumbers for the random copolymer (A2). This can be explained if we bear in mind the different environments for O–H groups in each case. In a block copolymer the hydroxyl environment is closer to that of PVA, where hydroxyl groups are surrounded by other hydroxyl groups, favoring multiple self-association. It is well-known that multiple hydrogen bonding between hydroxyl groups leads to a large shift of the OH band toward lower wavenumbers.[15] PVA exhibits a remarkable contribution of self-associated hydroxyl groups in the form of polymeric H-bonds (3200–3300 cm^{-1}); this contribution is also significant in the blocky copolymer but irrelevant (by steric reasons) in the random copolymer sample (see Figure 4).

The carbonyl stretching band for PVAc is located at 1738 cm^{-1}. For ACA copolymers, this band changes widely depending on composition and sequence distribution of repetitive units, as can be seen in Figure 5. The new contribution in ACA copolymers corresponds to hydrogen-bonded carbonyl groups. The higher the content of vinyl alcohol units, the higher the number of hydrogen-bonded

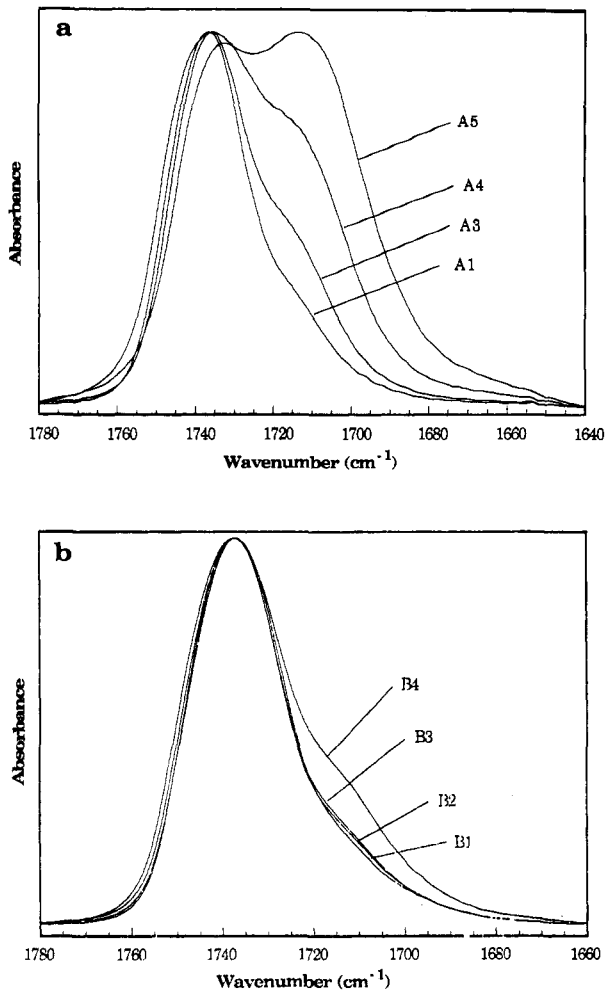

Figure 5. Autoscaled spectra in the 1640–1780-cm^{-1} region for (a) A samples and (b) B samples.

carbonyl groups, as expected. On the other hand, in the case of blockier ACA copolymers, the amount of associated carbonyl groups is clearly lower. Random comonomer distribution samples with higher hydroxyl contents show a slight shift toward low wavenumbers for the peak corresponding to "free" carbonyl groups. Although this shift can be considered as a spectral artifact originated by a simple superposition of the two peaks, a deeper analysis of the band by curve-fitting procedures seems to confirm the change on the free carbonyl peak position for the A5 sample. This can be explained by considering the hydroxyl-charged environment that surrounds carbonyl groups in these cases (this shift has been also confirmed for an ACA copolymer with a 97% degree of hydrolysis). In fact, the peak positions obtained as a result of curve-fitting procedures for blocky and random copolymers with low hydrolysis degrees matches that of pure PVAc (see below and Table 2).

The C–O–C stretching region for acetate units is located at 1240 cm^{-1} for pure PVAc. For ACA copolymers, it is split into two contributions; a new band, which appears at higher wavenumber (more than 15 cm^{-1} above), is attributed to hydrogen bonding with the neighboring carbonyl group.[4] This contribution becomes more important for copolymers of a high degree of hydrolysis. When comparing two different ACA with high contents of alcohol units, as A5 and B4, it can be seen that the B4 C–O–C stretching band resembles that of pure PVAc (1243 cm^{-1}), consistent with the lower amount of hydroxyl–carbonyl hydrogen bonding in the blockier copolymers.

The C–O stretching mode of vinyl alcohol units (≈1090 cm^{-1}) is also affected by hydrogen bonding. This band is

Table 2. Curve-Fitting Results for Carbonyl Stretching Bands in ACA Copolymers

	free carbonyl band			associated carbonyl band			
sample	wavenumber, cm^{-1}	width, cm^{-1}	rel area, %	wavenumber, cm^{-1}	width, cm^{-1}	rel area, %	f_F
A1	1737.9	22	73.1	1715.8	26	26.9	0.802
A2	1737.5	23	65.8	1714.3	25	34.2	0.742
A3	1737.5	21	61.6	1715.7	26	38.4	0.706
A4	1737.6	22	61.3	1715.4	25	38.7	0.704
A5	1735.7	19	33.4	1712.5	28	66.6	0.429
B1	1738.3	24	80.3	1714.1	24	19.7	0.859
B2	1738.2	22	73.5	1715.6	26	26.5	0.807
B3	1738.5	22	75.0	1715.9	26	25.0	0.818
B4	1738.5	21	65.3	1716.5	30	34.7	0.738
C1	1737.7	21	63.4	1715.5	26	36.6	0.723
C2	1738.5	22	69.5	1716.3	26	30.5	0.774
C3	1738.4	21	53.2	1716.2	29	46.8	0.631

the addition of two contributions, one corresponding to free groups and other in which the oxygen atom is involved in a hydrogen bond, resulting in a weaker C–O bond. Thus, a larger hydrogen-bonding effect is expected for random ACA copolymers with high acetate contents. This is experimentally confirmed, though the resolution of this band is poorer for these copolymers. More important is the effect of crystallinity of samples on this band, especially in the cases of PVA and blocky copolymers. The C–C–C stretching band (1144 cm^{-1}) is related to the crystalline regions of PVA.[1,2] For random ACA copolymers, this sharp band is only present for the samples with higher hydrolysis degrees (A5). On the contrary, it is present for all the saponified ACA samples and increases when the samples are annealed above 400 K (see below).

As is well-known, hydrogen bonds are widely influenced by temperature. Parts a and b of Figure 6 show the thermal behavior of the O–H stretching region for A2 and B2 copolymers, respectively. As the temperature is increased, a progressive shift toward higher wavenumbers and a narrowing of O–H band is observed, indicating the rupture of hydrogen bonds in the copolymers. It is remarkable that for all the temperatures studied, hydroxyl stretching bands in blocky copolymers are broader than those of random copolymers. In other words, blocky copolymers always exhibit higher contents in multiple or polymeric H-bonds.

After this thermal treatment, a different shape for O–H region at 298 K was noticed, especially for random copolymers. The peak is now narrower and more symmetrical because of the loss of lower wavenumber contribution. For instance, the mean width at half-height of the hydroxyl stretching band changes from 281 to 223 cm^{-1} for the random copolymer and from 345 to 333 cm^{-1} for the blocky copolymer. This effect, previously detected for vinyl chloride–vinyl acetate–vinyl alcohol terpolymers,[16] can be attributed to a change in the hydrogen-bonding distribution in the copolymer. Although the initial shape of the O–H band could be attributed to moisture sorption, this is not the case as shown in this way: humidification of annealed samples does not change the final band shape but produces an increase of the intensity of the symmetrical O–H band. On the other hand, the effect of heat treatments is not so evident for blocky samples (Figure 6b), a new proof of the influence of sequence distribution. In fact, as can be expected, hydroxyl self-association in the form of multiple polymeric H-bonds (contributions at lower wavenumbers) are more easily recouped after thermal treatments in the blocky copolymer than in the random one.

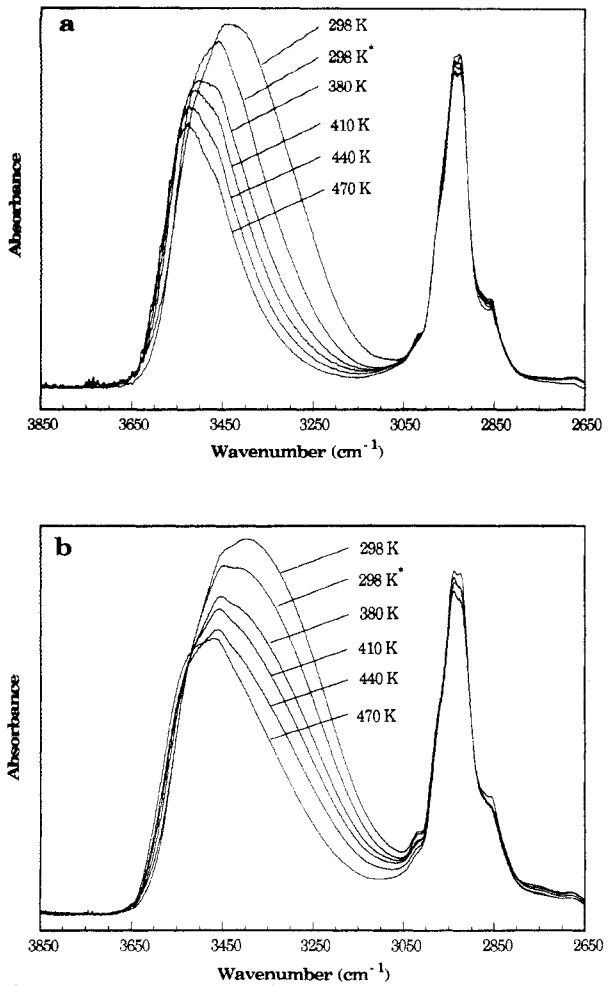

Figure 6. Infrared spectra in the 2650–3850-cm^{-1} region for (a) A2 sample and (b) B2 sample at different temperatures. (*) Spectra for annealed samples.

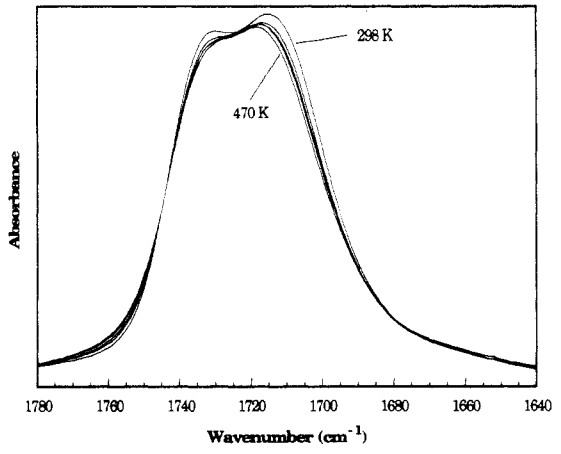

Figure 7. Infrared spectra in the 1640–1780-cm^{-1} region for the A5 sample between 298 and 470 K.

As far as carbonyl groups are concerned, Figure 7 shows their particular thermal behavior: the carbonyl groups remain hydrogen bonded at high temperatures, indicating the high stability of this type of interaction. This is an uncommon behavior for carbonyl–hydroxyl hydrogen bonding in polymers. Usually this type of interaction exhibits a dramatic decrease for temperatures above 400 K. The hydrogen-bonded blend poly(vinyl acetate)/poly(vinyl phenol),[17] involving similar chemical groups, is a good example of this kind of behavior. Moreover, the dimer self-association in polyacids as ethylene–methacrylic acid copolymers also exhibits unstability at these high temperatures.[18] The particular thermal stability of the

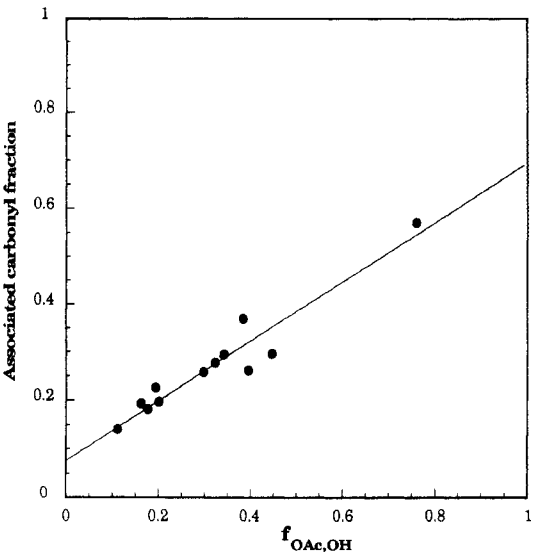

Figure 8. Plot of the fraction of hydrogen-bonded carbonyl groups f_{CO}^{HB} against the mole fraction of vinyl acetate units with adjacent vinyl alcohol units, $f_{OAc,OH}$.

carbonyl–hydroxyl interactions in these systems could be explained by taking into account that if they involve adjacent units, as has been suggested,[4] then cyclic structures involving 8-membered ring are formed, and they are probably thermally stable. Anyway, regarding Figure 7, we can conclude that the hydrogen bonds broken at high temperature are those involving hydroxyl–hydroxyl interactions.

Knowing that vinyl alcohol units do not show absorbance in the 1640–1780-cm^{-1} region, quantitative measurements of hydrogen bonding can be performed for the carbonyl absorption band by curve-fitting analysis. In order to obtain the fraction of hydrogen-bonded carbonyl groups, the absorptivity ratio for free and hydrogen-bonded carbonyl contributions is required. We have employed a value of $a_{HB}/a_F = 1.5$, which has been previously calculated by Moskala et al.[17] The results of such a curve-fitting procedure are summarized in Table 2. As can be seen, the results for the location and half-height of the hydrogen-bonded and non-hydrogen-bonded contributions are similar for copolymers with different composition and/or sequence distribution. FTIR analysis shows a strong dependence of hydrogen bonding in ACA copolymers with their sequence distribution. When comparing copolymers with a similar degree of hydrolysis, random copolymers show, in all cases, a larger level of association degree than blockier samples. On the other hand, the copolymers obtained from the combined method show intermediate values, in agreement with their sequence distribution. The most important reason for this event seems to be related to the special stability of the hydrogen bonds formed between hydroxyls and carbonyls in this system. In fact, it seems that carbonyl association is independent of the solvent employed for sample preparation. We have assayed with methanol and DMF solvents with a marked donor and acceptor character, respectively, and the results for carbonyl association are coincident.

According to these ideas, the relative intensity of the two carbonyl bands is therefore an indication of the sequence distribution of the copolymer, which is related to the number of VAc–VA pairs, i.e., (OH,OAc) diads. Curve fitting of carbonyl bands allows then the correlation of FTIR and ^{13}C-NMR results. In Figure 8, the fraction of hydrogen-bonded carbonyl groups, f_{CO}^{HB}, is plotted vs the mole fraction of vinyl acetate units with adjacent vinyl alcohol units, $f_{OAc,OH}$:

$$f_{OAc,OH} = \frac{(OH,OAc)}{2(OAc)} \quad (3)$$

A remarkable linearity is obtained for this plot, which confirms the correlation between hydrogen-bonding association and sequence distribution in the ACA copolymers. As was mentioned before, it has been suggested that hydrogen bonding in ACA copolymers involves hydroxyls and carbonyls of adjacent units. Although intramolecular hydrogen bonding generally occur in 5-, 6-, or 7-atom rings, 8-membered rings have been also reported.[19] As can be observed, the intercept (the case of completely block copolymers) is not zero; this fact can be attributable to carbonyl groups hydrogen bonded to nonadjacent hydroxyl groups. Anyway, our results are not conclusive about this particular point, and the possibility of hydroxyl protons bonding to penultimate acetate groups cannot be neglected.[20] Nevertheless, in our opinion the particular thermal stability of hydrogen bonding in these copolymers could be better explained if intramolecular H-bonds involve 8-membered rings, due to larger rings being more unstable as the temperature increases.

Conclusions

An almost random sequence distribution for ACA copolymers obtained by acidic hydrolysis has been confirmed. Also, it has been confirmed that the combination of acid and basic hydrolysis permits the synthesis of ACA copolymers with a wide range of sequence distributions.

FTIR spectroscopy has pointed out that hydrogen-bonding distributions in ACA copolymers strongly depend on sequence distribution. Block copolymers exhibit an association behavior close to PVA (hydroxyl–hydroxyl self-association is preferred); however, in random ACA copolymers a strong competition between hydroxyl–hydroxyl and hydroxyl–carbonyl association is observed. On the other hand, hydroxyl–carbonyl association presents a high thermal stability, suggesting the formation of cyclic structures, probably involving adjacent repetitive units.

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