

Influence of the degree of hydrolysis of poly(styrene-*alt*-maleic anhydride) on miscibility with poly(vinyl acetate)

M. Bosma, E. J. Vorenkamp, G. ten Brinke and G. Challa*

Department of Polymer Chemistry, University of Groningen, Nyenborgh 16, 9747 AG Groningen, The Netherlands

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The influence of the hydrolysis of anhydride groups in poly(styrene-*alt*-maleic anhydride) (PSMA) on its miscibility with poly(vinyl acetate) (PVAc) is investigated. The cloudpoint curves of these blends are determined as a function of the degree of hydrolysis. The miscibility is shown to improve with increasing number of carboxylic acid groups in PSMA. Specific interaction between the acid groups of PSMA and the ester groups of PVAc, together with the so-called copolymer effect, is put forward as an explanation for this observation.

(Keywords: miscibility; poly(styrene-*alt*-maleic anhydride); poly(vinyl acetate))

INTRODUCTION

In recent years considerable attention has been paid to the development of new polymer blends. From a commercial point of view this is quite understandable, since it is far more easy to prepare a new blend than to synthesize a completely new polymer. A commercially attractive polymer blend is the homogeneous blend of poly(styrene-*alt*-maleic anhydride) (PSMA) and poly(vinyl acetate) (PVAc), which is known to form a non-disintegrating hydrogel, capable of absorbing water up to 80 times its own weight¹. Heterogeneous blends of these polymers do not show the same stability towards water.

Miscibility between PVAc and PSMA, as in all mixtures, requires the Gibbs free energy of mixing to be negative. Since the entropy of mixing for high-molar-mass components is very small, this implies that the enthalpy of mixing has to be negative. In general, two basically different mechanisms can lead to exothermic mixing. First, it can result from strong specific intermolecular interactions, like hydrogen bonding, which for instance is the case between the carbonyl group of polyesters like poly(ϵ -caprolactone) or poly(β -propiolactone) and the hydroxyl group of polyvinylphenol. As a consequence, shifts of the C=O and OH vibrations in the infra-red absorption spectra of these blends are found². Secondly, exothermic mixing in blends consisting of one or two random copolymers can be the result of an intramolecular 'repulsion' between the repeating units of the copolymer(s), which outranges the possible presence of other unfavourable interactions³⁻⁵.

According to the equation-of-state theory, miscible polymer blends will phase-separate at temperatures sufficiently above the so-called lower critical solution temperature (LCST). This is in general attended by the

occurrence of a cloudpoint. In the present paper miscibility in blends of PSMA, which is an alternating copolymer of styrene and maleic anhydride, and PVAc is investigated by measuring these cloudpoints. By varying the degree of hydrolysis of PSMA, the number of carboxyl groups is varied, which enables us to investigate the influence of the specific interaction between the acid groups and the carbonyl groups of PVAc. However, at the same time the composition of the copolymer is also varied. This will have an additional effect on the miscibility and will be discussed in terms of the recently developed copolymer theory³⁻⁵.

The existence of specific interactions was already mentioned by Greidanus *et al.*⁶ in a preprint dealing with 20% w/v solutions of these polymers in butanone. At a fixed overall polymer concentration they found an increase of the LCST in this ternary system with the degree of hydrolysis of the anhydride groups of PSMA. This was attributed to the formation of hydrogen bonds involving the acid groups generated during hydrolysis of the anhydride groups.

EXPERIMENTAL

Materials

The PSMA sample was made by copolymerization of equal amounts of styrene and maleic anhydride in acetone at reflux temperature, using benzoyl peroxide as an initiator. The molar mass of the sample, determined with a Hewlett-Packard 302B vapour-pressure osmometer, was $\bar{M}_n = 8100$. From this polymer, samples with different degrees of hydrolysis were prepared by refluxing 20 wt % solutions in butanone with 2 wt % water for different times of reaction. The determination of the degree of hydrolysis was done by titration of maleic acid units in an aprotic medium according to the method of Greenhow

* To whom correspondence should be addressed

and Jones^{7,8} at the Plastics and Rubber Research Institute TNO in Delft, The Netherlands.

The PVAc sample was obtained from Hoechst (Mowolith 20). The molar mass, determined by g.p.c. (Waters ALC/GPC 150C), was $\bar{M}_w = 22\,000$ and $\bar{M}_n = 9500$, using tetrahydrofuran (THF) as an eluent, relative to polystyrene standards. The Mark-Houwink constants used for PVAc⁹ were $K = 1.59 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.70$, and for PS¹⁰ $K = 1.14 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.72$.

Glass transitions

The glass transition temperatures were measured with a Perkin-Elmer differential scanning calorimeter (DSC-2) at a heating rate of $10^\circ\text{C min}^{-1}$, using an Apple IIe microcomputer for the data handling. Polymer blends were prepared by precipitation from butanone solution into hexane. The onset of the T_g jump in the second scan was taken as the glass transition temperature.

Cloudpoint curves

Cloudpoints were determined on thin films, which were directly cast onto glass microscope slides from butanone solution, using two different methods:

(1) By visual inspection of blends after annealing on a hot plate (Mettler FP5) at a constant temperature, which was increased 2.5 or 5°C every hour.

(2) By measuring the scattered light at an angle of 30° , using a modified Cenco-TNO light scattering photometer, equipped with a heating block, which could be controlled electrically at a heating rate of $0.375^\circ\text{C min}^{-1}$.

Infra-red spectroscopy

The infra-red spectra were recorded with a Pye Unicam SP3-300 spectrophotometer, using an Apple IIe microcomputer for the data handling. The samples were prepared by casting thin films of the blends from butanone solution directly on KBr discs.

RESULTS AND DISCUSSION

Figure 1a demonstrates that, for a suitable chosen molar mass of PSMA, blends of PVAc and PSMA (degree of hydrolysis = 0.13) show a single T_g . It was determined as the onset of the T_g jump in the second scan. The maximum temperature reached during the first scan was approximately $T_g + 30^\circ\text{C}$. In this way thermal history is erased. A single T_g intermediate between those of the two pure components is believed to be the most unambiguous criterion of polymer miscibility and implies that these blends of PSMA and PVAc are homogeneous within the limits of detection of this technique¹¹. In Figure 1b the onset of the T_g jump vs. the composition of the blends is plotted, together with the theoretical curve according to the equation of Couchman^{12,13}:

$$\ln T_{gm} = \frac{X\Delta C_{p,1} \ln T_{g,1} + (1-X)\Delta C_{p,2} \ln T_{g,2}}{X\Delta C_{p,1} + (1-X)\Delta C_{p,2}}$$

In this equation the indices 1 and 2 indicate the two polymer components, X is the weight fraction of component 1 and $\Delta C_{p,i}$ gives the value of the specific heat jump at the T_g . The agreement with the experimental values is reasonably good. Annealing of the same blends

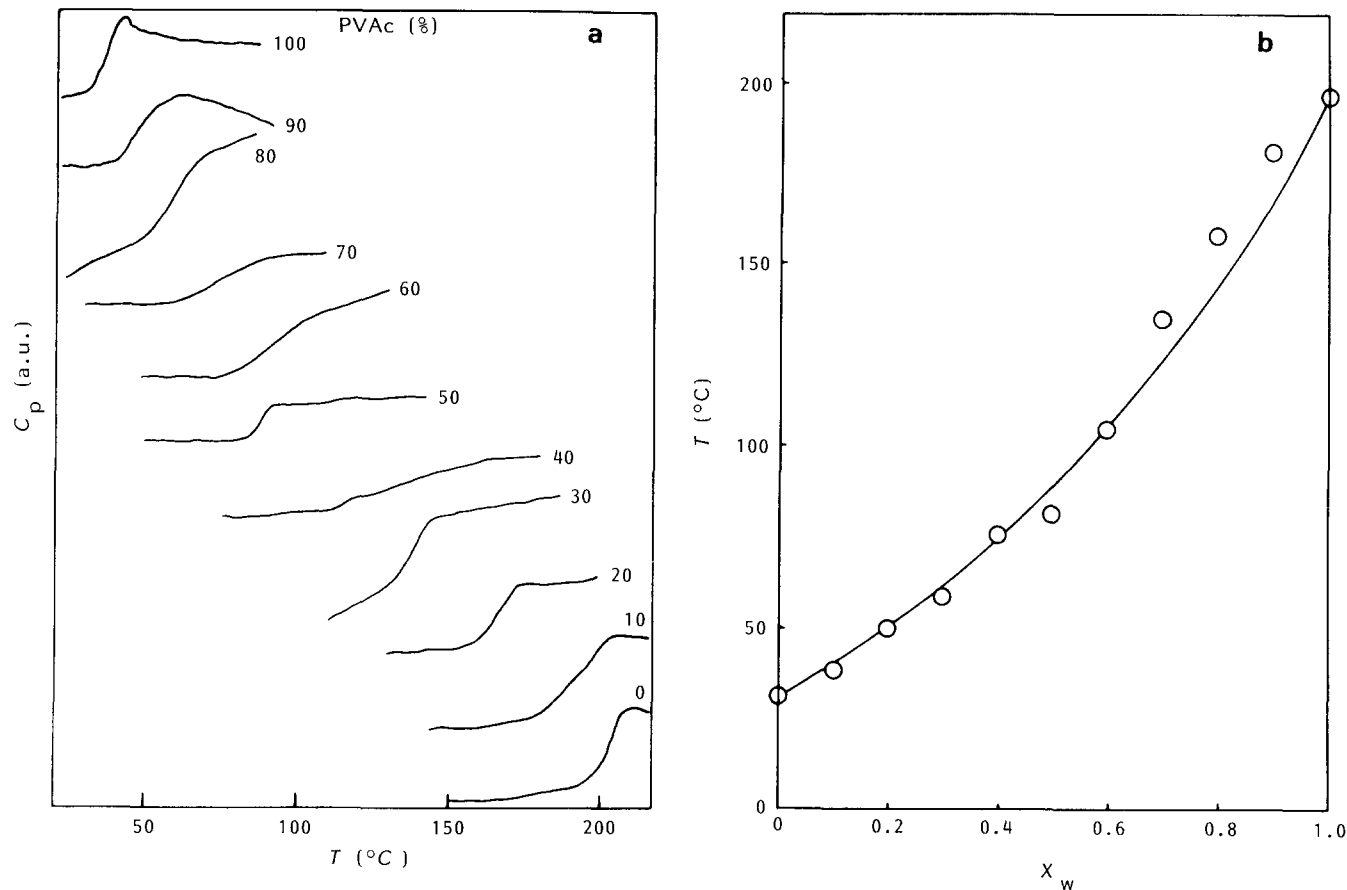


Figure 1 (a) Thermograms for blends of PVAc and PSMA (13% hydrolysed). (b) Glass transition temperatures vs. weight fraction of PSMA (X_w) for blends of PVAc and PSMA. The full curve was calculated using the equation of Couchman

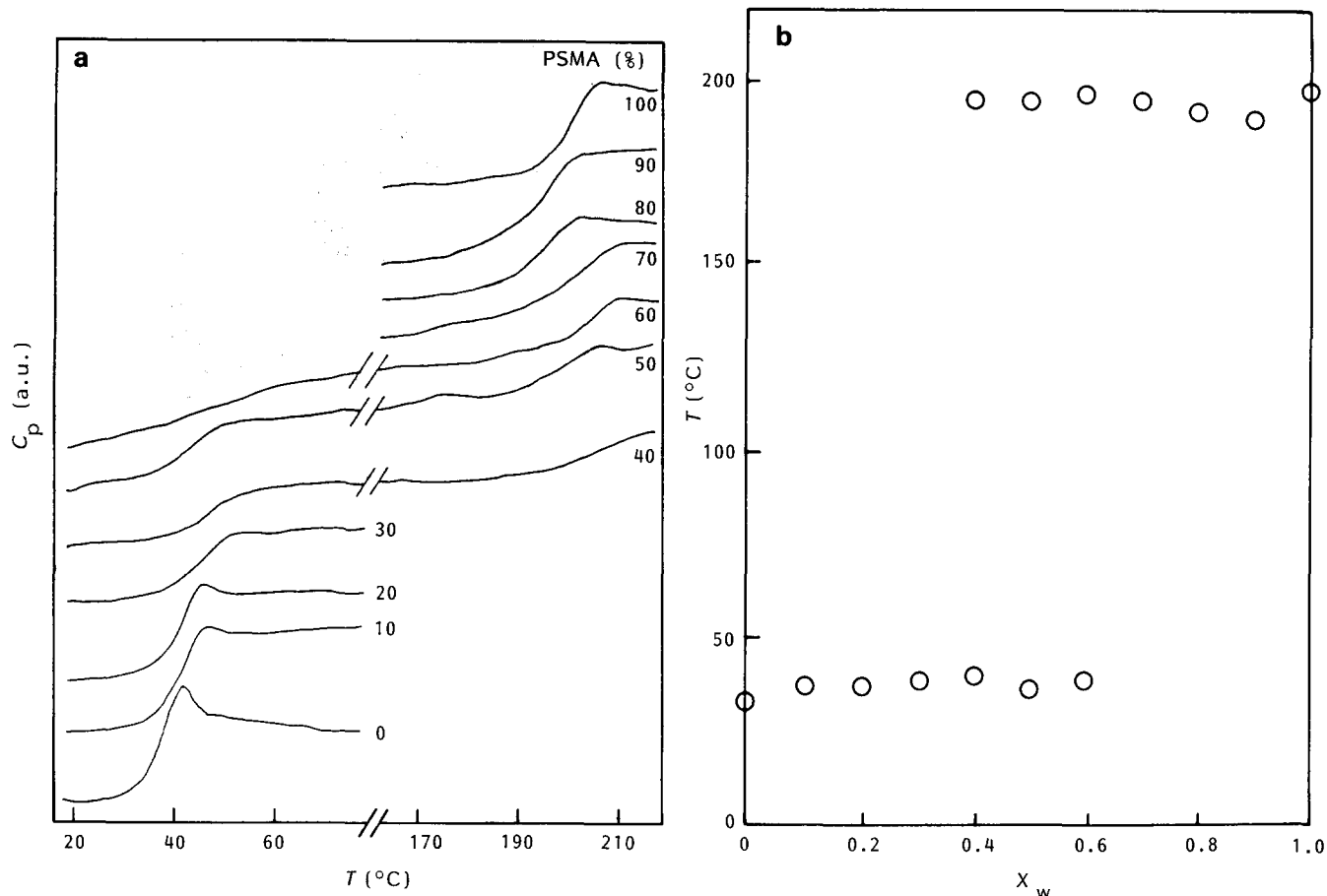


Figure 2 (a) Thermograms for blends of PVAc and PSMA after annealing at 220°C for 45 min. (b) Glass transition temperatures vs. weight fraction of PSMA (X_w) for blends of PVAc and PSMA after annealing at 220°C for 45 min

at 220°C for 45 min results in phase separation. This can be seen in *Figure 2a*, showing the thermograms of blends of various compositions after quenching from 220°C to room temperature. In *Figure 2b* the onset T_g values of these blends are plotted. From the fact that the T_g values of the pure components are found, we conclude that at 220°C a separation into phases consisting almost completely of either component has taken place. Since, as will be shown, the annealing temperature is far above the *LCST*, this is completely in line with observations on various other polymer systems, such as the much studied polystyrene/poly(vinyl methyl ether) blends¹⁴.

To study the effect of hydrolysis of PSMA on its miscibility with PVAc the intensity of the scattered light as a function of temperature was observed. The PSMA samples used were all prepared by hydrolysis of the same sample, which means that, ignoring the minor increase due to hydrolysis, the molar mass of the PSMA samples remained the same.

In *Figure 3* the cloudpoint curves of these blends are plotted as a function of the degree of hydrolysis. Because of the low mobility of the blends at temperatures just above T_g , the cloudpoints were determined using the 'anneal' method (see 'Experimental' section). In *Figure 4* the cloudpoints determined for blends containing 10 wt % PSMA, which is near the minima of the cloudpoint curves of *Figure 3*, are plotted as a function of the degree of hydrolysis. They were measured using an extremely low heating rate of 0.375°C min⁻¹. Cooling these samples using the same low rate resulted in remixing of the blends at approximately the same temperature, which indicates that the measured cloudpoints are fairly good

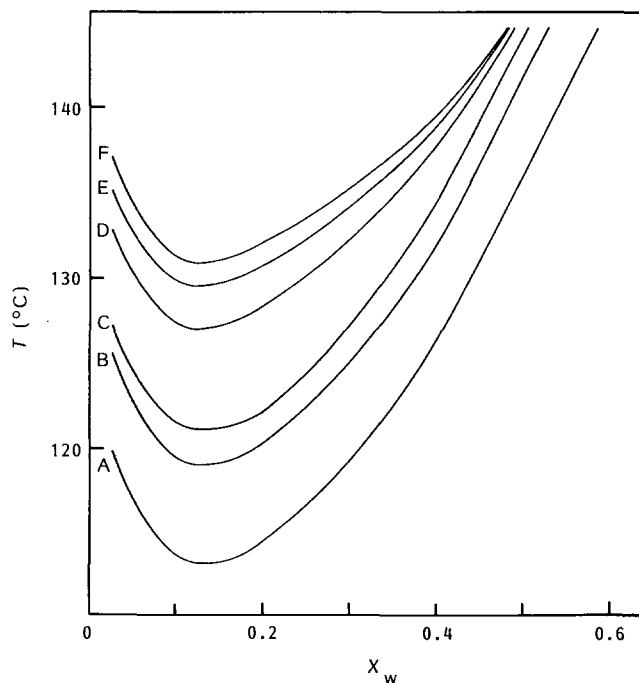


Figure 3 Cloudpoint curves for blends of PVAc and PSMA (X_w = weight fraction of PSMA) as a function of the percentage of hydrolysis: A, 1.8%; B, 2.1%; C, 8.2%; D, 11.4%; E, 13.0%; F, 14.2-43.0%

approximations for the location of the thermodynamic phase-separation temperatures.

Figures 3 and *4* show that up to a certain point the miscibility between PVAc and PSMA increases with the number of acid groups in the blends. However, above

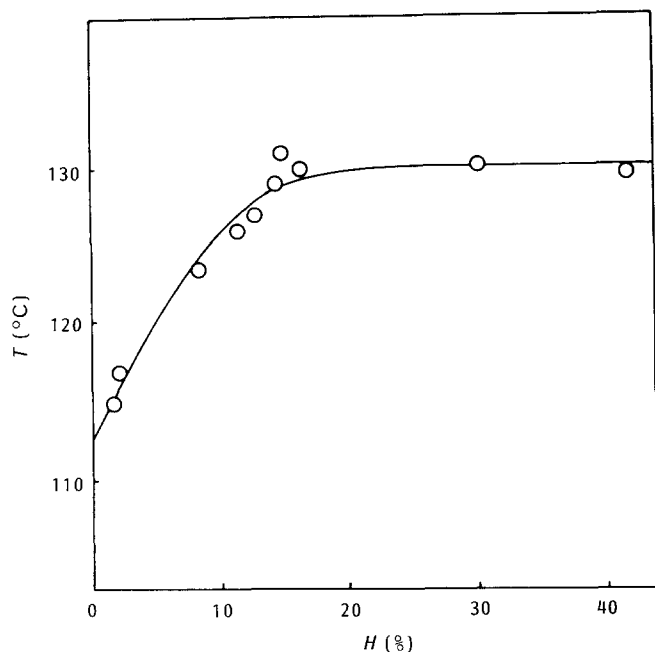


Figure 4 Cloudpoints for blends of PVAc with 10 wt% PSMA vs. percentage of hydrolysis (H)

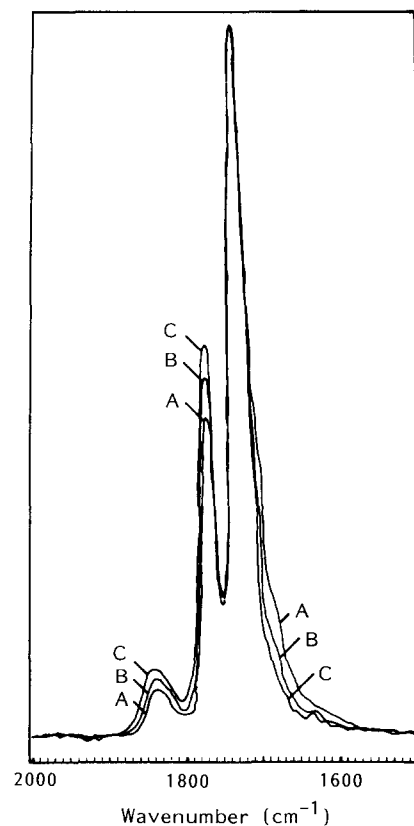


Figure 5 Infra-red absorption spectra of a blend of PVAc with 40 wt% PSMA (percentage of hydrolysis = 30%) after annealing at 110°C (A), 120°C (B) and 130°C (C), respectively, for 45 min

15 wt% hydrolysis the cloudpoints occur at the same temperature, a somewhat unexpected result which we think is due to the re-formation of anhydride groups favoured in hydrolysed PSMA at higher temperatures. Apparently, under the given conditions this back-reaction takes place at about 130°C and as a consequence the miscibility between hydrolysed PSMA and PVAc does not improve anymore.

The number of acid and anhydride groups can be determined by studying the infra-red spectra of the blends. In Figure 5 the infra-red spectra in the region 2000–1500 cm^{-1} are plotted for a blend of PVAc and 40 wt% PSMA (percentage of hydrolysis = 30%) which was annealed for 45 min at 110, 120 and 130°C, respectively. During the annealing process the number of acid groups reduces, decreasing the absorption at 1700–1620 cm^{-1} , while the number of anhydride groups increases, enhancing the absorptions at 1770 and 1840 cm^{-1} . The absorption band at 1730 cm^{-1} of the ester carbonyl group did not change, providing an opportunity to use this peak for scaling of the plots. Figure 5 clearly shows that a re-formation of anhydride groups takes place at temperatures between 110 and 130°C. From all these observations we conclude that the miscibility of hydrolysed PSMA and PVAc improves as a function of the number of hydrolysed anhydride groups.

Recently, considerable progress has been made in understanding the factors governing miscibility in polymer blends involving random or alternating copolymers. Although the theoretical description of these systems is still very elementary and oversimplified, it seems at least to contain the basic ingredients^{3-5,15,16}. In our case hydrolysed PSMA consists of three different repeating units and PVAc has one repeating unit. Let the subscripts 1–4 denote these units:

- 1 = styrene
- 2 = maleic anhydride
- 3 = maleic acid
- 4 = vinyl acetate

Let ϕ_B denote the volume fraction of PVAc in the blend and $\phi_A = 1 - \phi_B$ the volume fraction of hydrolysed PSMA. Furthermore, let ϕ_1 denote the volume fraction of styrene in hydrolysed PSMA and h denote the degree of hydrolysis. In that case the free energy of mixing in the familiar Flory–Huggins formulation^{17,18} is given by:

$$\frac{\Delta G_m}{RT} = \frac{\phi_A}{r_A} \ln \phi_A + \frac{\phi_B}{r_B} \ln \phi_B + \chi_{\text{eff}} \phi_A \phi_B \quad (1)$$

Here r_A and r_B are proportional to the degrees of polymerization, and χ_{eff} depends on all components involved in a way that will be discussed later. Assuming χ_{eff} is independent of ϕ_A and ϕ_B , phase separation will occur as soon as:

$$\chi_{\text{eff}} > \frac{1}{2} (1/\sqrt{r_A} + 1/\sqrt{r_B})^2 \quad (2)$$

Since we will use this simple description to discuss phase separation at elevated temperatures (LCST behaviour), here and in the following it has to be understood that χ_{eff} is a free energy rather than an interaction parameter. A discussion with respect to the corresponding more complicated temperature dependence of χ_{eff} in terms of the equation-of-state theory^{19–22} could be given, but is not warranted here because of the limited amount of experimental data available.

In terms of the repeating units χ_{eff} is given by:

$$\begin{aligned} \chi_{\text{eff}} = & \phi_1 \chi_{14} + (1-h)(1-\phi_1) \chi_{24} + h(1-\phi_1) \chi_{34} \\ & - \phi_1(1-\phi_1)(1-h) \chi_{12} - \phi_1(1-\phi_1)h \chi_{13} \\ & - (1-\phi_1)^2 h(1-h) \chi_{23} \end{aligned} \quad (3)$$

where the various χ parameters are again free energy rather than interaction parameters. Because for all blends investigated the values of r_A and r_B remain fixed, it is reasonable to assume that improved miscibility at higher degrees of hydrolysis corresponds to smaller, and in the light of equation (2) probably more negative, values of χ_{eff} at a given temperature. Equation (3) is rather complicated and given the limited amount of experimental data available not very suitable for a more detailed discussion. However, certain conclusions can be drawn by looking at the h dependence of χ_{eff} :

$$\frac{d\chi_{\text{eff}}}{dh} = (1 - \phi_1)(\chi_{34} - \chi_{24}) + \phi_1(1 - \phi_1)(\chi_{12} - \chi_{13}) - (1 - \phi_1)^2(1 - 2h)\chi_{23} \quad (4)$$

The first term is expected to be negative because $\chi_{34} < 0$ owing to hydrogen bonding. Moreover χ_{24} is probably positive. Since maleic anhydride is soluble in toluene, in contrast to succinic acid, we also expect $\chi_{12} < \chi_{13}$, in which case the second term in equation (4) is also negative. Finally it is expected that χ_{23} , although it may be small, is positive. Therefore all three contributions to $d\chi_{\text{eff}}/dh$ are probably negative. Although somewhat speculative it is not unreasonable to conclude that the improved miscibility as a function of the degree of hydrolysis h is primarily due to a combination of two effects: an increase in the number of specific interactions (χ_{34}) and an enhanced copolymer effect (mainly χ_{13}). A more detailed interpretation is only possible once the various χ -parameters involved are determined by additional experimental studies.

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