

Miscibility behaviour of PVC/polymethacrylate blends: temperature and composition analysis

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The miscibility behaviour of poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PPMA), poly(*n*-butyl methacrylate) (PBMA), and poly(*n*-amyl methacrylate) (PAMA) with poly(vinyl chloride) (PVC) was investigated using differential scanning calorimetry. All of the blends are miscible, i.e. they show a single glass transition temperature, when subjected to an appropriate thermal history. A lower critical solution temperature was detected in PVC/PBMA and PVC/PAMA blends, but not in PVC/PEMA and PVC/PPMA blends (although it must exist at temperatures higher than 200°C, which was not accessible experimentally due to severe degradation of PVC). These observations lead to the conclusion that there is a miscibility window in terms of the polymethacrylate structure; the greater degrees of miscibility are found in the PEMA and PPMA blends.

(Keywords: miscibility behaviour; polymethacrylate blends; PVC; d.s.c.)

INTRODUCTION

Several authors have investigated blends of poly(vinyl chloride) (PVC) with various poly(*n*-alkyl methacrylates), mainly methyl (PMMA), but also ethyl (PEMA), propyl (PPMA), butyl (PBMA), pentyl (PAMA) and hexyl (PHMA). It was found that PMMA is miscible with PVC, whatever its tacticity and the composition of the blend. However, this system exhibits a lower critical solution temperature (LCST) at temperatures which decrease with an increase of the isotactic content of PMMA^{1,2}. Furthermore, the presence of some non-random segment distribution, in other words the beginning of some aggregation, was detected by non-radiative energy transfer fluorescence spectroscopy, which is sensitive to a 2.0 nm scale. This non-random distribution was observed to increase with the isotactic content of PMMA³. For atactic PMMA, the LCST was reported to be 180¹ and 145°C (ref. 2) for PMMA number-average molecular weights of 38 000 and 80 000, respectively.

Polymethacrylates with longer alkyl side chains were reported to be miscible with PVC^{4,5}, although there is a 'miscibility window' as a function of the size of the alkyl group, which means that immiscibility is again found with hexyl and longer side groups^{4,6}. With polymethacrylates with substituents different from *n*-alkyl, the situation appears to be more complex. It has been mentioned that poly(isopropyl methacrylate) is immiscible with PVC⁷. Similarly, using d.s.c. and solid state n.m.r. spectroscopy, it has been shown that poly(benzyl methacrylate) is immiscible but not poly(cyclohexyl methacrylate)⁸.

In the course of a study on the miscibility behaviour of ternary polymer blends involving two polymethacrylates and a chlorinated polymer, and which will be reported elsewhere⁹, we had the opportunity to re-

investigate the miscibility behaviour of PVC/polymethacrylate blends and the existence of LCST values. For this purpose, we used differential scanning calorimetry (d.s.c.). We found variations of the glass transition temperature as a function of composition which differ from those that have been reported before and which can be explained with the Gordon-Taylor equation. We also determined the co-existence curves of this series of mixtures and have simulated them with the Flory-Prigogine equation-of-state theory. More specifically, we have analysed polymethacrylates with ethyl, *n*-propyl, *n*-butyl and *n*-pentyl (*n*-amyl) substituents.

EXPERIMENTAL

Table 1 gives the list of polymers used in this study: poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PPMA), poly(*n*-butyl methacrylate) (PBMA), poly(*n*-amyl methacrylate) (PAMA) and PVC. Their weight-average molecular weight is also given. They are in a range where most properties, including miscibility, depends little upon molecular weight. Molecular weights were determined by size exclusion chromatography (SEC) using μ -styrigel columns and a Waters chromatograph. The measurements were conducted at 298 K in tetrahydrofuran, and the apparatus was calibrated with polystyrene standards.

Blends were prepared by slowly casting films from solution by using distilled methylethylketone. In all cases, solvent evaporation was conducted at room temperature. The resulting films were removed from Petri dishes and dried in a vacuum oven at 50°C until they reached constant weight. The resulting films had a thickness of about 60 μ m.

Differential scanning calorimetry (d.s.c.) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS microcomputer. The d.s.c. was calibrated with ultrapure indium. The glass

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Table 1 Polymers used

Polymer	Repeat unit	T_g (°C)	M_w (kg mol ⁻¹)	M_n (kg mol ⁻¹)	Source
Polymethacrylate	$\left\{ \text{CH}_2 - \underset{\text{O}=\text{C}-\text{O}(\text{CH}_2)_x-\text{CH}_3}{\text{C}}(\text{CH}_3) \right\}$				
PMMA	$x = 0$	93	84	47	Fisher Scientific
PEMA	$x = 1$	71	206	101	Polysciences
PPMA	$x = 2$	52	315	94	Polysciences
PBMA	$x = 3$	32	155	88	Aldrich
PAMA	$x = 4$	6	62	27	Polysciences
PVC	$\left\{ \text{CH}_2 - \text{CHCl} \right\}$	82	72	43	Shawinigan Chemicals

transition temperatures, T_g , reported in this paper were recorded at the half-height of the corresponding heat capacity jump.

After their insertion in the d.s.c. apparatus, all samples were first heated up to 363 K for 90 s, in order to remove the last traces of solvent, quenched to 223 K, and maintained at that temperature for 5 min. A first scan was made at a heating rate of 20 K min⁻¹ up to 363 K. Each sample was maintained 90 s at that temperature and quenched again to 223 K. It was again left 5 min at this temperature before a second scan performed at a heating rate of 20 K min⁻¹. The T_g values reported in this paper were recorded during the first scan; but the values of the first and second scans are usually the same. A third scan was run on some selected samples to check the reproducibility of the measured values.

In this paper, the following terminology is retained: a sample is considered miscible if it gives at each composition a single T_g value intermediate between those of the individual components. Thus, a sample exhibiting two T_g values at a given composition is considered immiscible, even if the possibility of observing a single T_g value at other compositions is not excluded.

The phase separation occurring between polymethacrylates and PVC was studied with the following annealing cycle. The samples were heated up, at a rate of 40 K min⁻¹ to an annealing temperature higher by 10 K to the T_g of the homopolymers considered, maintained 90 s at that temperature, and quenched to 223 K. It was left 5 min at this temperature before a first scan was recorded at a heating rate of 20 K min⁻¹, the annealing temperature for this scan being 5 K higher than the annealing temperature of the previous scan. This heating-cooling cycle was repeated until two well-defined T_g values could be observed. The annealing temperature at which two T_g values begin to be observed corresponds approximately to the temperature where phase separation occurs.

RESULTS

T_g analysis

Figure 1 gives the T_g -composition curves of PVC/PEMA, PVC/PPMA, PVC/PBMA, and PVC/PAMA blends. In each case, a regular variation of T_g is observed as a function of composition, indicating that these systems are miscible. Moreover, the width of the transition zone is intermediate between those of the two polymers which are involved giving no indication at any microscale phase separation, at least at the level of resolution of the d.s.c. experiment¹⁰. Also, it is obvious

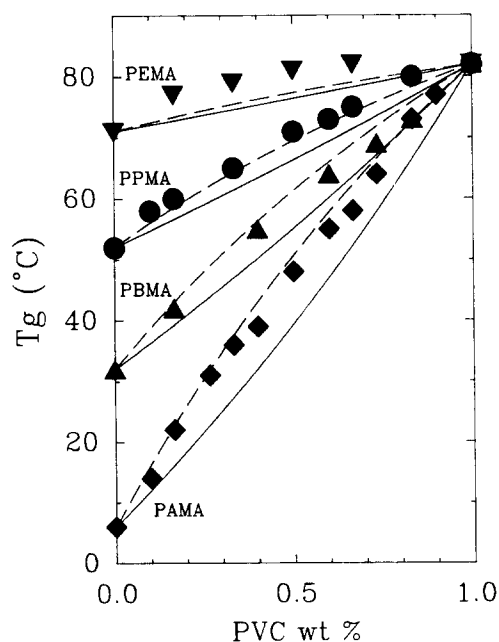


Figure 1 Glass transition temperature as a function of the PVC weight fraction of PVC/polymethacrylate blends: —, Fox equation; ---, Gordon-Taylor equation; filled symbols, experimental data

from Figure 1 that each of these series of points gives a positive deviation relative to the Fox equation¹¹ (indicated in Figure 1 by the continuous lines), although the importance of this deviation varies from one series to the other. We may note immediately that it is unusual to observe such positive deviations¹²⁻¹⁵ with few exceptions¹².

In order to understand the meaning of these curves and their variation as a function of the structure of the polymethacrylates, we have used the Gordon-Taylor equation¹⁶ which assumes no discontinuity in specific volume at T_g :

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

where w_i is the weight fraction of component i and T_{gi} its glass transition temperature; k is the so-called Gordon-Taylor coefficient defined by:

$$k = v_2 \Delta \alpha_2 / v_1 \Delta \alpha_1 \quad (2)$$

where v_i is the specific volume of component i and $\Delta \alpha_i$ the difference between its volume expansion coefficient in the liquid and glassy states. If assumptions are made that the specific volumes of the two polymers are equal (their

Table 2 Parameters used in equation (2)

Polymer	T_g (°C)	v^a (cm ³ g ⁻¹)	$\Delta\alpha^a$ (deg ⁻¹)	k^b
PVC	82	0.726	4.8	—
PEMA	71	0.904	2.8	1.38
PPMA	52	0.925	2.7	1.40
PBMA	32	0.946	2.6	1.42
PAMA	6	0.974	2.5	1.43

^aReported at T_g

^bFor the corresponding PVC/polymethacrylate blend

ratio is never very far from unity), and that $\Delta\alpha_i T_{g_i}$ is a constant, one gets the Fox equation mentioned above which reads¹¹:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (3)$$

In order to use equation (1), the parameters of equation (2) are needed. For PVC, those are taken from ref. 17 and reported in Table 2. For the polymethacrylates, we used the values of α_G and α_L given in ref. 18 and interpolated those values at the corresponding T_g (ref. 10). The $\Delta\alpha$ values thus calculated are also given in Table 2. For v_i , we started with the values given at 120°C in ref. 18 and calculated the corresponding values at T_g . From those values, k was calculated (Table 2) and the corresponding Gordon–Taylor curve is given in Figure 1. A fair agreement is obtained in all cases. This means that, despite the fact that the Gordon–Taylor equation is more or less an additivity rule which does not take into account deviations due to specific interactions, it can still represent adequately this series of results.

At this point several remarks must be made. First, the equation proposed by Kwei¹⁹ was used to simulate the T_g -composition data of PVC/PEMA (which is the system where the greatest deviation is observed in Figure 1). Kwei's equation is an expansion of equation (1), with a second term added on the righthand side. This term has the form qw_1w_2 where q is an adjusting parameter which accounts for the presence of specific interactions. With k taken in Table 2, we got a value of q equal to 16.5 (Figure 2) which indicates, according to Kwei, the presence of strong interactions between the polymer components.

Second, for the PVC/PEMA data, a better agreement could be obtained between experiment and theory by considering k as an adjusting parameter and by using k values larger than the ones given in Table 2 (Figure 2) but, in this case, the shape of the calculated curve is always different from the shape of the experimental one¹⁰(this problem does not occur with the other systems).

Third, the equation proposed by Brekner, Schneider and Cantow²⁰ was also used to simulate the T_g -composition behaviour of each system¹⁰. However, this equation contains two parameters and their meaning is not very clear, unless the second one is made equal to zero. But, in such a case, this expression reduces to Kwei's equation. We then preferred to use equation (1).

Fourth, we have not used in this study a free volume equation that we recently favoured in the analysis of T_g -composition data of PVC/polyester blends^{21,22}. This equation can be used uniquely if the T_g values of the two polymers involved are different by at least 100 degrees, which is obviously not the case here. Finally, PVC/

PMMA data were not considered here because these systems have already been investigated by several groups^{1,2}.

Temperature analysis

The behaviour reported in the preceding section was obtained for blends prepared in methylethylketone and annealed at 363 K. It is the purpose of this section to investigate the effects of other thermal treatments on the same systems.

Figure 3 shows, for a PVC/PAMA blend containing 67 wt% PVC, a clear indication of phase separation, with the appearance of two T_g values, which begin to occur at 100°C (the 95°C curve is ambiguous). Annealing at higher temperatures leads to better defined T_g values and their shift towards the values of pure PVC and pure PAMA (for an annealing time of 90 s). Similar experiments were conducted at several compositions leading to the phase separation curves given in Figure 4 for the PVC/PBMA and PVC/PAMA blends. A LCST is clearly defined at about 170°C with the PVC/PBMA blend, and at about 100°C with the PVC/PAMA blend. Similar experiments did not show any variation of T_g with PVC/PEMA and PVC/PPMA blends for annealing temperatures up to 200°C. Experiments made at higher

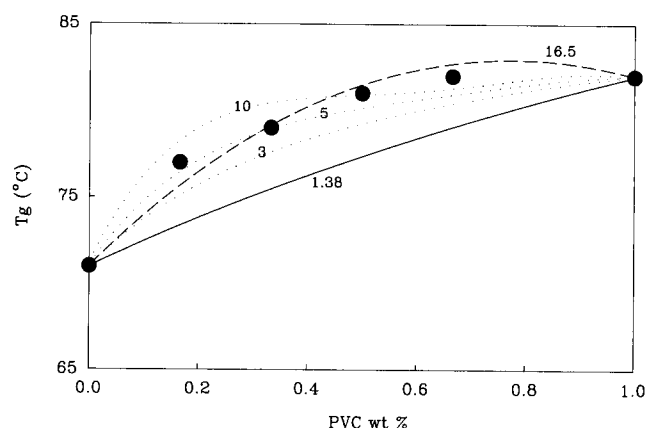


Figure 2 Glass transition temperature as a function of the PVC weight fraction of PVC/PEMA blends: —, Gordon–Taylor equation with $k = 1.38$; ···, Gordon–Taylor equation with $k = 3, 5$ and 10 ; ---, Kwei equation; (●) experimental data

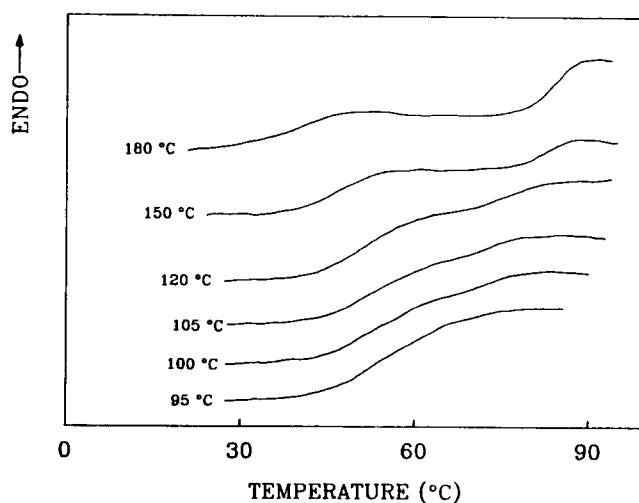


Figure 3 D.s.c. curves of PVC/PAMA blends (with a 67/33 composition) after annealing 90 s at the temperature indicated

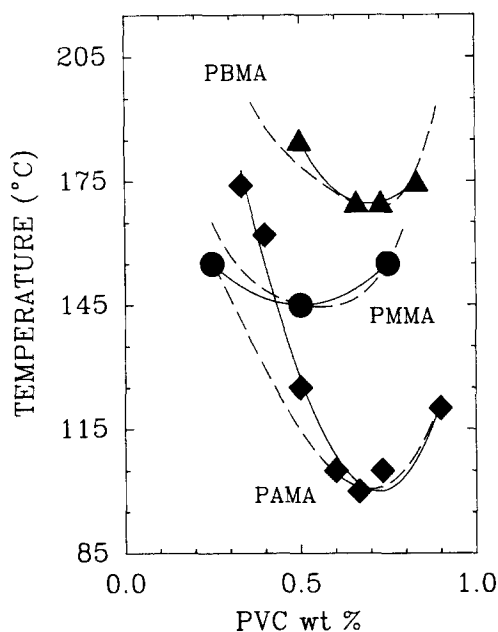


Figure 4 Experimental phase separation data of PVC/PMMA, PVC/PBMA and PVC/PAMA blends. The dashed lines are the simulated curves and \bullet — the experimental data. See text for details

temperatures are meaningless because there is too much degradation of PVC under these conditions. Let us recall that PVC/PMMA blends also exhibit phase separation at 145°C (ref. 2). It appears then that the LCST of PVC/polymethacrylate blends goes through a maximum, being low with PMMA, high (above 200°C) for PEMA and PPMA, and thereafter decreasing with the size of the alkyl side chain group. With poly(n-hexyl methacrylate) (PHMA), this LCST is so low that immiscibility is observed whatever the conditions of preparation of the PVC/PHMA blends⁶.

These phase separation curves can be simulated with the Flory-Prigogine equation of state. Details about the origin of these equations can be found in refs. 23, 24 and 25.

Here it suffices to give the resulting equation which allows the calculation of the spinodal:

$$\begin{aligned} \partial^2(\Delta G_M)/\partial\phi_2^2 = & -1/\phi_1 + (1 - (r_1/r_2)) \\ & + (P_1^*V_1^*/RT_1^*)(-D/(\bar{v} - \bar{v}^{2/3})) \\ & + (P_1^*V_1^*D/RT\bar{v}^2) + (PV_1^*D/RT) \\ & + (2V_1^*X_{12}\theta_1\theta_2^2/RT\bar{v}\phi_1\phi_2) \\ & - (V_1^*X_{12}D\theta_2^2/RT\bar{v}^2) \\ & - (2V_1^*Q_{12}\theta_1\theta_2^2/R\phi_1\phi_2) = 0 \end{aligned} \quad (4a)$$

where

$$\begin{aligned} D = \partial\bar{v}/\partial\phi_2 \\ = \{(\partial\bar{P}/\partial\phi_2) - (1/\bar{T})P + (1/\bar{v}^2)(\partial\bar{T}/\partial\phi_2)\} \\ + \left(\frac{2}{\bar{v}^3} - \frac{\bar{T}(\bar{v}^{1/3} - 2/3)}{\bar{v}^{5/3}(\bar{v}^{1/3} - 1)^2} \right) \end{aligned} \quad (4b)$$

$$\partial\bar{P}/\partial\phi_2 = (P/P_2^*)[P_1^* - P_2^* - X_{12}\theta_2(1 - (\theta_1/\phi_2))] \quad (4c)$$

and

$$\begin{aligned} \partial\bar{T}/\partial\phi_2 = T/P^*[(P_2^*/T_2^*) - (P_1^*/T_1^*)] \\ + (\bar{T}/P^*)[P_1^* - P_2^* - X_{12}\theta_2(1 - (\theta_1/\phi_2))] \end{aligned} \quad (4d)$$

where ΔG_m is the free enthalpy of mixing; r_i is the chain length of molecule i ; P_i^* is the hard core pressure of species i ; V_i^* is the molar hard core volume of species i ; T_i^* is the hard core temperature of species i ; \bar{P} is the reduced pressure of the mixture; \bar{v} is the reduced volume of the mixture; \bar{T} is the reduced temperature of the mixture; θ_i is the site fraction of species i ; ϕ_i is the segment fraction of species i ; X_{12} is the interaction parameter; Q_{12} is the interaction entropy parameter; R is the gas constant; T is the temperature, and P is the pressure of the system.

In order to solve equation (4) to find the theoretical phase separation temperature, the hard-core and reduced variables, which can be obtained from the following parameters, are required: the specific volume v , the thermal expansion coefficient $\alpha = (1/v)(\partial v/\partial T)_p$, and the thermal pressure coefficient $\gamma = (\partial P/\partial T)_v$. The following binary parameters are also needed: the surface per unit of core volume ratio $s_1/s_2 = s$, and the interaction parameter X_{12} . The temperature dependence of v , α and γ at atmospheric pressure is given by^{23,25,26}:

$$v = v_0 e^{\alpha\Delta T} \quad (5)$$

$$\alpha = \alpha_0 + \alpha_0^2(7 + 4\alpha_0 T)\Delta T/3 \quad (6)$$

$$\gamma = \gamma_0 - \gamma_0(1 + 2\alpha_0 T)\Delta T/T \quad (7)$$

Values of \bar{v} , P^* and \bar{T} could be found for each component at zero pressure from

$$\bar{v}_i^{1/3} = 1 + \alpha_i T/(3 + 3\alpha_i T) \quad (8)$$

$$P_i^* = \gamma_i T \bar{v}_i^2 \quad (9)$$

$$\bar{T}_i = (\bar{v}_i^{1/3} - 1)/\bar{v}_i^{4/3} \quad (10)$$

and for the mixture

$$P^* = P_1^*\phi_1 + P_2^*\phi_2 - \phi_1\theta_2 X_{12} \quad (11)$$

where

$$T^* = P^*/[(\phi_1 P_1^*/T_1^* + \phi_2 P_2^*/T_2^*)] \quad (12)$$

$$\bar{T} = T/T^* \quad (13)$$

$$\theta_2 = \phi_2/(s\phi_1 + \phi_2) \quad (14)$$

and, by iteration, \bar{v} for the mixture can be found from the reduced equation of state: $\bar{v}^{1/3} = 1/(1 - \bar{T}\bar{v})$.

Alternatively, at a single temperature where both α and γ are known, P_i^* and \bar{T}_i can be calculated from equations (9) and (10), and hence T_i^* . One can then calculate P^* and T^* for the mixture; \bar{T} for either the mixture or its components can be found from equation (13) at any temperature, and hence \bar{v} . This procedure would give the same result except when the ratio of the two components is very large or very small; then, the equations become very sensitive to small errors in \bar{v} .

Equation (4) can be solved because all parameters can be measured or calculated, except X_{12} and Q_{12} which are fitting parameters. For PVC, several values of α , γ and v are available^{1,12,27,28}; they are different but all of the same order of magnitude. We have preferred the values given in ref. 1 because the PVC used in that paper has a molecular weight very similar to that used in this study (values given in Table 3). For PMMA, values of α , γ and v are known¹ (Table 3). For the other polymethacrylates, values of v_i were extrapolated at 120°C, as indicated in the previous section. Values of γ were calculated from the accepted values of PMMA (0.267 cal cm⁻³ K⁻¹ at 120°C, ref. 1) and assuming the

Table 3 Parameters used in equation (4) (at 120°C)

Polymer	T_g (°C)	$\alpha \times 10^4$ (K ⁻¹)	γ (cal cm ⁻³ K ⁻¹)	v (cm ³ mol ⁻¹)	X_{12} (J cm ⁻³)	$Q_{12} \times 10^{-4}$ (J cm ⁻³ deg ⁻¹)
PVC	82	5.00	0.272	0.740	–	–
PMMA	93	5.40	0.267	0.894	–0.25	–4.90
PEMA	71	5.62	0.250	0.928	–0.37	–5.08
PPMA	52	5.80	0.250	0.959	–0.44	–5.08
PBMA	32	5.97	0.245	0.990	–0.26	–1.22
PAMA	6	6.18	0.240	1.032	–0.23	–0.41

same dependence as a function of the size of the alkyl side chain as for the corresponding polyacrylates¹². Finally, the analogy between the series of polyacrylates and polymethacrylates also gives the ratios s_1/s_2 (ref. 12): a value of 0.952 has been used for PVC/PBMA and PVC/PAMA blends and 0.90 in the other cases. A variation of this parameter by 10% does not change the curve very much so that the following discussion is not affected by this assumption.

All these parameters are listed in Table 3. Although there are two fitting parameters, X_{12} and Q_{12} , the former has a profound influence on the shape and flatness of the spinodal curve and the second one very little. X_{12} is then chosen to give the best shape of the curve and Q_{12} is then adjusted in order to obtain the proper LCST. The parameters used to fit the curves are also given in Table 3. Figure 4 shows that a satisfactory agreement can be obtained, although the calculated curves are generally broader than the experimental ones (keeping in mind a non-negligible uncertainty of the experimental points). As expected, values of X_{12} and Q_{12} are negative because the miscibility between PVC and polymethacrylates is due to the presence of specific interactions between blend components. The values found for these three systems are not very different indicating quite similar interactions. Also given in Table 3 are the parameters which have been used to simulate the phase diagrams of PVC/PEMA and PVC/PPMA binary mixtures. In both cases, the LCST values are located at approximately 200°C, which is the experimental limit encountered. These simulations confirm the adequacy of the Flory–Prigogine theory in explaining the PVC/polymethacrylate phase diagrams. It is immediately noticed that, in both cases, X_{12} is more negative than in the other cases indicating stronger interactions in these systems.

Finally, let us recall the effect of some important parameters on the simulated curves. The LCST decreases (hence, the miscibility decreases) with an increase of the difference between the α values of the two polymers¹⁰, with an increase of the molecular weight of the polymers, and with a decrease of the ratio r_1/r_2 (V_1^* remaining constant). A decrease of the r_1/r_2 ratio (keeping again V_1^* constant) also shifts the LCST to the component 1 side. This variation is similar to that generated with the Flory–Huggins theory. This result is expected because this variation corresponds to an increase in molecular weight of component 2 (ref. 10). Furthermore, decreasing X_{12} increases the LCST (more miscible) whereas introducing a more negative value of Q_{12} leads to the opposite effect. A variation of X_{12} also influences the shape of the simulated curve, which becomes flatter when X_{12} becomes more negative, whereas the shape and position of the curve are not affected by Q_{12} (ref. 10). Finally, the effect of various other parameters, like γ , the thermal

pressure coefficient, s_1/s_2 , the surface per unit of core volume ratio, have been studied in detail in other publications^{10,12,29}.

CONCLUSIONS

A series of atactic polymethacrylates, with ethyl, n-propyl, n-butyl and n-amyl substituents, was found to be miscible with PVC. Two additional interesting features were noticed. First, the T_g –composition curves give positive deviations, as compared to negative deviations for most systems^{12–15}. These positive deviations can be monitored using the Gordon–Taylor equation (except for the PVC/PEMA system where the deviation is larger) because values of k larger than unity were calculated. It is interesting to note that a similar positive deviation was recently observed by Parmer *et al.*⁸ with poly(cyclohexylmethacrylate)/PVC blends. Second, no phase separation curve can be observed up to 200°C with PVC/PEMA and PVC/PPMA blends, but it occurs at 145, 170 and 100°C with, respectively, PMMA, PBMA and PAMA. There is, therefore, a sort of miscibility window with this polymethacrylate series, the miscibility extending to a much broader temperature range (for similar molecular weight) with ethyl and n-propyl substituents, than with methyl, n-butyl and n-pentyl substituents, as we have suggested before⁶. This behaviour suggests stronger specific interactions with ethyl and n-propyl substituents.

In the simulation of the spinodal curves, it appeared that a good fit of the experimental data (which are not in fact spinodal curves, but quasi-cloud-point curves, and probably located somewhere between the spinodal and the binodal) can only be achieved by using appropriate values of X_{12} and Q_{12} : no satisfactory agreement can be achieved by neglecting Q_{12} . As already mentioned by Sham and Walsh¹², in the Flory–Prigogine theory, X_{12} is considered as a purely enthalpic parameter and does not consider the fact that the stronger the specific interactions, the larger the entropic perturbation. In other words, the larger the specific interactions, the larger the necessary correction brought about by having a negative value of Q_{12} which opposes to miscibility.

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