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Poly(4-vinylpyridine)/poly(vinyl acetate-*co*-vinyl alcohol) blends: effect of sequence distribution on miscibility

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The miscibility of blends of poly(4-vinylpyridine) (P4VP) with blocky copolymers of vinyl alcohol/vinyl acetate (ACA) of different compositions has been investigated and compared to that of the blends with random ACA copolymers. The miscibility window found in both cases is narrower for the blocky ACA blends, indicating the influence of the comonomer sequence distribution. Fourier transform infra-red spectroscopy shows a lower level of pyridine–hydroxy hydrogen-bonding interactions in the case of blends with blocky ACA copolymers. Cloud point curves have been obtained from optical microscopy measurements for several P4VP/ACA blends. Finally, the binary interaction model including the influence of the copolymer sequence distribution has been applied using Balazs and Cantow–Schulz approximations.

(Keywords: P4VP/ACA blends; sequence distribution; miscibility)

INTRODUCTION

Polymer blends including copolymers have been extensively studied since the 1980s in order to understand their phase behaviour. The binary interaction model[1-3] has been successfully applied to copolymer blends. For instance, the miscibility window phenomenon can be explained by this mean-field theory for the case of A/BC-type blends in which A, B and C are immiscible in their binary homopolymer combinations but a 'repulsion' in the BC copolymer may lead to miscible blends with homopolymer A. Nevertheless, the influence of the sequence distribution of the comonomer units in the copolymer on miscibility cannot be neglected, as has been discussed[4]. It is obvious that if BC 'repulsive' interactions in the copolymer can be considered as responsible for miscibility, the number and distribution of such 'repulsions' will significantly influence the phase behaviour. Balazs *et al.*[4] explain these ideas in terms of the polarizability of a group: since the χ_{ij} parameter is related to the product of the electronic polarizabilities for units i and j, the interaction energy for the AB pair is then influenced by the units that are chemically bonded to B.

Nevertheless, the effect of the copolymer microstructure does not have to be explained always in terms of neighbouring repulsions. In the case of poly(vinyl acetate-*co*-vinyl alcohol) (ACA) copolymers, in which the specific interactions between acetate carbonyls and vinyl alcohol hydroxys compete with hydroxy self-associations, the sequence distribution effect has been proved to be mainly responsible for the distribution of hydrogen bonds in the copolymer[5]. When these copolymers are blended with a proton acceptor such as poly(4-vinylpyridine) (P4VP), a competition between these A units with carbonyls of C units (vinyl acetate) for the hydroxy groups is detected[6]. The possibility of hydrogen bond formation between hydroxys (B units) and neighbouring carbonyls in the copolymer implies a short scale competition of specific interactions. The phase behaviour of P4VP/ACA blends has been extensively studied for the case of quasi-random ACA copolymers and the binary interaction model has been applied successfully[7]. These copolymers are very interesting for sequence distribution studies since, as has been reported[5], they can be obtained with a wide range of microstructures, and small differences in sequence distribution for similar total comonomer compositions can be obtained.

EXPERIMENTAL

Materials

The ACA copolymers studied in this work were prepared by different routes as described elsewhere[5] (acid alcoholysis for rACA samples; saponification for bACA samples; and a combined method for cACA samples) from the same parent poly(vinyl acetate) (PVAc) sample ($M_w = 255\,000\,\mathrm{g\,mol^{-1}}$). Therefore, all the copolymers were atactic and had the same degree of polymerization, allowing the effects on microstructure due only to sequence distribution differences to be studied.

Table 1 shows the sequence distributions of several ACA copolymers employed in this work obtained by ^{13}C n.m.r. as described in a previous paper[5]. The samples are named according to their sequence distribution character; the number at the end denotes the molar percentage of vinyl alcohol units determined by chemical titration.

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Table 1 Molar fractions of dyads, vinyl alcohol molar fractions (OH) and values of η for several ACA copolymers obtained by different methods (rACA*x*, acid alcoholysis; bACA*x*, saponification; cACA*x*, combined method)

Sample	(OH,OH)	(OH,OAc)	(OAc,OAc)	(OH)	η
rACA24	0.0789	0.3079	0.6132	0.233	0.861
rACA35	0.1456	0.3916	0.4628	0.341	0.871
rACA39	0.1871	0.4139	0.3990	0.394	0.867
rACA55	0.3240	0.4172	0.2587	0.533	0.838
rACA88	0.8771	0.1063	0.0166	0.930	0.816
bACA18	0.1433	0.1713	0.6854	0.229	0.485
bACA35	0.2878	0.1985	0.5136	0.387	0.418
bACA47	0.3837	0.1851	0.4312	0.476	0.371
bACA82	0.8214	0.1012	0.0774	0.872	0.445
cACA51	0.3508	0.3167	0.3325	0.509	0.634
cACA32	0.1924	0.2618	0.5457	0.323	0.599
cACA48	0.2829	0.3976	0.3195	0.482	0.796

Poly(4-vinylpyridine) (P4VP) was a commercial sample, kindly supplied by Reilly Chemicals (sample 450). Its weight average molar mass determined by light scattering was 49 000 g mol^{-1}. The sample was purified by precipitation from methanol into ether.

Calorimetric measurements

Thermal analysis was performed on a Mettler TA 4000 system equipped with a DSC30 measuring cell. A heating rate of 20 K min^{-1} was used if not specified otherwise. Sample sizes ranged from 10 to 15 mg. All the thermograms correspond to a second scan after melting of the crystalline phase at 500 K.

Optical microscopy

Cloud point curves for P4VP/ACA blends were obtained by means of thermo-optical analysis. The films were cast onto glass microscope slides from 2% (w/v) methanol solutions and were placed in a Mettler FP82 hot stage device. The system was placed under a Jenapol microscope (Carl Zeiss, Jena, Ltd) equipped with a photoelectric cell. All the scans started from 403 K after 3 min of annealing at this temperature in order to eliminate moisture and solvent residues. The cloud point was detected as the onset of the jump in transmitted light intensity.

Infra-red measurements

The infra-red spectra for the blends were recorded on a Nicolet-520 Fourier transform infra-red (*FT*i.r.) spectrometer with a resolution of 2 cm^{-1} and using the average of 100 scans. Films for *FT*i.r. measurements were cast from methanol solutions (0.02 g ml^{-1}) directly onto KBr pellets, or onto Teflon for samples dissolved in water/methanol mixtures. All films were vacuum dried and they were thin enough to be within the absorbance range where the Beer–Lambert law is obeyed.

RESULTS AND DISCUSSION

Miscibility of blocky P4VP/ACA blends

In our previous work, a miscibility window was found for the P4VP/ACA system between 21 and 97 mol% of vinyl alcohol units in the ACA copolymer[7,8]. The calorimetric results reported in *Table 2* illustrate the phase behaviour of the different blends of P4VP with an ACA copolymer having 82% of vinyl alcohol units. Although its composition is well below the upper miscibility limit proposed, this blend shows only partial miscibility. In contrast, P4VP/rACA88 blends were presented as examples of a totally miscible system in our previous work. This discrepancy arises from the fact that the phase behaviour of the bACA82 copolymer cannot be regarded only in terms of its chemical composition: the comonomer sequence distribution in this ACA sample is quite different from that corresponding to the previously studied ACA. Thus, the comonomer sequence distribution seems to play a decisive role in the phase behaviour of P4VP/ACA blends. Taking into account that this paper is dealing with the influence of the sequence distribution in the ACA copolymer on its miscibility with P4VP, a remark about the character of our samples is needed. The ACA copolymers employed in our previous work were obtained by acid alcoholysis of poly(vinyl acetate), and they can be considered as quasi-random in character (see *Table 1*). In contrast, blocky ACA samples are produced if basic saponification is used as the modification method.

Although n.m.r. is the best experimental tool to give a quantitative description of the sequence distributions of the polymers (see *Table 1*), thermal analysis gives a qualitative idea since just by comparing the thermal behaviour of the pure copolymers their differences are

Table 2 Glass transition temperatures, melting points and heats of fusion for different blends between P4VP and bACA copolymers as a function of the blend composition. Reported temperatures correspond to the second scan, except for bACA35 and bACA47 blends (first scan)

Polymer	P4VP content (wt%)	T_g (K)	T_m (K)	ΔH_m (J g^{-1})
bACA18	0	324	468	3.0
	20	321,422	468	1.5
	40	322,421	468	0.6
	60	321,424		
	80	315,420		
	100	424		
bACA35	0	325	469	5.5
	20	332	468	1.0
	40	351	470	0.9
	50	353		
	60	361		
	80	417		
bACA47	0	325	471	4.2
	20	325	477	4.3
	40	350	475	1.6
	50	358		
	60	363		
	80	414		
bACA70	0	329	491	18.4
	40	343	485	5.3
	60	354	484	3.5
	80	412	476	0.4
bACA82	0	331	493	40
	20	347	494	20
	40	365	488	9.0
	60	338,417	488	6.1
	80	355,419	483	1.5
bACA94	0	353	501	45
	20	358,423	501	40
	40	356,423	498	32
	60	356,421	498	22
	80	355,426	498	9.3

evident. The crystallinity of the sample increases as the blocky character of the copolymer increases. This is an indication of a higher level of self-association of the hydroxy units in the 'blocky' copolymers. Besides, the shape of the jump corresponding to the glass transition in the calorimetric curve (*Figure 1*) seems to reflect the same microphase separations in the case of the blocky copolymers, a typical effect in semicrystalline polymers.

The thermograms of *Figure 2* allow comparison of the behaviour of blocky and random ACA copolymer (samples bACA and rACA, respectively) blends with P4VP as a function of copolymer composition. Only the blends with intermediate bACA copolymers (bACA35 and bACA47) show miscibility, although the glass transitions are wide and imprecise. Nevertheless, a second glass transition attributable to a P4VP-rich phase (close to 423 K) is not detected. These blends can be considered miscible since, as in the case of the random ACA blends, two distinct glass transitions corresponding to the pure polymers are clearly detected after thermal annealing of these samples, as can be seen in *Figure 3*. Moreover, in our previous study, exothermic peaks of demixing were detected for miscible blends close to phase separation during a high heating rate scan[7]. The same behaviour (see *Figure 3*) has been found for blends of P4VP with bACA35 and bACA47 with a value of 6.8 J g^{-1} for the heat of demixing associated with *LCST* behaviour, comparable to the value previously obtained. The glass

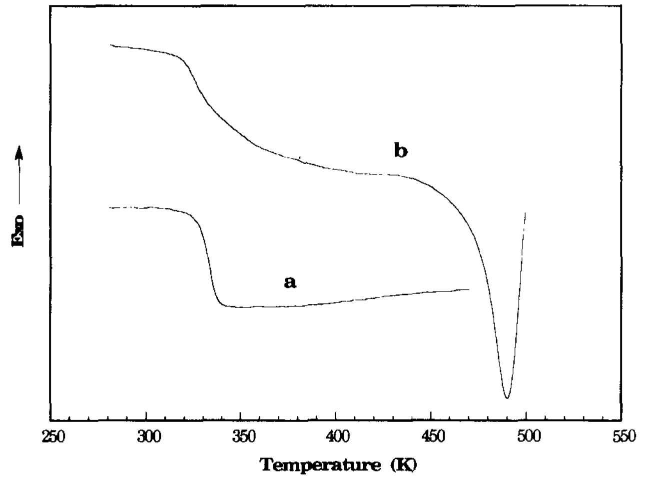

Figure 1 Differential scanning calorimetry (d.s.c) curves for rACA55 (a) and bACA70 (b) copolymers

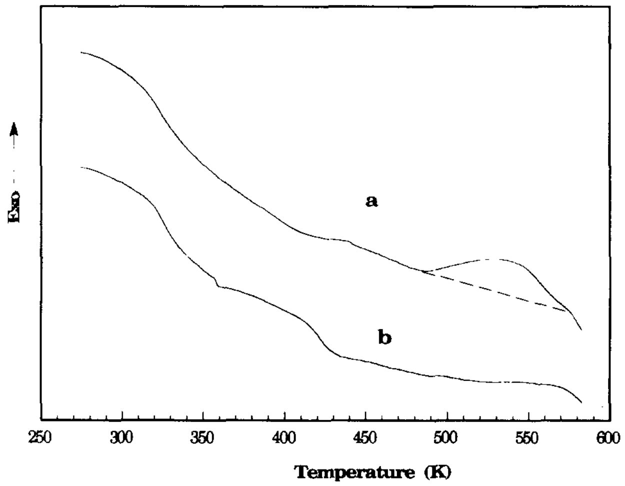

Figure 3 D.s.c. curves for a 50/50 P4VP/bACA35 blend: (a) first scan; (b) second scan

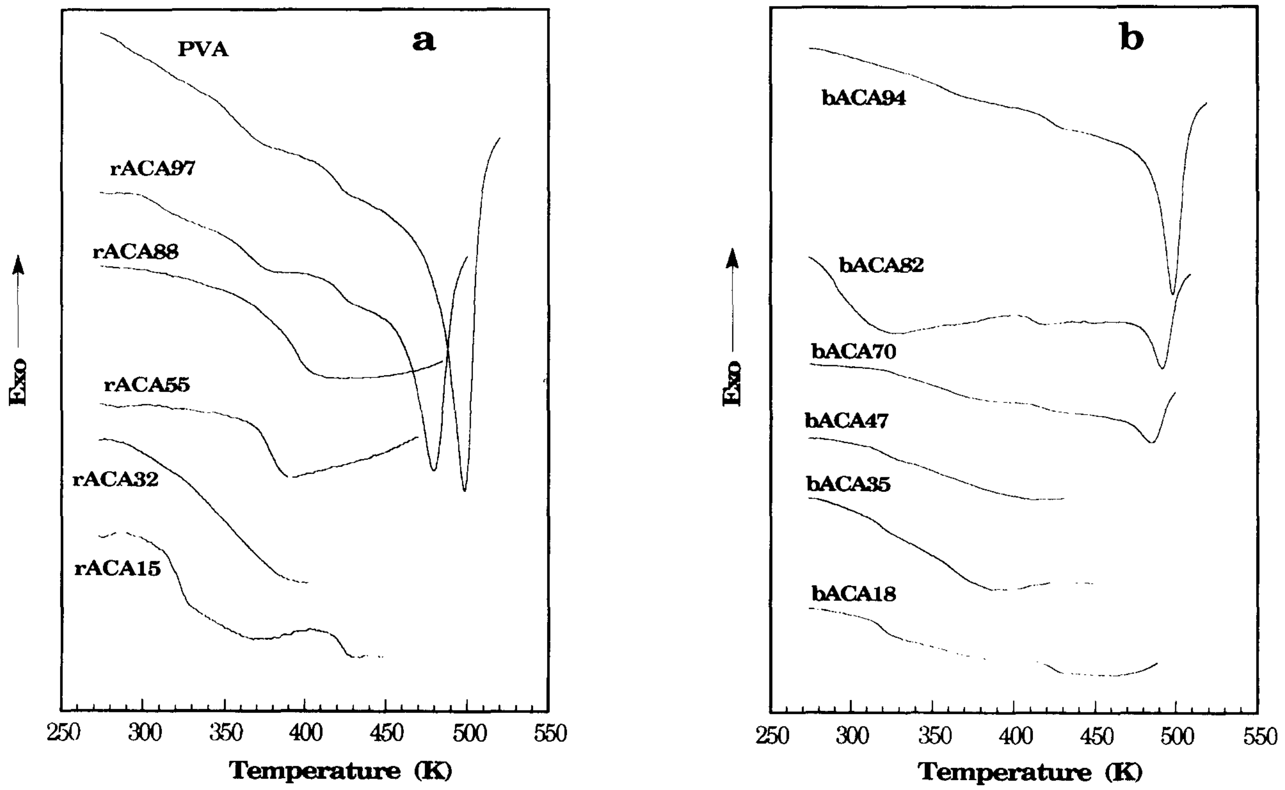

Figure 2 D.s.c. curves for blends of P4VP (60 wt%) with rACA (a) and bACA (b) copolymers. All the thermograms correspond to the second scan, except for the blends with bACA35 and bACA47

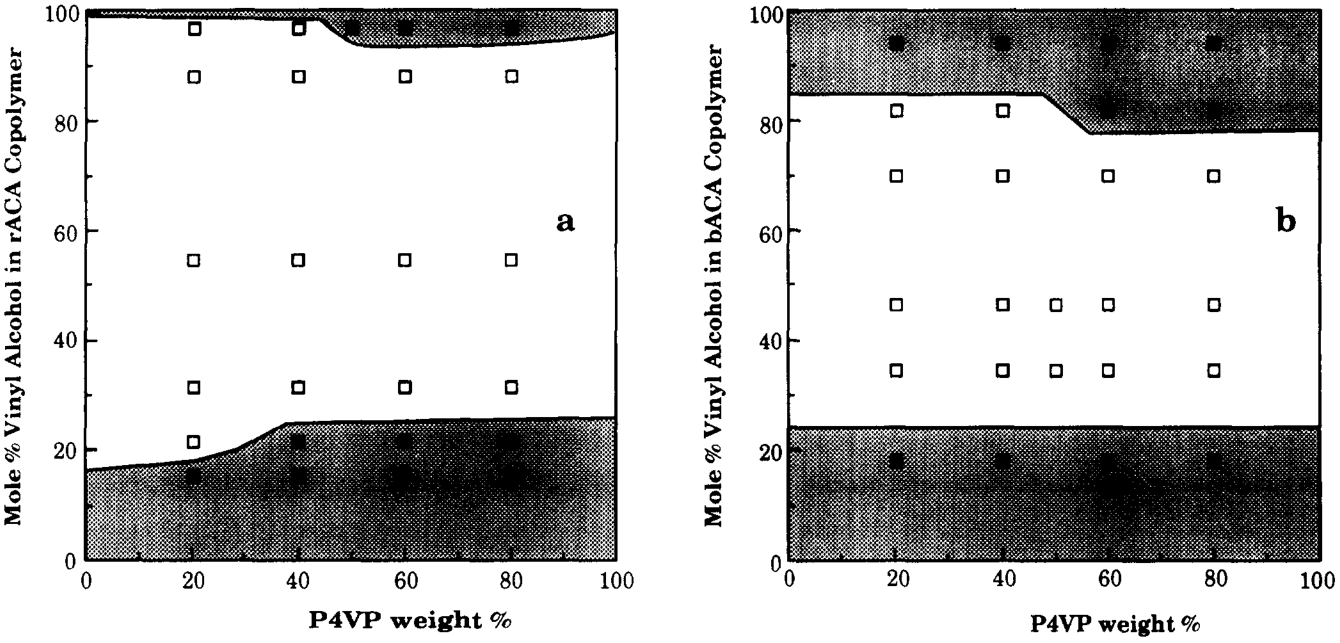

Figure 4 Phase diagrams of P4VP/ACA blends for rACA copolymers (a) and bACA copolymers (b) at room temperature: (■) immiscible; (□) miscible

transition temperatures and other calorimetric data for the P4VP/bACA blends are displayed in *Table 2*. As far as melting point depression is concerned, a remarkable effect seems to occur in the case of miscible blends such as P4VP/bACA70. Nevertheless, an adequate analysis of such an effect requires a study of the equilibrium melting temperature as a function of the blend composition[9]. Unfortunately, poly(vinyl alcohol) (PVA) and ACA copolymers exhibit thermal degradation processes at temperatures close to their melting points (~500 K), complicating the data analysis.

Results from the calorimetric study are shown in *Figure 4*. This figure shows the phase diagrams of P4VP/ACA blends for blocky and quasi-random copolymers. As can be seen, the miscibility window is considerably reduced in the case of the blocky copolymers, especially at the upper limit. This is clear evidence of the influence of the sequence distribution in these blends and the relevance to miscibility of self-association processes in ACA copolymers.

Infra-red study of specific interactions

Hydrogen bonding between hydroxy, carbonyl and pyridine groups and its effects on the most significant modes of the infra-red spectra of P4VP/ACA blends have been extensively studied previously[6]. The pyridine ring mode at 993 cm^{-1} has been proven to be the most sensitive mode in the qualitative study and detection of hydroxy–pyridine hydrogen bonding. When the blend exhibits hydrogen bonding, this spectral mode splits into two components: one corresponding to the non-bonded pyridine rings (~993 cm^{-1}) and the other at a higher wavenumber (~1003 cm^{-1}). *Figure 5* shows this spectral region for different rACA and bACA blends with the same P4VP contents. It is interesting to compare the spectral behaviour shown in *Figure 5* with the phase behaviour in *Figure 4*. First, the blends in the immiscible regions do not show appreciable contributions from associated pyridine rings, except those close to the upper miscibility boundaries (probably owing to interfacial effects). On the other hand, miscible blends exhibit clear contributions from associated pyridine groups. It must be pointed out that rACA blends present a higher level of molecular interactions than bACA blends for similar copolymer compositions.

Cloud point curves

In order to obtain the cloud point curve for each blend, the onset of the decay in transmitted light as a function of temperature at different heating rates (from 12 to 0.2 K min^{-1}) was extrapolated to zero heating rate, since a significant dependence on this parameter has been found for these systems. As in the case of quasi-random P4VP/ACA blends[7], coalescence of the domains after phase separation has been detected in several cases. This phenomenon becomes evident as an increment in the transmitted light intensity through the sample film. In the case of quasi-random ACA blends, we showed that this process depends on the ACA copolymer composition: blends with ACA copolymers whose degrees of hydrolysis are below 40% (molar percentage of vinyl alcohol units) show this process, while for those of rACA53 the clearing is not detected. For the blockier ACA copolymers (bACA35 and bACA47), the coalescence cannot be detected except in the case of blends of bACA35 with higher contents of P4VP and at high heating rates. We can conclude that although coalescence is favoured in the case of ACA copolymers with lower contents of vinyl alcohol units, the blocky character of the sequence distribution can prevent it.

Table 3 contains cloud point data for all the studied blends. Although in the case of quasi-random ACA blends the cloud points are higher for higher vinyl alcohol contents, the situation is not so simple for the other blends. Nevertheless, it becomes evident that the ACA copolymer composition is not the only variable involved, and so its sequence distribution must also be considered. *Figure 6* shows some selected cloud point curves obtained by a fitting procedure (see below). These curves correspond to blends of P4VP with ACA copolymers differing

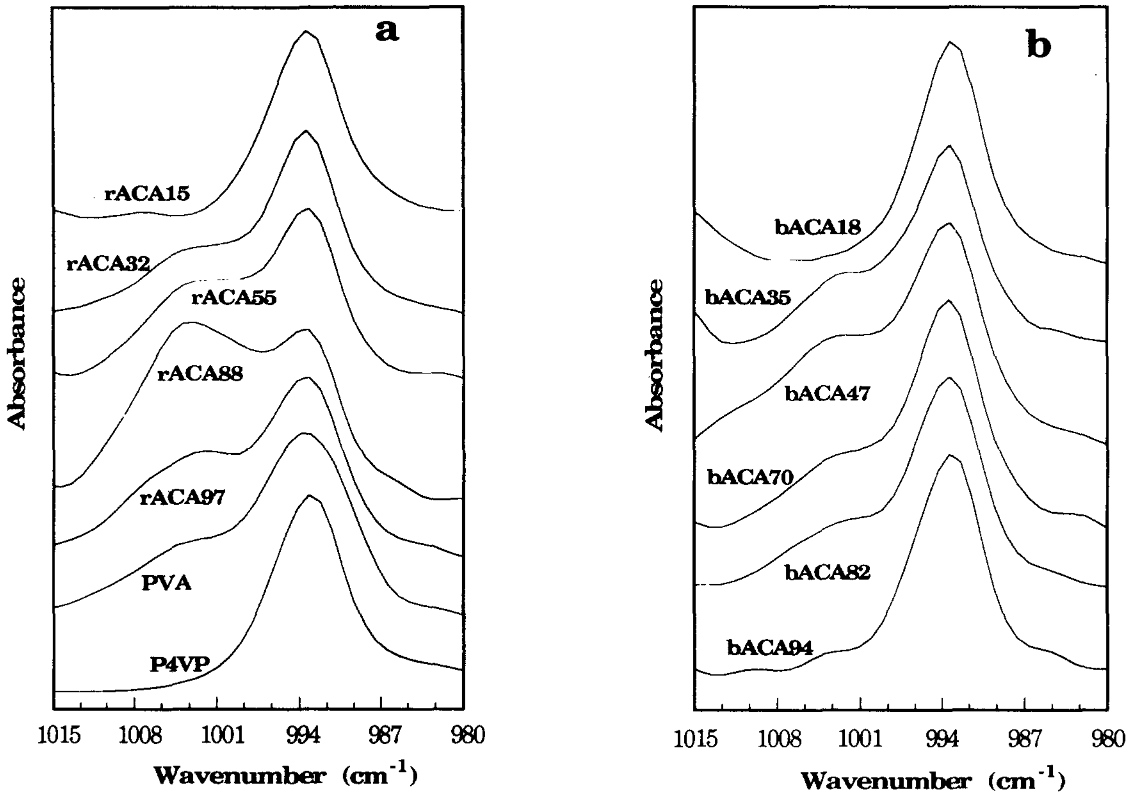

Figure 5 Scale-expanded infra-red spectra in the range 980–1015 cm^{-1}: (a) P4VP and blends of PVA and different rACAs with 40 wt% P4VP; (b) blends of different bACAs with 40 wt% P4VP. The spectra of the blends have been digitally subtracted[6]

Table 3 Cloud point temperatures (K) extrapolated to a 0 K min^{-1} heating rate for different P4VP/ACA blends as a function of P4VP content. Values of the density interaction parameter for the blends (B_{blend}) at 298 K and a volume fraction of 0.5 are also indicated

P4VP content (wt%)	rACA23	rACA35	rACA39	rACA55	P4VP content (wt%)	bACA35	bACA47	P4VP content (wt%)	cACA51	cACA32	cACA48
20	416	428	452	471	20	450	425	20	465	459	453
35	410	426	456	469	40	440	444	35	459	455	451
50	418	428	455	471				50	465	450	463
65	431	433	453	473	60	456	431	65	471	450	465
80	438	449	464		80	455	439	80	469	448	475
B_{blend}	−0.032	−0.14	−0.24	−0.37	B_{blend}	−0.20	−0.087	B_{blend}	−0.27	−0.20	−0.16

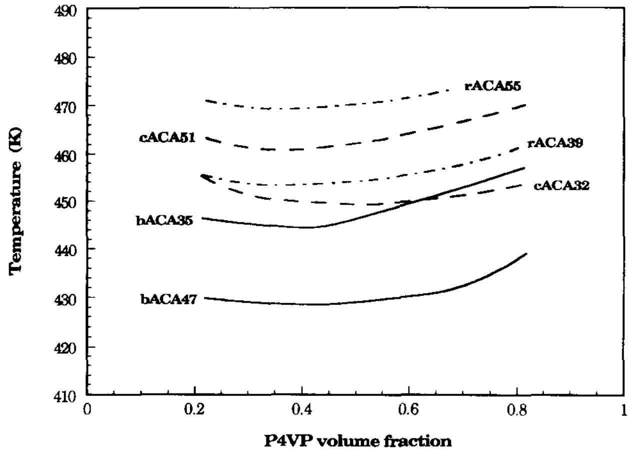

Figure 6 Cloud point curves for blends of P4VP with several ACA copolymers differing in their sequence distribution character

in their sequence distribution character. As can be seen, rACA cloud point curves are above bACA curves, while cACA curves are in between.

Therefore, qualitative evidence for the influence of the sequence distribution in this blend has been shown. Other systems involving large sequence distribution differences[10–12] also exhibit this influence, but experimental studies dealing with small differences are limited[13] and most of them include chlorinated polyethylene as a component[14–17]. Some systems in which sequence distribution effects are unimportant have also been reported[14].

Application of the binary interaction model

A quantitative description can be attempted by means of the binary interaction model[1–3] and its extension to consider sequence distribution effects on miscibility[4]. The postulated treatment assumes that since interactions between two monomer units depend on their corresponding intramolecular adjacent units, triad interactions must be considered. In the case of a binary mixture of homopolymer A (P4VP) with copolymer BC (vinyl alcohol and vinyl acetate, respectively), all the possible triplets with B or C in the central site are taken into account. Their corresponding probabilities of occurrence are calculated and different energy values are assigned (for instance, by means of their interaction parameters $\chi_{CBC;A}$, $\chi_{CBB;A}$, etc.).

Balazs *et al.*[4] have introduced two simplifications in order to reduce the number of χ parameters necessary to describe the system. All the possible B–C interactions are assumed to be equivalent with an average interaction parameter $\bar{\chi}_{BC}$, and all B–B and C–C interactions are equivalent and equal to zero. Secondly, all the triads with equal centres have the same interaction energy with A except for the homoblock triads

$$\bar{\chi}_{BA} = \chi_{CBC;A} = \chi_{BBC;A} = \chi_{CBB;A} \neq \chi_{BBB;A} \tag{1a}$$

$$\bar{\chi}_{CA} = \chi_{BCB;A} = \chi_{CCB;A} = \chi_{BCC;A} \neq \chi_{CCC;A} \tag{1b}$$

Their corresponding differences are defined as

$$\Delta\chi_B \equiv \chi_{BBB;A} - \bar{\chi}_{BA} \tag{2a}$$

$$\Delta\chi_C \equiv \chi_{CCC;A} - \bar{\chi}_{CA} \tag{2b}$$

Cantow and Schulz[18], also using the triad interaction approach, have made a different simplification: the energy of interaction changes as the number of repeat units in the triad does, but the differences between interaction energies are equal

$$\Delta\chi_B = \chi_{BBB;A} - \chi_{BBC;A} = \chi_{BBC;A} - \chi_{CBC;A} \tag{3a}$$

$$\Delta\chi_C = \chi_{CCC;A} - \chi_{CCB;A} = \chi_{CCB;A} - \chi_{BCB;A} \tag{3b}$$

In order to consider the sequence distribution of the comonomer units, a parameter θ is defined as a function of the probabilities of finding BB, BC and CC pairs along the chain (f_{BB}, f_{BC} and f_{CC}, respectively)

$$f_{BC} = 2\theta f_{BB} f_{CC} \tag{4}$$

This θ parameter is analogous to the η parameter obtained from ^{13}C n.m.r. analyses of ACA copolymers (*Table 1*) since they are simply related by $\eta = 2\theta$; so, for example, a random copolymer corresponds to $\theta = 1/2$, $\eta = 1$ and an alternating copolymer corresponds to $\theta = 1$, $\eta = 2$.

Interaction parameters for the blends can be expressed in terms of the defined interaction energies, the fractions of molecules in the chain f_B and f_C, and the η parameter. The Balazs and Cantow–Schulz assumptions are, respectively

$$\chi_{blend} = f_B\bar{\chi}_{BA} + f_C\bar{\chi}_{CA} - f_B f_C\bar{\chi}_{BC} + f_B(1-\eta f_C)^2\Delta\chi_B + f_C(1-\eta f_B)^2\Delta\chi_C \tag{5}$$

$$\chi_{blend} = f_B\chi_{BBB;A} + f_C\chi_{CCC;A} - f_B f_C\bar{\chi}_{BC} - 2\eta f_B f_C(\Delta\chi_B + \Delta\chi_C) \tag{6}$$

From now on we will consider interaction energy densities (B_{blend}, B_{ij}) instead of χ parameters to describe our results.

The values of B_{blend} for the blends studied in this work (see *Table 3*) were calculated from cloud point curve data following the procedure described previously[7]. The Flory–Huggins equation enables the B value to be obtained at the temperature of phase separation as a function of composition. A subsequent fit to the expression $B = b_0 + b_1\phi_1 + b_T T$ gives, by extrapolation, the B value at room temperature for a blend composition $\phi_1 = 0.5$.

The value for the blend with bACA82 was obtained by taking into account that this is a critical blend (i.e. a miscibility limit), so $B_{blend} = B_{crit}$

$$B_{crit} = \frac{RT}{2}\left(\frac{1}{V_1^{1/2}} + \frac{1}{V_2^{1/2}}\right) \tag{7}$$

where V_1 and V_2 are the molar volumes of the two polymers.

Then, another fitting procedure was performed according to equations (5) and (6) using the experimental data for copolymer compositions, sequence distributions

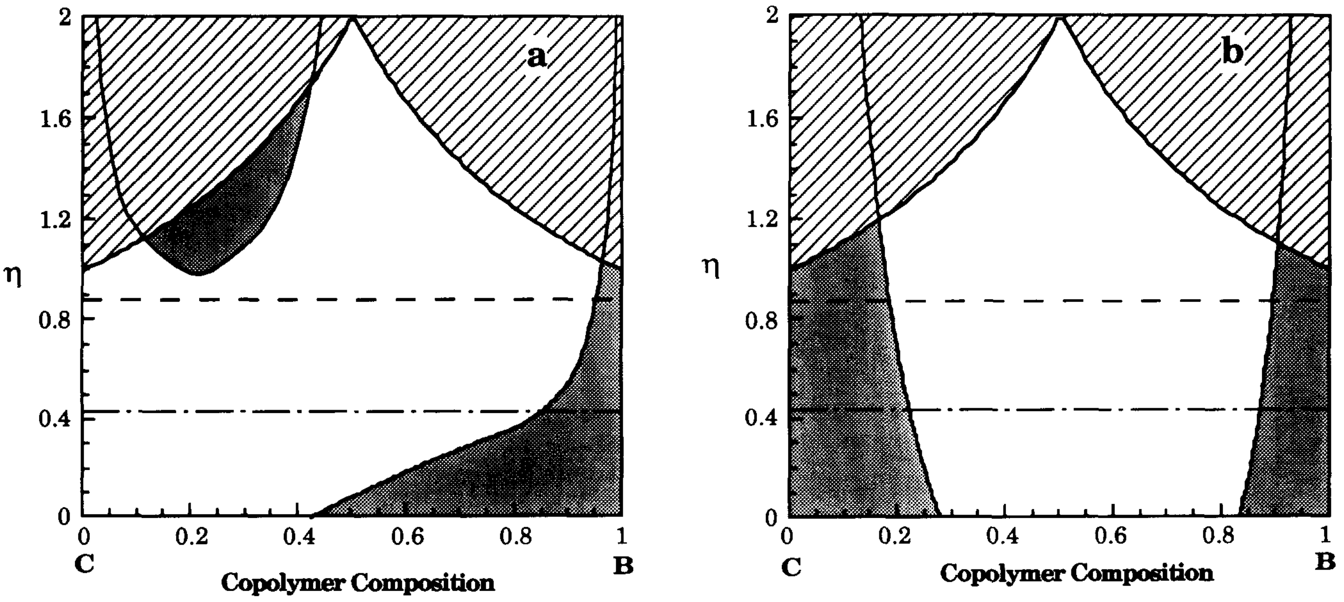

Figure 7 Miscibility behaviour as a function of sequence distribution η and copolymer composition for 50/50 (v/v) P4VP/ACA blends: (a) the Balazs model; (b) the Cantow–Schulz model. Shaded regions represent immiscible blends and hatched regions correspond to impossible copolymer cases. The dashed lines represent the two sets of copolymers employed (rACA, - - - - -; bACA, -·-·-·-·-)

(*Table 1*) and interaction parameters (*Table 3*). After these calculations, we used the results obtained to plot the miscibility windows, or boundaries, as a function of copolymer composition for different sequence distributions, as shown in *Figure 7*. We applied the condition $B_{\mathrm{blend}} - B_{\mathrm{crit}} < 0$, taking $B_{\mathrm{crit}} = 0.02$ obtained from equation (7) as a mean value valid for all possible ACA copolymers.

In the phase diagrams of *Figures 7a* and *7b*, the dashed lines represent the locations of the two sets of copolymers studied (rACA and bACA). Although both treatments agree on showing a lower level of miscibility for blocky sequence distributions, the Balazs model cannot predict the experimental miscibility windows, while the Cantow–Schulz model is in good accordance with the experimental results. We can conclude that the results obtained from the Cantow–Schulz model are quite satisfactory despite the simplifications used in this model, and especially in our case where specific interactions between components are present.

Another way of calculating B_{blend} arises from considering that dyads are the interacting units instead of monomers[19]. Then we have to consider the case of a homopolymer A mixed with a terpolymer BCD in which B, C and D correspond to the dyads BB, CC and BC, respectively, with their respective molar fractions g_{BB}, g_{CC} and g_{BC} coming from the n.m.r. dyad data. The equation for the blend is then

$$B_{\mathrm{blend}} = g_{\mathrm{BB}}B_{\mathrm{BB;A}} + g_{\mathrm{BC}}B_{\mathrm{BC;A}} + g_{\mathrm{CC}}B_{\mathrm{CC;A}} - g_{\mathrm{BB}}g_{\mathrm{BC}}B_{\mathrm{BB;BC}} - g_{\mathrm{BB}}g_{\mathrm{CC}}B_{\mathrm{BB;CC}} - g_{\mathrm{CC}}g_{\mathrm{BC}}B_{\mathrm{CC;BC}} \qquad (8)$$

The first disadvantage of this approach is that six parameters must be calculated (one more than in the previous models). Besides that, two more aspects must be considered: first, interactions between the two copolymer components are differentiated; and secondly, dyad instead of triad interactions are considered, which represents a poorer characterization of the sequence distribution.

The result of the fitting procedure shows again an improvement in miscibility for random copolymers, but it does not predict immiscibility for P4VP and PVAc as occurs in the case of the Balazs treatment.

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