Mapping Phases of Poly(vinyl alcohol) and Poly(vinyl acetate) Blends by FTIR Microspectroscopy and Optical Fluorescence Microscopy

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ABSTRACT: Fluorescence optical microscopy (FOM) of poly(vinyl alcohol) (PVA) and poly(vinyl acetate) (PVAc) blends in compositions 9/1, 1/1, and 1/9 (w/w) show that these blends present phase separation in the solid state. Each domain of the solid samples was identified by FOM as PVA-richer domains by green fluorescence of fluorescein and PVAc-richer domains by the blue fluorescence of anthracene. The dimensions, shapes, and distributions of these domains were dependent on the initial composition of the polymeric mixtures in the solution. Specific interactions between both homopolymers were studied using FTIR microspectroscopy, which allowed us to obtain spectra for both PVA-richer and PVAc-richer domains. These spectra demonstrated that partial miscibility could occur only for blends with a higher PVAc content and, in these cases, we observed interchain hydrogen-bonded carbonyl groups. Fluorescence microscopy of blends with this partial miscibility exhibited small interconnected domains produced by coalescence of droplets during the polymer phase separation process. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 645–655, 1998

Key words: polymer blends; fluorescence; microspectroscopy

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a commercial polymer usually produced by acidic or basic hydrolysis of poly(vinyl acetate) (PVAc). Its properties depend on its molecular weight, total degree of hydrolysis, sequence distribution of the monomer units, and tacticity. PVA is a semicrystalline polymer and its crystalline index depends on the synthetic process and physical ageing.[1] Hydrogen bonds keep together the polymer chains, even in the amorphous phase,[2] and the glass transition temperature of this polymer is ∼ 350 K.

Hydrogen-bonding interactions between different polymers can be conveniently studied using near-infrared spectroscopy.[3] Near-infrared spectra of PVA exhibit some characteristic bands centered at 4800 cm^{-1} (assigned to CO stretching); 5200 cm^{-1} (assigned to $\delta_{OH} + v_{OH}$); a doublet at 5800 cm^{-1} (a combination band of symmetric and antisymmetric CH stretching); and very broad and complex bands from 6700 to 7200 cm^{-1} attributed to a combination of ($\delta_{OH} + 2v_{OH}$) and an overtone of $2v_{OH}$ bands. These absorption bands were resolved into three lines, assigned to vibrations of hydroxyl groups associated with intramolecular, intermolecular, and nonhydrogen-bonding, toward a higher wavenumber. We demonstrated that the relative intensities of these bands were dependent on the temperature and involved changes of the interactions between hydroxyl groups.[4] We also observed that the glass transition temperature of PVA homopolymer is $T_g \cong 350$ K, from the relative intensities of the bands

at 5200 cm^{-1} and 5800 cm^{-1}. On the other hand, PVAc is an amorphous polymer, with a $T_g \sim 305$ K, depending on its molecular weight.

Shibayama et al.[5] showed that Fourier-transform infrared (FTIR) spectroscopy is one of the most powerful techniques to investigate a multicomponent system because it provides information for both blend composition and polymer–polymer interactions. Studies of polymer–polymer interactions and of polymer miscibility can be performed using those vibrational modes attributed to "free" and hydrogen-bonded hydroxyl and carbonyl groups. Many examples of these studies have been reported: cellulose and PVA,[5] poly(4-vinyl phenol) with poly(vinyl acetate) and ethylene–vinyl acetate copolymers,[6–8] poly(hydroxyl ether of bisphenol A) and poly(caprolactone),[9] polypyrrole and PVA.[10] Significant changes in vibrational wavenumbers occurred for these polymer blends involving the following vibrations: OH-stretching (3400–3000 cm^{-1}), carbonyl stretching (1800–1650, 1240 and 1090 cm^{-1}) and crystalline vibrations for PVA (1140 cm^{-1}).

The development of FTIR in recent years improved the studies in material science since it provides a direct method for analysis and mapping of molecular species in materials.[11–13] Therefore, this technique should be very conveniently applied in studies of polymer blends in order to analyze specific interactions in well-defined sites.

Blends of PVA and PVAc should be immiscible since the solubility parameters are $\delta(\text{PVA}) = 12.6$ cal$^{1/2}$ cm$^{-3/2}$ and $\delta(\text{PVAc}) = 9.1$ cal$^{1/2}$ cm$^{-3/2}$.[14] However, if partially hydrolyzed PVA is used instead of 100% hydrolyzed samples, one would expect a partial miscibility of these homopolymers.

We studied the miscibility of PVA/PVAc blends through optical fluorescence microscopy.[15] Partial miscibility was also evidenced by fluorescence spectroscopy since there were significant changes in the nonradiative deactivation processes of the fluorophores dissolved in the material compared with the homopolymers.[16] Although these studies demonstrated the existence of a partial miscibility of these homopolymers they did not show the molecular mechanisms of the interactions between them.

Therefore, the goal of this article is to study the molecular interactions between the PVA and PVAc homopolymers in polymer blends of different compositions (9 : 1, 1 : 1, and 1 : 9 w/w). We performed this study using FTIR microspectroscopy since it is expected that some vibrational modes of each homopolymer are modified by polymer–polymer interactions producing shifts of the absorption bands. Selection of different parts of the samples was done by the microscope.

EXPERIMENTAL

PVA [Aldrich Chemical Co., average molecular weight (M_w) = 124,000–186,000, 87–89% hydrolyzed], $T_g \cong 350$ K, and PVAc (Aldrich Chemical Co., high M_w = 237,000), $T_g \cong 305$ K, were used as received.[4,16]

Blends of PVA/PVAc in three proportions by mass (9/1, 1/1, and 1/9) (w/w) were prepared in the form of films by casting from the appropriate solutions of both homopolymers over a polystyrene plate covered by a polyethylene film. A mixture of ethanol and water was used as solvent to dissolve both homopolymers. All of the films used for measurements were dried at room temperature and normal pressure and were kept in a desiccator under vacuum.[15,16] Phase separation processes were observed in these blends for all initial compositions, producing a visibly heterogeneous material, with thicker ($\sim$100 μm) and thinner ($\sim$20–40 μm) areas.[15,16] Thinner part of the samples could be directly analyzed by FTIR, but the thicker parts had to be re-dissolved in order to reduce its thickness.

FTIR spectra were recorded on a Perkin–Elmer model 16PC spectrometer coupled with a Perkin–Elmer microscope with a resolution of 4 cm^{-1}. Sixty-four scans were averaged. The selected slits of the spectrophotometer allow us to probe regions of the sample with an area of 268 μm $\times$ 143 μm. The software used for the data collection and analysis was the standard IRDM-Perkin–Elmer.

We obtained fluorescence photomicrographs of different parts of these samples for a complete description of the material. Fluorescence optical microscopy (FOM) was performed using a standard Zeiss Jena universal microscope with the microscope in a reflection configuration as described earlier. A magnification of 100$\times$ was used for all of the micrographs. Since these polymers are not fluorescent upon UV excitation, they were dyed with fluorescein (green fluorescence), mapping PVA-richer domains, and anthracene (blue fluorescence), mapping PVAc-richer domains.[15]

RESULTS AND DISCUSSION

Infrared spectra of both PVAc [Fig. 1(a,b)] and PVA homopolymers in order of crescent hydrolysis
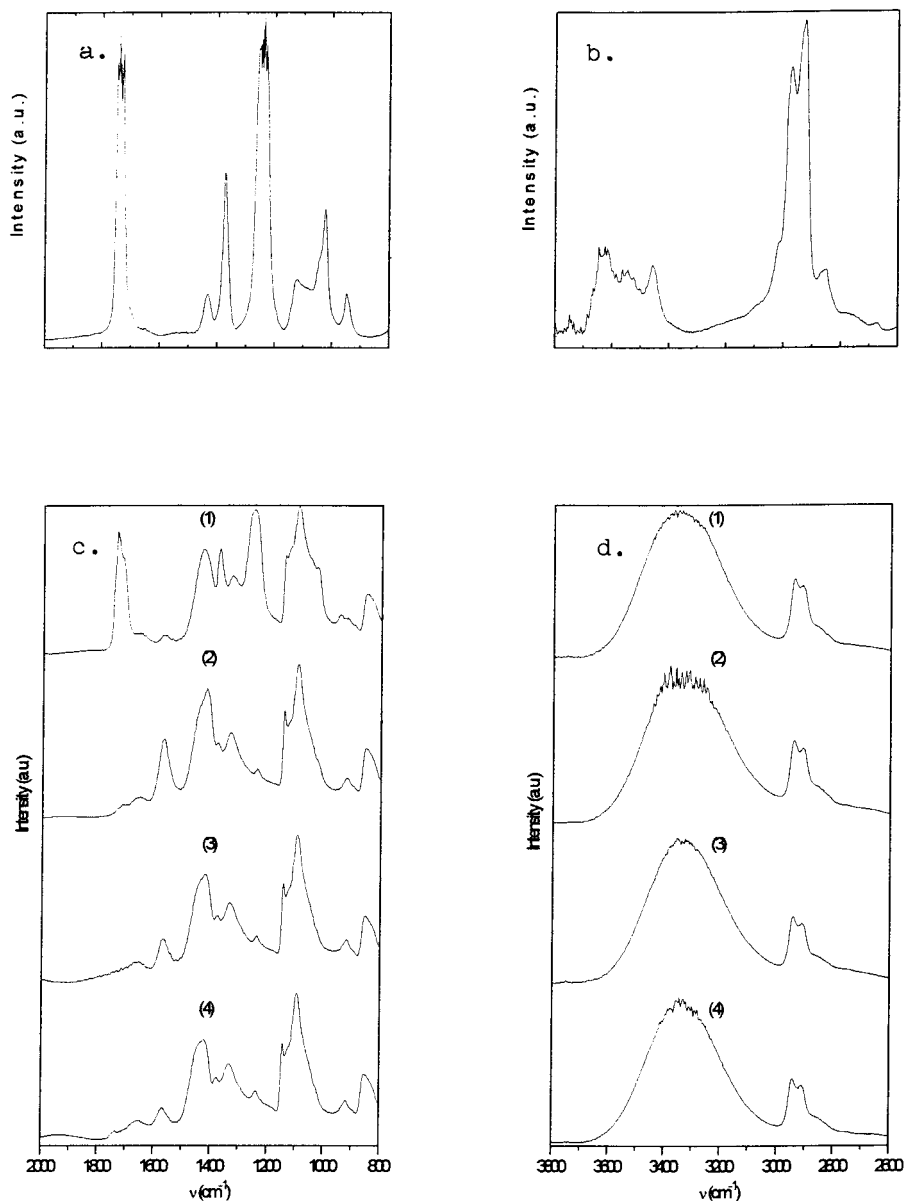
Figure 1 FTIR spectra in the range of 2000–800 cm^{-1} (left side) and 3800–2600 cm^{-1} (right side) of PVAc (a and b) and PVA (c and d) homopolymers. In parts c and d, (1) M_w = 124,000–186,000 (87–89%) (sample used for blend preparation); (2) M_w = 124,000–186,000 (98–99%); (3) M_w = 124,000–186,000 (99$^+$%); and (4) M_w = 115,000 (100%). Numbers between parentheses represent hydrolysis degree.

degrees {Fig. 1[c,d(1–4)]} are shown. These spectra are shared in two parts: from 2000 cm^{-1} to 800 cm^{-1} (left side, a and c) and from 3800 cm^{-1} to 2600 cm^{-1} (right side, b and d).

The assignments for the frequencies of different groups and vibrational modes were done following Tadokoro et al.[17–19] and Sokr and Schneider,[20] which define some structural properties of the materials.

Tacticity

The intensity ratio between the bands at 916 cm^{-1} and 849 cm^{-1} bands > 0.30 indicates syndiotacticity, whereas a value < 0.25 indicates isotacticity. For atactic polymers the density ratio values lie in the range 0.25–0.30.[21–23] According to our data we obtained that the PVA homopolymer (87–89%) was mainly an atactic-rich polymer {Fig.

Table I Crystallinity (χ %) and Tacticity Degrees of Certain PVA Homopolymers, Determined by FTIR Spectroscopy

M_w	Hydrolysis Degree (%)	Tacticity	χ (%)
124,000–186,000[a]	87–89	0.25	36
124,000–186,000	98–99	0.34	38
124,000–186,000	99†	0.41	42
115,000	100	0.34	42

[a] Homopolymer used in this work.

1[c(1)]}. It is noteworthy that the bands at 852 cm^{-1} and 918 cm^{-1} are absent in a PVAc-homopolymer [Fig. 1(a)] while that at 946 cm^{-1} is absent in a 100% hydrolyzed PVA-homopolymer {Fig. 1[c(4)]}.

Crystallinity

Although the nature of the band at 1138 cm^{-1} is still under speculation, it is recognized as a crystallization-sensitive band.[17–19,21,24] In Figure 1(c) we observe a sharp absorption band at 1142 cm^{-1} overlapped with a broad and complex band, suggesting that PVA is a semicrystalline polymer, in agreement with the X-ray diffraction pattern.[2,4] In Table I we show the crystallinity degrees estimated using the procedure described by Peppas and Merrill for every PVA sample.[24]

Hydrogen-Bonding Interactions

Since we used a partially hydrolyzed PVA, we could attribute the bands at 1740, 1256, 1028, and 946 cm^{-1} to the presence of acetate monomer units. They are also observed in PVAc-homopolymer [Fig. 1(a)]. The spectrum of PVA (87–89%) {Fig. 1[c(1)]} presents a strong absorption at 1740 cm^{-1} ("free" carbonyl groups) with a shoulder at lower wavenumber side due to hydrogen-bonded carbonyl groups.[5–8,23] These bands are absent in samples with higher hydrolysis degrees {Fig. 1[b(2–4)]}.

There are some other bands that should be shifted due to hydrogen bond interactions. For example, the C—O—C stretching region for acetate units is observed at 1240 cm^{-1} for pure PVAc [Fig. 1(a)],[20] and shifts to a higher wavenumber ($\cong$ 15 cm^{-1}) by hydrogen bonding with the neighboring carbonyl group.[23] A very intense and broad band centered at 3340 cm^{-1} was verified for all PVA

homopolymers, independent of the crystallinity degree. This band is attributed to a wide distribution of hydrogen-bonded hydroxyl groups (self association) {Fig. 1[d(1–4)]} and it is absent in PVAc-homopolymer [Fig. 1(b)].[22,23]

Another set of absorption bands in the region of 3000–2800 cm^{-1} is assigned to several types of C—H stretching mode.[21–23] Shibayama et al.[5] used the methylene stretching band (2908 cm^{-1} for PVA) as an internal reference band to estimate PVA crystallinity degree, defining the relative contribution of the crystalline phases of PVA to the pure or blend films as

$$I_{\mathrm{PVA}} = A_{1143}/A_{2908}$$

They also demonstrated that the crystallinity of both polymers decreased by blending.

We did not use this relation since the presence of PVAc in our blends introduces CH_3 groups, whose infrared active symmetric and antisymmetric normal modes are partially overlapped with those assigned to the CH and CH_2 stretching modes. Therefore, the profile of CH stretching bands in the 2950–2850 cm^{-1} changes significantly by the presence of methyl groups [Fig. 1(b,d)].

In conclusion, the PVA used in this work is characterized as an atactic semicrystalline polymer (χ = 36%), partially hydrolyzed, with T_g = 350 K and exhibiting free and hydrogen-bonded carbonyl groups, while PVAc is an amorphous polymer, with T_g = 305 K.

We reported earlier[15,16] that PVA/PVAc polymer blends exhibit a solid-phase separation producing, on the optical microscopic scale, two types of domains whose proportions, dimensions, and morphology are dependent on the initial composition. Furthermore, we observed by FOM of PVA/PVAc blends containing fluorescein and anthracene that the color emission of each domain is different (green or blue), showing that these fluorophores are located in different sites, controlled by specific dye–polymer interactions. Considering these specific interactions we concluded that the PVA-richer part of the sample is thinner and smooth (green fluorescence emission), and the PVAc-richer part is thicker with a corrugated surface (blue fluorescence emission).[15] We show the photomicrographs of these domains in Figure 2 (right side).

Although the phase diagram for this system has not been determined, we can assume that the morphology of the material is dependent on the phase separation mechanism during the solvent
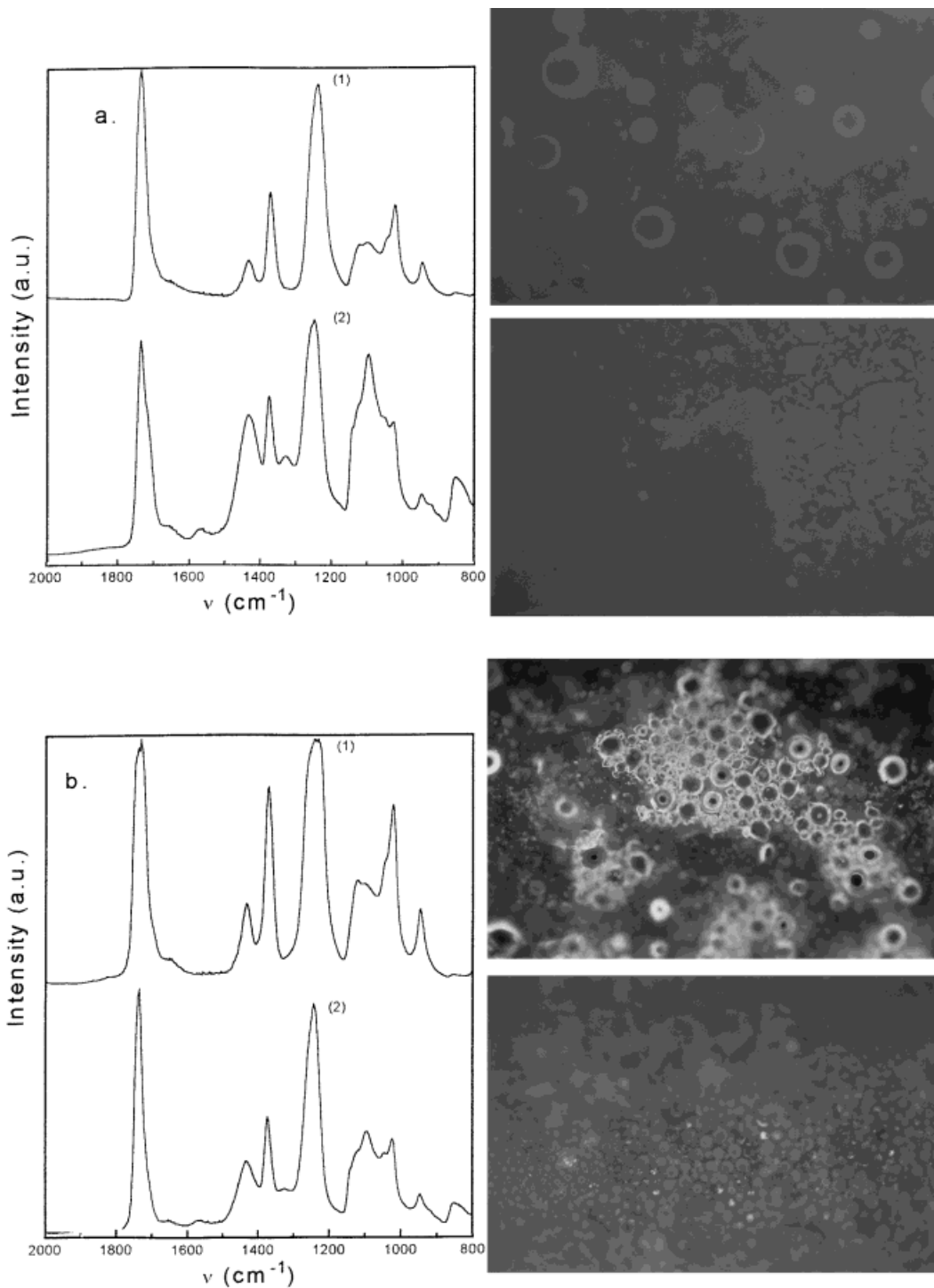
Figure 2 FTIR spectra in the range of 2000–800 cm^{-1} and fluorescence optical micrographs of PVA/PVAc blends in different proportions (w/w). (a) 9/1; (b) 1/1; (c) 1/9. In each part, spectrum and micrograph corresponds to: (1) top PVAc-richer region and bottom (2) PVA-richer region.

evaporation. The initial solution contained four components: PVA (water soluble), PVAc (ethanol soluble), water, and ethanol. A single phase is exists only while ethanol is present. Since ethanol

vapor pressure is higher than water, as this solvent evaporates, the system passes into a two-phase region forming a new system containing a PVA-richer solution and a PVAc-richer and swol-
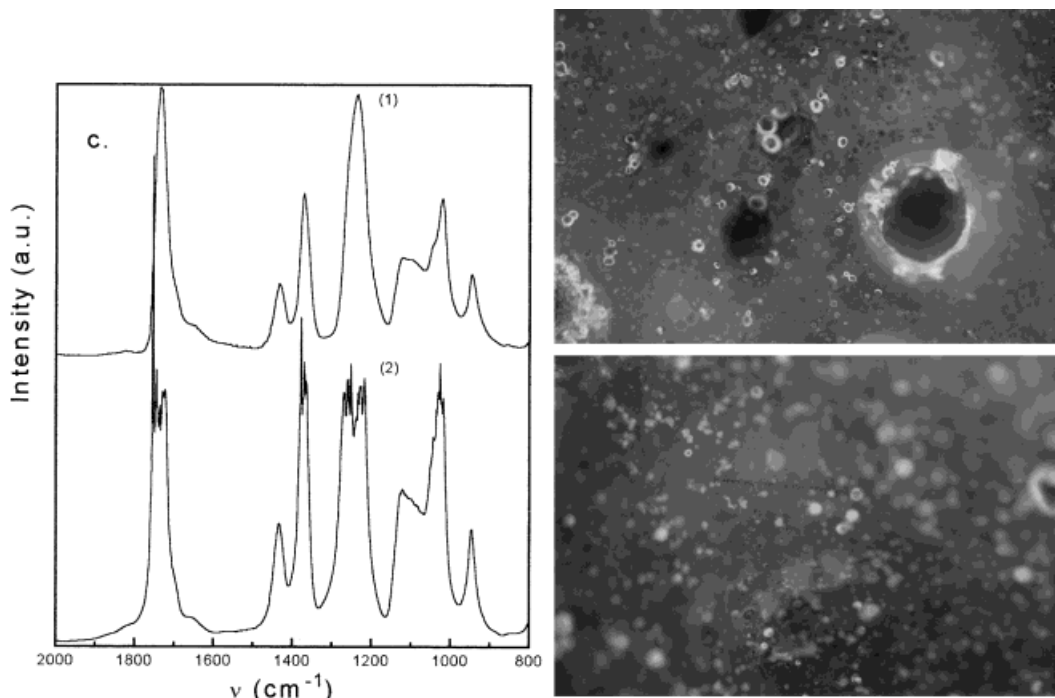
Figure 2   (*Continued from the previous page*)

len phase. Depending on the solvent concentration and on the solution viscosity, spherical droplets of PVAc-richer phase appear in the PVA-richer solution {photomicrographs in Fig. 2[a](2)} and in sequence they grow by coalescence {photomicrographs in Fig. 2[b,c]}. Since PVA is highly soluble in water, and since the solvent evaporation rate in this phase is very low, it gives a continuous solid phase.

Therefore, we expect that the whole material will always be formed by some spherical shape domains mainly composed by PVAc containing anthracene (blue emission) {photomicrographs in Fig. 2[a–c](1)} and a richer-PVA substrate containing fluorescein (green emission) {photomicrographs in Fig. 2[a–c](2)}.

Related with these photomicrographs we performed FTIR spectromicroscopy for those blends with different initial proportion of both homopolymers. The FTIR spectra for both the PVAc-richer (thicker) (1) and PVA-richer (thinner) (2) are shown in Figure 2. We also compared these spectra with those for PVAc and PVA homopolymers as shown in Figure 1(a) and (b), respectively. As expected, the infrared spectra of the thinner parts of the samples [PVA-richer regions (2)] are similar to that of PVA-homopolymer, and spectra of thicker parts [PVAc-richer regions (1)] are similar to PVAc-homopolymer, in agreement with the conclusions obtained by FOM.

In order to get more information about each part of the samples, we obtained the difference FTIR spectra using a conventional software program. A difference spectrum is obtained by subtracting the sample from a reference spectrum using an adjustable scaling factor, defined by

$$A_{iS} - kA_{iR} = 0 = a_{iS}C_Sb_S - ka_{iR}C_Rb_R \quad (1)$$

where $A_{iR} = a_{iR}C_Rb_R$ and $A_{iS} = a_{iS}C_Sb_S$ are the absorbances of the internal thickness bands for the reference (R) (homopolymer) $(\nu_{OH} = 3340$ cm^{-1} for PVA and $\nu_{C=O} = 1740$ cm^{-1} for PVAc) and samples (S); a_i are the absorptivity coefficients, at wavenumber i, for references $[a_{OH}$ (PVA) or $a_{C=O}$(PVAc)] and samples; C is the concentration, which is equal to 1 for homopolymers and for samples is dependent on the composition and thickness; and b is the thickness of the homopolymer (R) and blend samples (S), which is different for each part of the PVA/PVAc blends.[19] The spectrum must be within the linear optical range scale and the vibrational bands should remain independent of the polymer–polymer interactions. Then, the scaling factor $k = C_S(b_S/b_R)$ will be dependent only on thickness and composition of each sample.

Difference infrared spectra for PVA/PVAc blends in concentrations of 9/1, 1/1, and 1/9 are shown in Figures 4 and 5 for ranges 2000–800
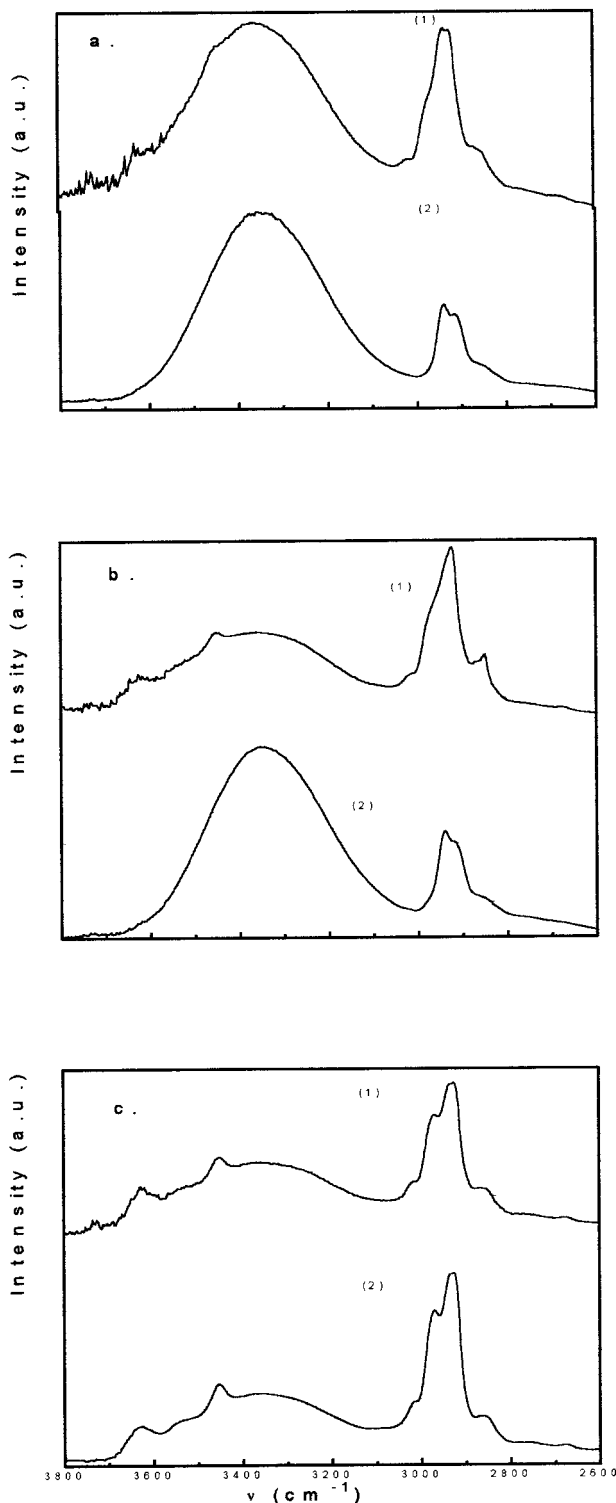
Figure 3 FTIR spectra, in the range of 3800–2600 cm^{-1} of PVA/PVAc blends in different proportions (w/w) using the same notation as Figure 2.

cm^{-1} and 3800–2600 cm^{-1}, respectively. In these figures, we designated (1) as the PVAc-richer and (2) as the PVA-richer parts of the blends. On the left side of these figures the spectra scaled using PVA homopolymer as a reference (sample minus PVA) is shown, and on the right side we used PVAc homopolymer (sample minus PVAc). Using the appropriate scaling factor the resultant difference spectrum should be the purified spectrum of one homopolymer (PVA or PVAc), only if no wavenumber shift would be produced by the polymer–polymer interactions. However, we noted remarkable differences in the spectra of the PVA-richer parts (2) which is more evident for higher compositions of PVAc [Figs. 4 and 5(d) and (f)]. When the initial PVA concentration was very low (1/9 PVA/PVAc blend), the morphology of some parts was very complex and we were not able to separate the PVA-richer and PVAc-richer domains. This suggests a partial miscibility in the solid phase as shown in photomicrographs 2[c] (1) and (2) and in the difference FTIR spectra {Fig. 4[f](1) and (2)}.

In addition we were only able to calculate the crystallinity degrees for the PVA-richer parts of the samples {Fig. 4[b](1) and [d](1)} because there is no spectral evidence for the presence of crystalline bands for different parts of the 1/9 PVA/PVAc blend {Fig. 4[f](1)}. These values were 27% for both 9/1 and 1/1 PVA/PVAc blends, which is lower than the pure PVA homopolymer (36%). As we explained earlier the crystallization of PVA should be produced by slow solvent evaporation from a PVA-richer solution allowing nucleation and growth of crystallites from the solution.

Infrared spectra of PVA-richer phase of a 9/1 PVA/PVAc blend {Fig. 2[a](2)} exhibits a shoulder on the lower wavenumber side a band at 1740 cm^{-1}. This is similar to partially hydrolyzed PVA-homopolymer [Fig. 1(c)]. Since this shoulder is only noted for PVA-richer domains of the 9/1 blend {Fig. 1[c](1)}, we concluded that this hydrogen-bonded carbonyl was characteristic of intramolecular interactions in partially hydrolyzed PVA chains and not due to PVA/PVAc interchain interactions in the blends. This result together with the presence of PVA crystallites suggests that PVA-richer domains in the 9/1 PVA/PVAc blend are formed by a complete phase separation process of these polymers.

Analyzing the infrared spectrum of PVA-richer parts of the 1/9 PVA/PVAc blend [Fig. 2(c)] we observe some bands split into two components, assigned to acetate groups (1740 cm^{-1}, 1256 cm^{-1}, and 1090 cm^{-1}). These splitting are most clearly noted in the difference spectra in Figures 4[e](2) (PVA-richer part minus PVA-homopolymer) and 4[f](2) (PVAc-richer part minus PVAc-
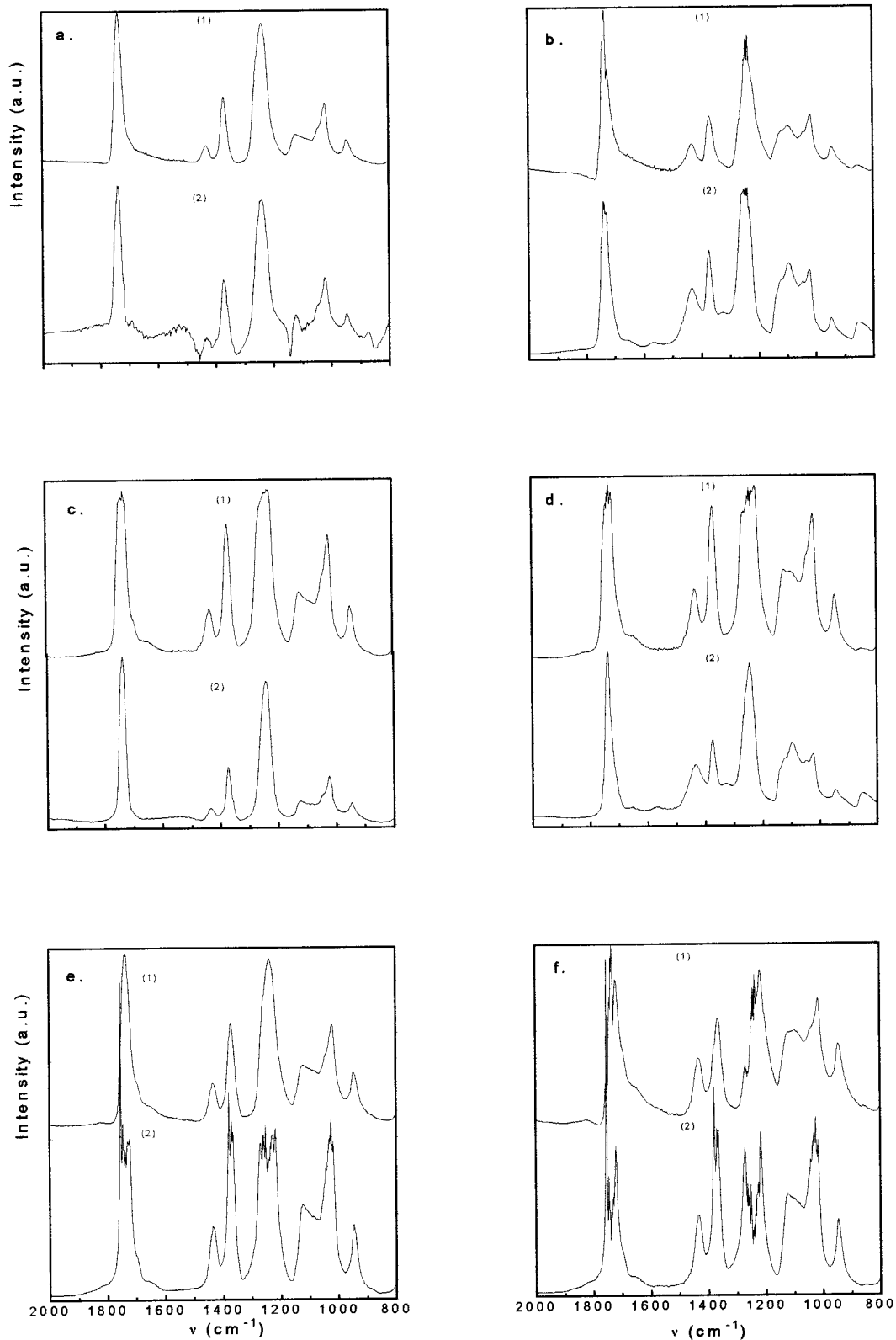
Figure 4   Difference spectra of PVA/PVAc blends in the range of 2000–800 cm^{-1} with different proportions. (a) and (b) 9/1; (c) and (d) 1/1; (e) and (f) 1/9. The top (1) spectrum corresponds to the richer-PVAc parts and the bottom (2) spectrum to the richer-PVA one. The left side corresponds to differences from PVA; right side from PVAc.
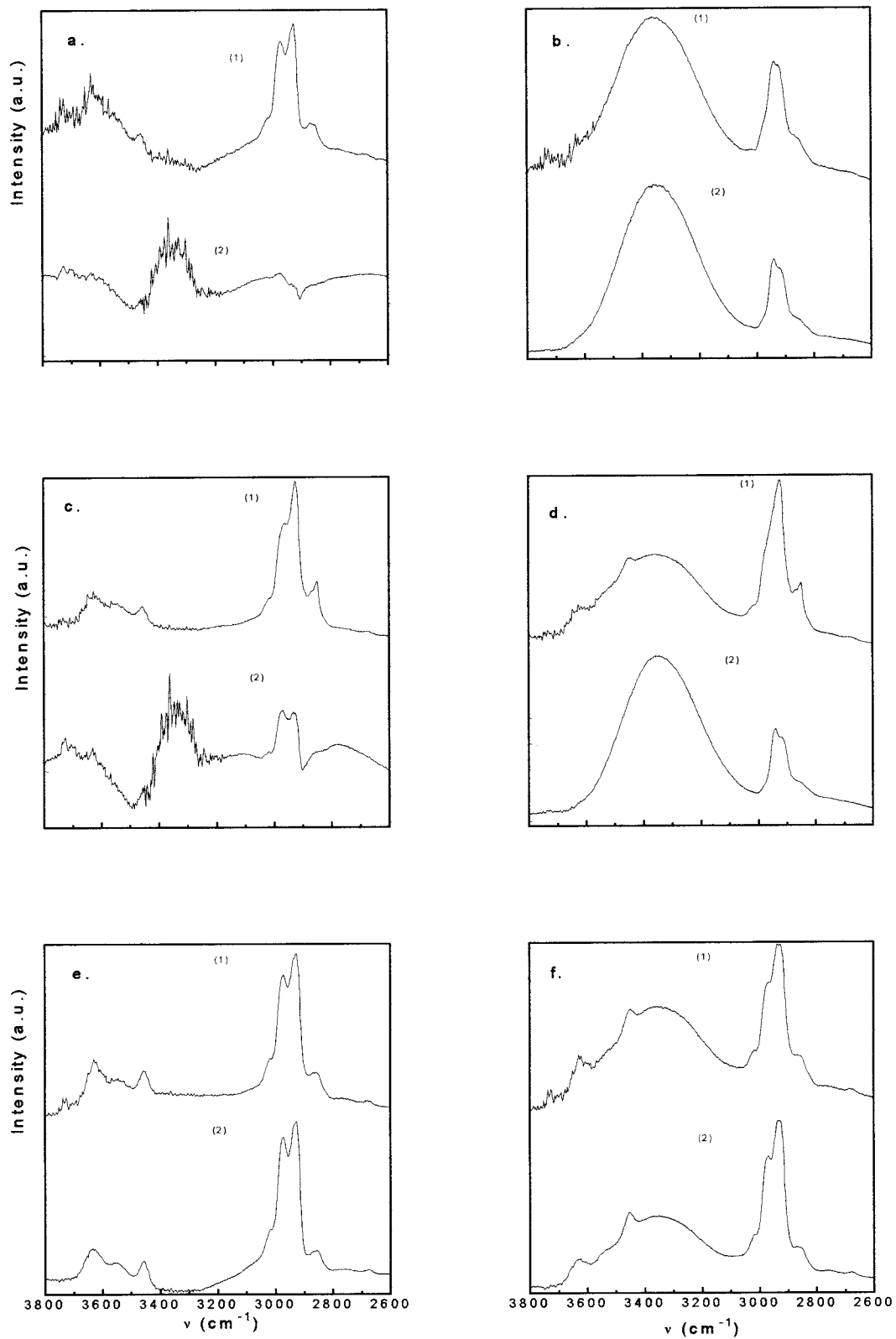
Figure 5 Difference spectra of PVA/PVAc blends in the range of 3800–2600 cm^{-1} with different proportions using the same notation as in Figure 4.

homopolymer) and is revealing a significant interactions between hydroxyl and carbonyl groups. Considering together, this polymer–polymer interaction, the absence of crystallinity, and the FOM images of these samples we can conclude that 1/9 PVA/PVAc blends {Fig. 2[c](1) and (2)} presents some miscibility degree.

As described earlier the components at 1738 cm^{-1} and 1714 cm^{-1} can be assigned to the free and hydrogen-bonded carbonyl groups produced by interchain interactions.[5–8,23] In order to explain the nature of the shift obtained for the band at 1738 cm^{-1} for every part of the 1/9 PVA/PVAc blend we considered the following information: (1) Isasi, Cesteros, and Katime[23] reported that the band at 1738 cm^{-1} changes broadly toward lower wavenumbers in PVA commoners with higher content of vinyl alcohol units. (2) The band at a lower wavenumber is assigned to the hydrogen-bonded carbonyl groups. (3) We observed this shift for both PVA homopolymer (87–89%) and for blends with higher content of PVA homopolymer. In this case we are assuming that this shift is due to interaction between intrachain groups. (4) 1/9 PVA/PVAc blends exhibit interconnections between its domains. (5) Since it contains lower PVA-homopolymer content, the most plausible explanation for the presence of these bands is the chain interactions between the PVA and PVAc macromolecules.

Although we do not observe splitting of the band at 1240 cm^{-1} for the PVA homopolymer {Fig. 1[c](1)}, suggesting that this is a block copolymer,[23] there is a significant split of this band for PVA-richer part of 1/9 PVA/PVAc blend {Fig. 2[c](2)}. It is noteworthy that while there was not any shift of wavenumber (1240 cm^{-1}) for all PVAc-richer parts of the samples, independent of the initial composition of the blends {Fig. 2[a–c](1)}, there is a continuous shift toward higher wavenumbers for PVA-richer parts with the increase of PVAc-homopolymer concentration {Fig. 2[a–c](2)}. In order to explain these results we considered (1) PVA homopolymer is a block copolymer and as pointed out earlier hydrogen-bonded carbonyl groups are absent. (2) These interactions are also absent in all polymer blends with a higher degree of phase separation, as PVAc-richer domains {photomicrographs 2[a–b](1)}. Photomicrographs of samples with higher PVAc content present significant numbers of interconnected domains {Figs. 2[c] (1) and (2)} and, consequently, there is a concurrent increase of the probability of interchain interactions by hydrogen bonding. Therefore, we obtain spectral

shifts toward higher wavenumber values, in agreement with results reported in ref. 23. In addition, photomicrographs indicate that PVA-richer parts are more homogeneous and the 1/9 PVA/PVAc blend is more miscible.

Although it has been reported that the C—O stretching mode of vinyl alcohol units (≈ 1090 cm^{-1}) is also affected by hydrogen bonding,[23] we do not analyze this region because the spectra for all blends are complicated by overlapping between bands assigned to both homopolymers.

We mentioned previously that PVA homopolymers exhibit a very strong broad band centered at 3336 cm^{-1}, assigned to hydrogen-bonded hydroxyl groups (self-association) [Fig. 1(d)].[7] Figure 3 shows the FTIR spectra of different parts of the PVA/PVAc blends and we identified the PVA-richer and PVA-richer parts of the material by numbers (1) and (2), respectively. This figure also shows that there is a reduction of the intensity of the band centered at ~ 3340 cm^{-1} with the increment in the PVAc concentration [from 3(a) to 3(c)]. Concurrently, the maximum wavenumber of the hydrogen-bonded hydroxyl band slightly increases from ~ 3340 cm^{-1} to 3360 cm^{-1}. The wavenumber shift (≈ 20 cm^{-1}) is less than that observed for free hydroxyl groups compared with self-associated hydroxyl groups. Moreover, the relative intensity of the sharp band at 3450 cm^{-1} superimposed upon the broad hydrogen-bonded hydroxyl bands, assigned to overtones present in the PVAc-homopolymer spectrum [Fig. 1(a)], increases as the concentration of PVAc is increased and is also higher for all PVAc-richer parts of the blends, as expected. Therefore, we could conclude that we are not observing free hydroxyl groups, either because they are self-associated or because they are associated with carbonyl groups.

Figure 5 shows the difference spectra for PVA/PVAc blends, using PVA or PVAc homopolymers as references. It is noteworthy that FTIR spectra of different parts of 1/9 PVA/PVAc blends are quite similar [Figs. 3(c) and 5(e) and (f)] in both wavenumber and profiles of the bands. This result supports the evidence from fluorescence microscopy [Fig. 2(c)] that we could not isolate PVA-richer and PVAc-richer domains in this case.

CONCLUSIONS

We have mapped different parts of PVA/PVAc polymer blends prepared with initial compositions of 9/1, 1/1, and 1/9 combining FTIR micros-

pectroscopy and fluorescence microscopy. Domains in blends could be identified by fluorescence optical microscopy since we used two fluorophores that display specific interactions with PVA and PVAc. Photomicrographs show a phase separation during solvent evaporation during casting of these blends leading to domains whose dimensions, shapes, and distribution are dependent on the blend composition. Fluorescence microscopy allowed us to identify the PVA-richer domains by the green fluorescence of fluorescein and PVAc-richer domains by the blue fluorescence of anthracene. While for the 9/1 PVA/PVAc initial composition there is a very clear phase separation, with very well formed and isolated domains of each homopolymer, the same is not observed for the 1/9 blend, suggesting some degree of miscibility between these polymers at this initial composition.

FTIR microspectroscopy gives evidence that specific interactions between PVA and PVAc is occurring for blends containing higher PVAc-homopolymer content. In this case we obtained wavenumber changes of bands assigned to hydrogen-bonded carbonyl groups. For polymer blends with higher PVA-homopolymer content (9/1), changes of these wavenumbers are mainly produced by intrachain interactions, suggesting that there is an almost complete immiscibility between PVA and PVAc, which is in agreement with fluorescence optical microscopy results. However, partial miscibility is obtained for higher PVAc-homopolymer content, as demonstrated by the splitting of the bands assigned to hydrogen-bonded carbonyl groups.

We have reported earlier one study for miscibility of PVA/PVAc blends using fluorescence spectroscopy of fluorescein and anthracene dissolved on this matrix.[16] In this article we have demonstrated that the profiles of the curves for fluorescence intensity versus temperature for blends containing both fluorophores are different from those obtained for homopolymers. Moreover, the efficiency of fluorescence deactivation becomes higher with the increase of PVAc concentration in the blends, which also indicates a partial miscibility of both polymers in this case.

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