Influence of the tacticity of poly(methyl methacrylate) on the miscibility with poly(vinyl chloride)

E. J. Vorenkamp, G. ten Brinke, J. G. Meijer, H. Jager and G. Challa

Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands
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It can be concluded from the work of Schurer et al.[10] that poly(vinyl chloride) (PVC) is more miscible with syndiotactic than with isotactic poly(methyl methacrylate) (PMMA). By choosing different molar masses for the various tactic forms of PMMA it is possible to obtain blends with PVC with similar phase behaviour, i.e. in all cases a cloud-point curve with a minimum in the vicinity of 190°C. In this way a more quantitative statement about the influence of the tacticity of PMMA on its miscibility with PVC can be made. One of the principal differences between syndiotactic or atactic PMMA and isotactic PMMA is the higher flexibility of the latter. Using Flory's equation of state theory it will be shown that the effect of this difference is large enough to explain the difference in phase behaviour observed. Heats of mixing of low molar mass analogues were also measured and found to be negative.

INTRODUCTION

Blends of poly(vinyl chloride) (PVC) and a carbonyl-containing polymer are among the most studied polymer systems. Well-known carbonyl-containing polymers include poly(methyl methacrylate) (PMMA) and polyesters like poly(ε-caprolactone) (PCL). A necessary and sufficient condition for miscibility of a two-component system is that the second derivative of the Gibbs free energy with respect to the volume fraction of either component is positive. To fulfil this requirement the free energy of mixing has to be negative, which in turn for mixtures of high molar mass polymers implies that a stable one-phase system can be obtained only if the mixing is exothermic. This follows from the fact that in this case the entropy of mixing is very small positive or even negative (unfavourable).

Basically exothermic mixing may be the result of two essentially different properties. As shown recently[1-3], for blends of a random copolymer and a homopolymer, this requirement is satisfied if the 'repulsion effect' is strong enough. This refers to a situation where the exchange interaction between the two different monomers that make up the copolymer is positive and larger than the two other positive exchange interactions involved. As a result, the net exchange interaction between the two components becomes negative. Mixtures of homopolymers, on the other hand, form stable one-phase systems only if there is some kind of specific interaction. For the system we are dealing with, PVC and PMMA, the presence of a hydrogen bonding type of interaction involving the α-hydrogen of PVC and the carbonyl group of PMMA is expected. In various systems like PVC–PCL[4], PMMA–poly(vinylidene fluoride)[5] and ethylene–vinyl acetate copolymers with chlorinated polyethylene[6], the involvement of the carbonyl group is well established from a shift in the carbonyl infrared absorption frequency.

Besides hydrogen bonding, a dipole–dipole interaction between the carbonyl bond of PMMA and the carbon–chlorine bond of PVC is also possible[7]. However, recent results by Varnell et al.[4] strongly suggest hydrogen bonding to be the principal mode of interaction.

Direct measurements of the heat of mixing of high molar mass polymers are obviously impossible. An alternative way is to perform heat of solution measurements[8]. However, this is a rather inaccurate method, since the heat of mixing wanted is very small and equal to the difference between large heats of solution. A simpler method is to use low molar mass analogues. Walsh et al.[9] used commercial chlorinated paraffins and 1-methylheptyl acetate to model chlorinated polyethylene and ethylene–vinyl acetate copolymers respectively. Walsh et al.[41] used chlorinated octadecane and oligomeric methyl methacrylate as the low molar mass analogues of chlorinated polyethylene and PMMA. We will present similar results using 1,3-dichlorobutane and the methyl ester of iso-butyric acid as low molar mass analogues for PVC and PMMA.

Blends of PVC and PMMA were first studied by Schurer et al.[10], who concluded that PVC was partially miscible with atactic (at) and syndiotactic (st) PMMA but almost completely immiscible with isotactic (it) PMMA. Recently Jager et al.[11] showed that the partial miscibility of PVC and atactic PMMA for temperatures above a certain threshold value is caused by lower critical solution temperature (LCST) behaviour. At lower temperatures the viscosity of the blend is too high to observe equilibrium behaviour. The fact that PVC and at-PMMA are miscible for fairly large amounts of PMMA is of considerable technological importance. As in the case of st-PMMA[10], adding small amounts of at-PMMA to PVC may raise the glass transition temperature (T_g) 10–15°C above the T_g of pure PVC. Their partial miscibility is, furthermore, the reason that block copolymers of poly-

styrene (PS) and PMMA act as very efficient emulsifiers for mixtures of PVC and PS[12].

The main objective of this paper is to consider in more detail the influence of the tacticity of PMMA on the miscibility with PVC, experimentally as well as theoretically. According to the recent theories of polymer mixing, the free energy of mixing consists of three main contributions: the combinatorial entropy of mixing, the exchange interaction and the free-volume contribution. For high molar mass components all three are very small and the observed phase behaviour is the result of a very delicate balance between them. Large changes in behaviour may result from small changes in *any* of these three contributions. Striking examples are known.

In the case of PS–poly(o-chlorostyrene), for instance, a decrease in molar mass of PS from 30 400 to 26 700 turns a partially miscible system into a system that is miscible throughout the entire experimental temperature range from 150 to 400°C. Apparently, this is mainly due to the small increase in the combinatorial entropy of mixing[13].

Examples of cases in which a small change in exchange interaction lead to drastically different phase behaviour are frequently encountered. Usually random copolymers are involved. For instance, a very small change in copolymer composition in the case of blends of poly(2,6-dimethyl-1,4-phenylene oxide) and a random copolymer of o-fluorostyrene and p-chlorostyrene also turns a partially miscible system into a miscible one[14]. Theoretically, a change in copolymer composition corresponds to a different effective exchange interaction contribution[2].

Changing the tacticity of one of the components can also lead to very different phase behaviour. In the case of poly(ethyl methacrylate) (PEMA) and poly(vinylidene fluoride) (PVDF), st-PEMA and at-PEMA are completely miscible with PVDF, whereas it-PEMA is only partially miscible with PVDF[15]. As far as the influence of the tacticity is concerned the PVC–PMMA system behaves in a similar manner, as will be shown. Theoretically, a change in tacticity leads among others to a change in the free volume contribution. Arguments will be given, using Flory's equation of state theory, that this change is sufficiently large to explain the difference in phase behaviour between PVC and the various tactic forms of PMMA.

EXPERIMENTAL

Materials

Two commercial atactic poly(methyl methacrylate) samples were used: at-PMMA-1 was obtained from ICI (Diakon MO 900) and at-PMMA-2 from Aldrich as a so-called secondary standard. Poly(vinyl chloride) was a commercial product obtained from Péchiney et St. Gobain (Lucovyl RB 8010). The isotactic poly(methyl methacrylate) samples were obtained by fractionation of the crude product of a Grignard synthesis using phenylmagnesium bromide as initiator in toluene at 25°C, following the procedure of Goode *et al.*[16]. The fractionation was performed by repeated precipitation from acetone solution in methanol at decreasing temperatures. The syndiotactic poly(methyl methacrylate) samples were obtained by methylation with diazomethane of syndiotactic poly(methacrylic acid) (st-PMAA). The st-PMAA was obtained by Co-60

radiation polymerization of the monomer in isopropyl alcohol[17,18].

The molar masses were determined by g.p.c. (Waters alc/gpc 150 C) using THF as an eluent, relative to polystyrene standards. The Mark–Houwink constants used for PVC were: $K = 1.5 \times 10^{-2}$ cm^3 g^{-1}, $a = 0.77$; for PMMA: $K = 8 \times 10^{-2}$ cm^3 g^{-1}, $a = 0.75$ and for PS: $K = 1.14 \times 10^{-2}$ cm^3 g^{-1}, $a = 0.72$. *Table 1* contains the molar masses of the samples used.

The tacticities of the PMMA samples were determined from 5% solutions in o-dichlorobenzene at 160°C by 60 MHz n.m.r. spectroscopy with a Jeol C-60 HL instrument. For the isotactic and syndiotactic samples the percentage of isotactic and syndiotactic triads respectively exceeded 95%.

Preparation of blends

Blends of PVC and PMMA were prepared in two different ways: solution-blending and melt-mixing. The latter was carried out only for atactic PMMA. Solution-blending was performed by casting 3 wt% mixed solutions in butanone-2 on a hot plate (30°C). The films obtained were dried in vacuum for 24 h at room temperature. To remove the last traces of solvent the samples were kept at 120°C for 2 h under vacuum. Melt-mixing was performed as described previously by Schurer *et al.*[10]. To counteract degradation of PVC, 1 wt% stabilizer, di-n-octyltin-S,S'-bis(iso-octylmercaptoacetate) (Ciba-Geigy), based on PVC, was added to all blends.

Glass-transition

The glass-transition temperatures were measured with a Perkin-Elmer differential scanning calorimeter (DSC-2) at a heating rate of 10°C min^{-1}, using a liquid N$_2$ cooling device and a scanning auto-zero. The onset of the specific heat jump was taken as the glass transition temperature, T_g.

Cloud-point determination

Phase boundaries were determined by light scattering on thin films which were directly cast on to glass microscope slides. A modified Cenco-TNO lightscattering photometer, equipped with a heating block, which could be controlled electrically, was used with a heating and cooling rate of 4°C min^{-1}. The scattering angle was 30°.

Heats of mixing

The heats of mixing of low molar mass analogues were measured at 30°C with a Setaram Calvet-type microcalorimeter.

Table 1 Molar masses of polymers used

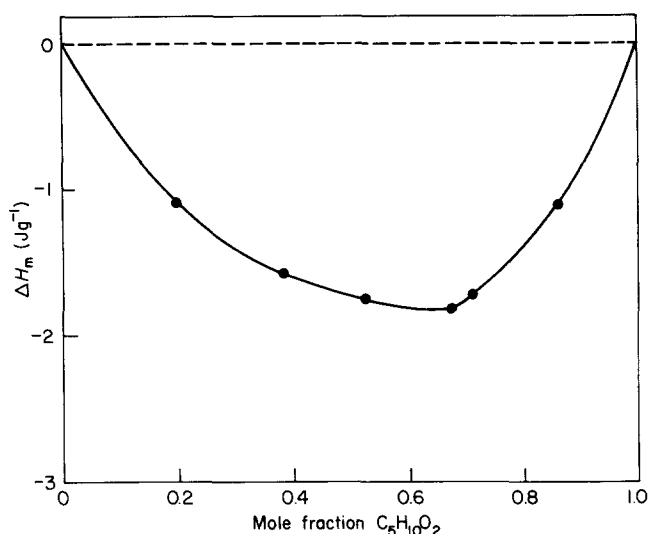|	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PVC	7.5 × 10^4	3.6 × 10^4	2.08
at-PMMA-1	10.0 × 10^4	4.5 × 10^4	2.22
at-PMMA-2	8.0 × 10^4	3.8 × 10^4	2.11
st-PMMA	9.1 × 10^4	5.3 × 10^4	1.72
it-PMMA-1	1.75 × 10^4	0.73 × 10^4	2.40
it-PMMA-2	0.8 × 10^4	0.41 × 10^4	1.95
it-PMMA-3	0.3 × 10^4	0.2 × 10^4	1.50

Figure 1 Plot of heat of mixing against composition for mixtures of 1,3-dichlorobutane with the methyl ester of isobutyric acid

RESULTS AND DISCUSSION

Heat of mixing

As the low molar mass analogues of PVC and PMMA we took 1,3-dichlorobutane, CH_3-$CHCl$-CH_2-CH_2Cl, and the methyl ester of isobutyric acid, CH_3-CH $(CH_3)(COOCH_3)$. The heats of mixing, ΔH_m, obtained with a microcalorimeter are presented in *Figure 1* as a function of mole fraction $C_5H_{10}O_2$. Mixing is exothermic, in agreement with the observations of Walsh et al.[40,41] that heats of mixing for oligomeric PMMA and chlorinated octadecanes are negative for a sufficiently large degree of chlorination (>43.2 wt% Cl). The absolute value of ΔH_m is largest for a composition corresponding to an approximately equimolar α-$H/C{=}O$ ratio. Expressed in joule per gram mixture it is somewhat larger than found by Walsh et al.[9] for chlorinated paraffins and 1-methylheptyl acetate. This was expected because the number of interacting groups is larger in our case.

Whether low molar mass analogues can model high molar mass mixtures accurately is an open question. Assuming a similar composition dependence of ΔH_m for PVC and PMMA as found for the low molar mass analogues, one expects that mixing should improve for increasing weight fractions of PMMA. In reality, as will be shown, exactly the opposite is found experimentally.

LCST behaviour

PVC–atactic PMMA. The phase behaviour in blends of PVC with atactic PMMA was investigated first by Schurer et al.[10] and more recently by Jager et al.[11]. Here we will summarize only those of their results which are pertinent to the subject of this paper: observation and explanation of the influence of the tacticity of PMMA on the phase behaviour in blends with PVC. It was shown that PVC and at-PMMA-1 form a homogeneous blend with a single glass-transition temperature if prepared from a suitable solution. Heating the sample resulted in phase separation above 190°C for compositions exceeding 60 wt% PMMA. Below 60 wt% PMMA no phase separation was observed. A decrease in temperature did not result in remixing of the phase-separated samples, most likely because of the high viscosity of the blend. To

circumvent this problem, an atactic PMMA of a somewhat lower molar mass was chosen (at-PMMA-2). Now a cloud-point curve was found with a minimum just above 190°C for approximately 70 wt% PMMA. Because of the relatively high value of this minimum, compared with the T_g of each component, it was possible to observe an equilibrium behaviour, i.e. demixing upon heating followed by mixing upon cooling. The cloud-point curve for PVC/at-PMMA-2 is presented in *Figure 2*. An interesting feature is the location of the phase boundary in the PMMA-rich side of the phase diagram. Based on the simple Flory–Huggins theory and the very similar molar masses of both components, a more symmetric cloud-point curve location was expected. This deviating behaviour was observed previously for blends of isotactic poly(ethyl methacrylate) and poly(vinylidene fluoride)[15]. It is called an irregular asymmetry and will be discussed more fully in the model calculation section.

PVC–syndiotactic PMMA

Based on the work of Schurer et al.[10], it was expected that an increase in syndiotactic triads would improve the miscibility with PVC. To confirm this a st-PMMA sample of a somewhat higher molar mass than at-PMMA-2 was
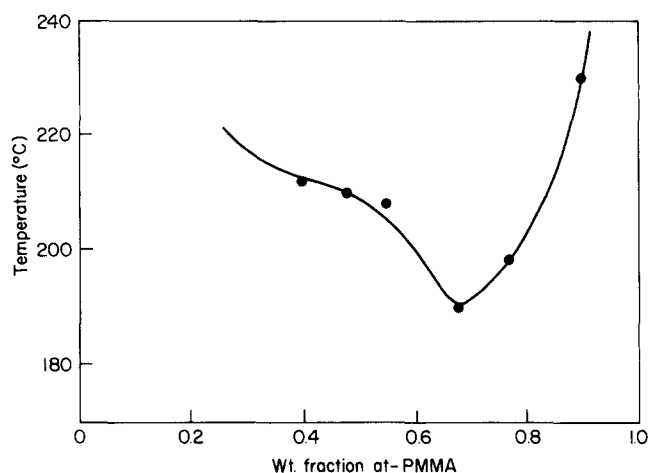

Figure 2 Cloud-point curve for blends of PVC and at-PMMA-2. ($M_w \simeq 80\,000$)
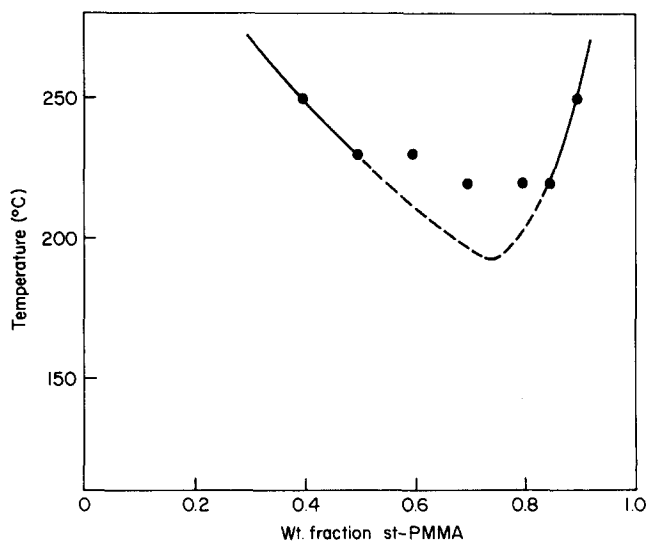

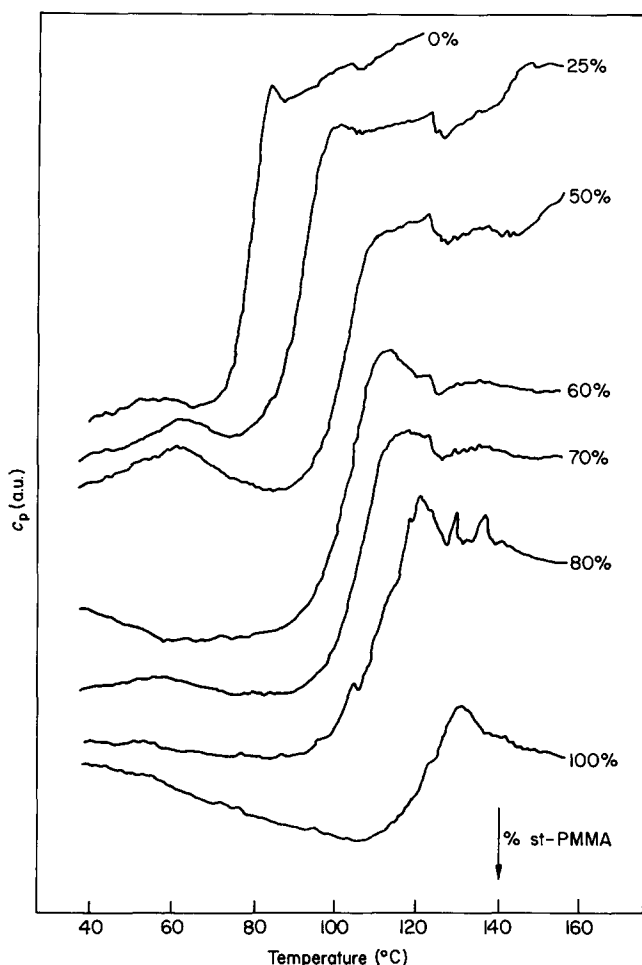**Figure 3** Cloud-point curve for blends of PVC and st-PMMA. ($M_w \simeq 91\,000$)

Figure 4 Thermograms for blends of PVC and st-PMMA before annealing

has a much lower T_g (40°C), giving rise to a higher mobility in the melt, but also because lower molar masses have to be used. It was already known from the work of Schurer *et al.*[10] that at about 180°C PVC is immiscible at almost all compositions with high molar mass isotactic PMMA samples. *Figure 7* presents the cloud-point curves for three different samples of rather low molar masses, 3000, 8000 and 17 500 respectively. For the last sample it was again
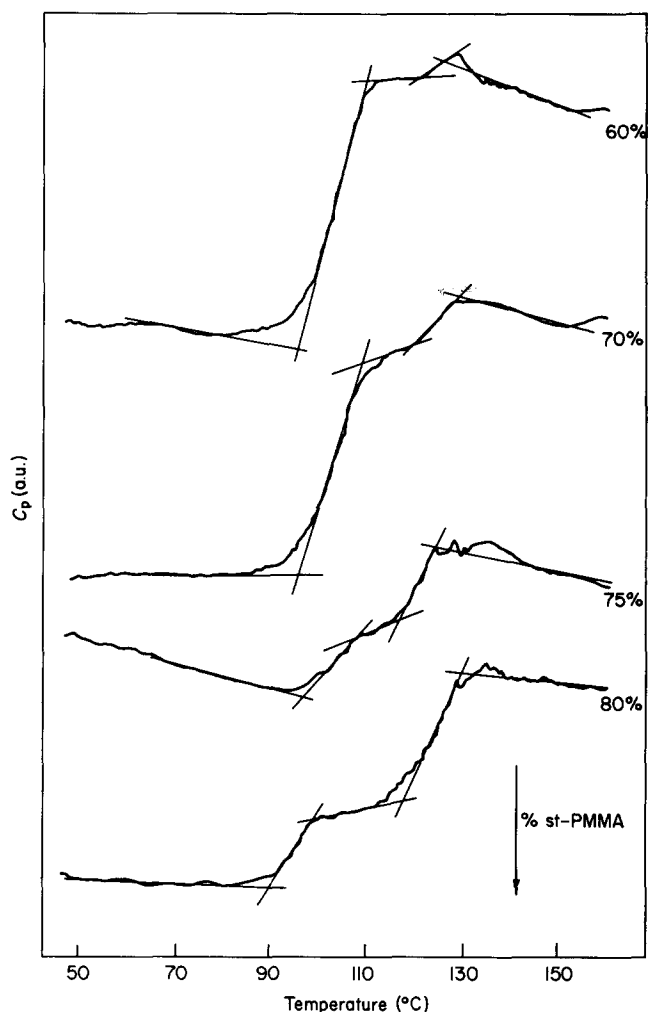
chosen. In this blend the viscosity threshold temperature, below which equilibrium behaviour could no longer be observed, was estimated to be at about 230°C, compared with 190°C for atactic PMMA. *Figure 3* presents the cloud-points found upon heating from homogeneous blends obtained by solution-blending. Most points do not represent the equilibrium situation, which is obvious from their location and supported by the fact that, experimentally, demixing upon heating is not followed by mixing upon cooling. The possible equilibrium cloud-point curve is indicated by the dotted line. Again the same irregular asymmetry as for at-PMMA is found. The miscibility of st-PMMA with PVC is confirmed to be somewhat better than that of at-PMMA. *Figure 4* shows the thermograms of the blends which were obtained by solvent blending and were never heated above 120°C. Clearly a single composition-dependent T_g is found. *Figure 5* shows the thermograms of the same blends after annealing for 5 min at 240°C. In this case two T_g's, indicative of phase separation, appear at compositions in between 60 and 90 wt% st-PMMA. The T_g-values of all blends before and after annealing are given in *Figure 6*. The results obtained by these annealing experiments are in complete agreement with the light scattering results.

PVC–isotactic PMMA

Of the different tactic forms of PMMA, isotactic PMMA offers the best prospects of observing equilibrium behaviour, in the first place, because the isotactic sample

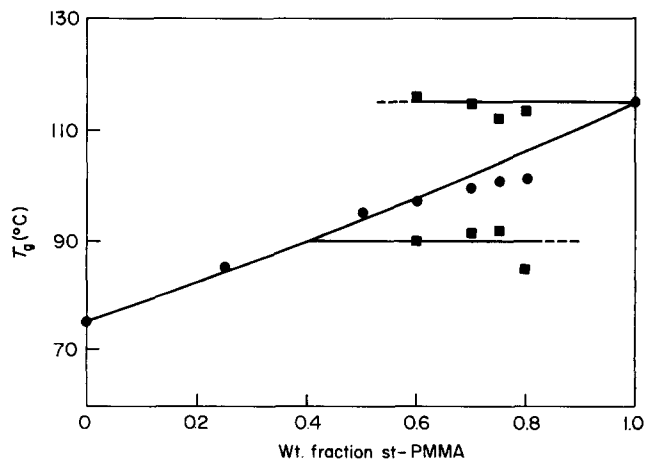**Figure 5** Thermograms for blends of PVC and st-PMMA after annealing at 240°C for 5 min

Figure 6 Glass transition temperatures vs. composition for blends of PVC and st-PMMA before (●) and after annealing (■) at 240°C for 5 min
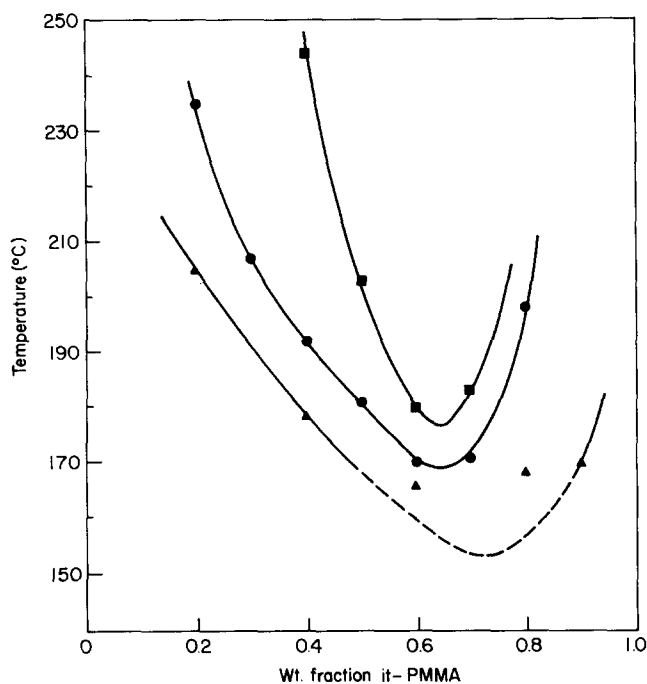
Figure 7 Cloud-point curves for blends of PVC and it-PMMA-1 (▲), it-PMMA-2 (●) and it-PMMA-3 (■) respectively.

not possible to observe equilibrium behaviour at all compositions. The viscosity threshold was found to be at approximately 165°C, which is somewhat lower than for the systems discussed before. The minimum of the cloud-point curves of the two lowest molar mass samples was above 165°C and for these samples phase separation and remixing upon heating and cooling with a rate of 4°C min^{-1}, respectively, occurred at all compositions very rapidly. The T_g of the blend with it-PMMA-2 is plotted against composition in *Figure 8*.

The main results of these light scattering experiments can now be summarized: In order to have a cloud-point curve with a minimum at 180–200°C, molar masses of about 91 000, 80 000 and 3000 for syndiotactic, atactic and isotactic PMMA respectively have to be used. This result clearly demonstrates that miscibility improves as a function of the syndiotactic triads content. In addition it was found that the viscosity threshold temperature, below which equilibrium behaviour could no longer be observed, occurred at 230, 190 and 165°C for the syndiotactic, atactic and isotactic PMMA samples respectively. This is in line with the differences in T_g and molar mass of the PMMA samples used.

Model calculation

Dielectric[20], acoustic[21] and n.m.r.[22,23] relaxation data for the various tactic forms of PMMA all show that the isotactic chain is more flexible than the syndiotactic chain. Moreover, Quach et al.[24] showed that the thermal expansion coefficient, the internal pressure and the reduction in internal energy upon compression are all larger for isotactic PMMA than for conventional PMMA. The effect of stereo-regularity on the compressibility in the liquid state is minimal. These results are in qualitative agreement with the existence of a weaker molar cohesion and/or greater chain flexibility, and closer packing in the isotactic polymer[24]. It is well known[25,26] that the difference in thermal expansivity between two polymers is a

very important factor in determining their mutual miscibility. Therefore, an obvious question to be asked is whether the difference in thermal expansivity between the various tactic forms of PMMA, alone, might be responsible for the difference in mixing behaviour with PVC observed. That this is indeed the case will be shown by a simple model calculation using Flory's equation of state theory[25].

Flory based his theory on an assumption of Prigogine[27] stating that the degrees of freedom of a polymer segment can be separated into internal and external degrees of freedom. The latter number is denoted by $3c$ with c in general smaller than one. For a system of the same molecules the equation of state is

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3}-1) - 1/(\tilde{v}\tilde{T}) \tag{1}$$

where $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$ and $\tilde{v} = v/v^*$. P^*, T^* and v^* are the characteristic pressure, temperature and volume respectively. They can be calculated from a knowledge of the thermal expansion coefficient α, the thermal pressure coefficient γ and the specific volume. In the low pressure approximation valid at atmospheric pressure, the necessary relations are given by

$$\tilde{v} = (1 + \alpha T/[3(1 + \alpha T)])^3 \tag{2}$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{3}$$

$$P^* = \gamma T \tilde{v}^2 \tag{4}$$

Extension to mixtures requires a set of combining rules. Basically mixing is assumed to be random between segments of equal hard core volume. Here the underlying assumption is also the additivity of the hard core volumes of both components. The interactions are supposed to take place between the surfaces of adjoining segments. In this way the number of interacting contacts of chain segments are (as suggested long ago by Staverman[28]) proportional to their specific surface area. This leads to a Flory–Huggins χ-parameter, which will in general be concentration dependent[29,30]. The mean intermolecular energy is taken to be inversely proportional to volume. As shown by Sanchez and Lacombe[31] this assumption is correct as long as the intermolecular potential is sufficiently short range. The exchange interactions are described by an interaction parameter X_{12}. In addition a non-combinatorial entropy parameter Q_{12} is introduced as an adjustable parameter, often necessary to obtain more quantitative agreement with experimental observa-
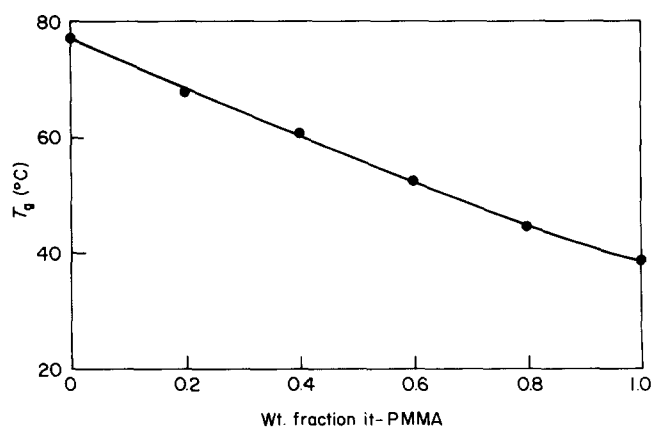

Figure 8 Glass transition temperatures vs. composition for blends of PVC and it-PMMA-2

tions[24]. In this study Q_{12} will be ignored. The equation of state for mixtures is in form identical to equation (1) provided the characteristic quantities for a mixture are defined by

$$P^* = \varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1 \theta_2 X_{12} \qquad (5)$$

$$\tilde{T} = T/T^* = (\varphi_1 \tilde{T}_1 P_1^* + \varphi_2 \tilde{T}_2 P_2^*)/P^* \qquad (6)$$

where φ_1 and φ_2 are the segment fraction of component 1 and 2 respectively, and θ_2 is the surface fraction of component 2. At atmospheric pressure, the spinodal of a binary mixture is given by[13,19]

$$1/(r_1 \varphi_1) + 1/(r_2 \varphi_2) - (2v^*/kT)(s_2/\bar{s})^2 (s_1/\bar{s}) X_{12}/\tilde{v}$$

$$- \left(\frac{\partial \tilde{v}}{\partial \varphi_1}\right)_{P,T} \{(c_1 - c_2)/[\tilde{v}^{2/3}(\tilde{v}^{1/3} - 1)]\}$$

$$- (v^*/kT\tilde{v}^2)[P_1^* - P_2^* - (s_2/\bar{s})(\varphi_2 - \theta_1)X_{12}]\} = 0 \qquad (7)$$

where component 1 and 2 have r_1 and r_2 segments of equal hardcore volume v^* and surface areas s_1 and s_2 respectively. $\bar{s}$ is defined by

$$\bar{s} = \varphi_1 s_1 + \varphi_2 s_2 \qquad (8)$$

As is clear from the foregoing, any application of the equation of state theory requires experimental data for the density, the thermal expansion coefficient α and the thermal pressure coefficient γ or compressibility β. The P-V-T properties of isotactic PMMA were thoroughly investigated by Quach et al.[24]. Conventional PMMA was investigated by Hellwege et al.[32] and by Heydemann and Guicking[33]. Reasonable values for α, γ and v at 120°C are presented in Table 2. This table also contains values for the characteristic quantities P^* and T^* and for the number of external degrees of freedom c calculated from equations (2)–(4) and from

$$c = P^* v^*/kT^* \qquad (9)$$

According to the equation of state theory the characteristic quantities are defined by[25]

$$T^* = s\eta/(2v^*ck) \qquad (10)$$

$$P^* = s\eta/(2v^{*2}) \qquad (11)$$

where η is a constant characterising the energy of interaction for a pair of neighbouring sites of the pure component. The higher flexibility of isotactic PMMA compared with conventional PMMA is therefore reflected in a lower value of T^* and a larger value of c of the former. The larger value of P^* for isotactic PMMA compared with conventional PMMA indicates that the larger expansion factor should be ascribed to flexibility rather than reduced cohesion, a conclusion reached before by Quach et al.[24].

The situation for PVC is less clear. Again the thermal expansion deserves most attention. Simha and Boyer[34]

quote a value of $5.18 \times 10^{-4} \text{ K}^{-1}$ for α. Dunlop[35], on the other hand, showed that PVC plasticized with phthalates and sebacates had in general a lower expansion coefficient than the abovementioned one. The thermal expansion coefficient, moreover, increased with increasing amounts of plasticizer. This suggests a smaller value for the thermal expansion coefficient of PVC. This conclusion seems to be confirmed by recent results of Rostami and Walsh[36] on chlorinated polyethylenes. Using a procedure described by Orwoll and Flory[37], a value of about $3.6 \times 10^{-4} \text{ K}^{-1}$ for the thermal expansion coefficient of a chlorinated polyethylene with a content of 52.65 wt% Cl was found. Based on these observations a value of $5 \times 10^{-4} \text{ K}^{-1}$ was chosen for α of PVC. The density and the thermal pressure coefficient are less important quantities and were taken from ref. 33. As can be seen from *Table 2* the flexibility of PVC is lower than the flexibility of isotactic and conventional PMMA.

According to the original Flory–Huggins theory, the difference in chemical potential of component 1 between the pure state and the mixture is given by

$$\Delta\mu_1/kT = \ln \varphi_1 + [1 - r_1/r_2]\varphi_2 + \chi_{12}\varphi_2^2 \qquad (12)$$

where χ_{12} is the Flory–Huggins parameter. Identifying this expression with the corresponding expression of the equation of state theory leads to a relation between χ_{12} and X_{12}[38]

$$\chi_{12}(\varphi_1) = (3c_1/\varphi_2^2) \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]$$

$$+ (v^*/kT\varphi_2^2)[P_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + \theta_2 X_{12}/\tilde{v}] \qquad (13)$$

where the concentration dependence of χ_{12} is explicitly indicated. As shown by Eichinger and Flory[29] this concentration dependence is, within the equation of state theory, almost completely due to the assumed proportionality between the number of interacting contacts of chain segments and their specific surface area, i.e. the last term of equation (13). A smaller part is caused by the free-volume contribution. Koningsveld et al.[39] argued that various other factors, not incorporated in the equation of state theory, like non-uniform segment density and difference in chain flexibility, can lead to additional concentration dependence. For a χ-parameter which varies only slightly with concentration the critical composition will be rich in the component with the shortest chain length. As shown before, for the system PVC–it-PMMA this is indeed the case. However, the systems of PVC with atactic PMMA and syndiotactic PMMA have a cloud-point curve with a so-called irregular asymmetry. As is well known[19,30], such behaviour can be the result of the combination $s_1/s_2 < 1$ and $X_{12} < 0$, where PVC is component 1. In our case the condition $X_{12} < 0$ holds because of the specific interactions whereas $s_1/s_2 < 1$ follows from the geometry of the chain molecules. Zhikuan et al.[40] reported a value of 0.94 of the latter ratio for chlorinated polyethylene with a content of 51.6 wt% chlorine and PMMA. In order to obtain reasonable agreement between the simulated spinodal and the observed cloud-point curve for the PVC-at-PMMA system a value of about 0.8 had to be used. Since, as has been said before, there are several other factors, not taken into account by the equation of state theory, which can lead to additional concentration dependence, this value is considered to be acceptable. To predict an $LCST$ near 190°C for a molar mass of at-PMMA of 80 000 a value of

Table 2

	$\alpha \times 10^3$ (K^{-1})	γ (cal cm^{-3})	v $(\text{cm}^3 \text{ g}^{-1})$	P^* (cal cm^{-3})	T^* (K)	c
PVC	0.500	0.272	0.740	142	8809	0.51
at-PMMA	0.580	0.267	0.870	150	8075	0.59
it-PMMA	0.615	0.280	0.863	160	7788	0.66

[a] Mixture properties: $s_1/s_2 = 0.8$, $X_{12} = -0.1 \text{ cal cm}^{-3}$, $Q_{12} = 0$
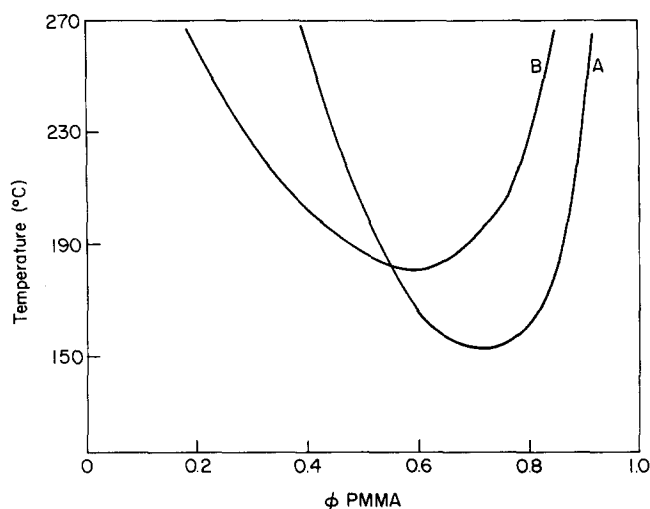
Figure 9 Simulated spinodals for blends of PVC and it-PMMA-2 (curve A) and PVC and at-PMMA-2 (curve B)

-0.1 cal cm^{-3} for X_{12} was required. *Figure 9* shows the calculated spinodal. The same values were taken for the PVC–it-PMMA system. The calculated spinodal for a molar mass of 8000 of it-PMMA is also presented in *Figure 9*. Both spinodals closely resemble the observed cloud-point curves shown in *Figures 2* and *7* respectively and clearly demonstrate that the difference in flexibility between the various tactic forms of PMMA, alone, might be responsible for the difference in phase behaviour with PVC observed. There is no need to invoke any difference in strength of the specific interactions.

According to the equation of state predictions, the *LCST* in the PVC–it-PMMA system is more sensitive to a change in molar mass of it-PMMA than observed experimentally. Theoretically an increase in molar mass from 8000 to 10 000 shifts the *LCST* downwards to about 100°C, whereas a decrease in molar mass to 6000 results in an *LCST* at 220°C. In these calculations the P-V-T properties were kept the same for all molar masses. In reality, however, a lower value of the molar mass of it-PMMA, in the molar mass range employed, will result in a higher expansivity, which in turn will lead to more unfavourable free-volume contributions. Consequently the *LCST* will be lower than expected on the basis of the chain length reduction. By varying the thermal expansion coefficient of it-PMMA with molar mass it was possible to obtain an indication of the influence and likelihood of this effect. *Figure 10* shows that the simulated spinodals for PVC with it-PMMA-3 and it-PMMA-1 are in good agreement with the experimental observations presented in *Figure 7* provided α is taken to be 0.650×10^{-3} K^{-1} and 0.600×10^{-3} K^{-1} respectively. Compared with the molar mass dependence reported by Orwoll and Flory[37] for the thermal expansion coefficient of n-alkanes, the above variations seem very reasonable indeed. Additional support is provided by the fact that the thermal expansion coefficient of oligomeric methyl methacrylate ($\bar{M}_n = 434$) equals 0.976×10^{-3} K^{-1} [40].

CONCLUSIONS

Isotactic PMMA was found to be miscible with PVC for relatively low molar masses only. For atactic and syndiotactic PMMA much higher molar masses could be

tolerated. Within the framework of Flory's equation of state theory it was possible to attribute this difference in phase behaviour to the free-volume contribution. Clearly other explanations are possible. Huggins[42], for instance, introduced another way of including differences in flexibility in a lattice type theory. One could also speculate about the influence of the difference in conformation and radius of gyration of the various tactic forms of PMMA on the total number and strength of the exchange interactions. Nevertheless, we believe the difference in free-volume to be one of the principal reasons for the difference in phase behaviour observed.

An indication that other factors not properly taken into account by the equation of state theory are important is given by the irregular asymmetry for blends of PVC with at-PMMA or st-PMMA. We modelled it by treating the ratio of the specific surface areas s_1/s_2 more or less as an adjustable parameter. This seemed to be justified by the fact that our main interest is the temperature location of the minimum of the phase boundary for the various tactic forms of PMMA. The choice made for s_1/s_2 implies that, as far as the exchange interaction is concerned, mixing is more favourable for increasing amounts of PVC. The heat of mixing results of the low molar mass analogues, on the other hand, suggest that mixing should improve for higher contents of PMMA. Hence, unlike Walsh et al.[9], who found that heat of mixing results for 2-octyl acetate and commercial chlorinated paraffins compared favourably with the asymmetrical cloud-point curves for mixtures of chlorinated polyethylene with vinyl acetate copolymers, we are unable to combine both observations. Zhikuan et al.[41] measured cloud-point curves for blends of PMMA and chlorinated polyethylene (CPE) (49.8 and 51.6 wt% Cl). The minima also occurred at the PMMA rich side of the phase diagram. However, the molar mass of PMMA is smaller than the molar mass of CPE and the asymmetry is, just as in our case of PVC and it-PMMA, as expected.
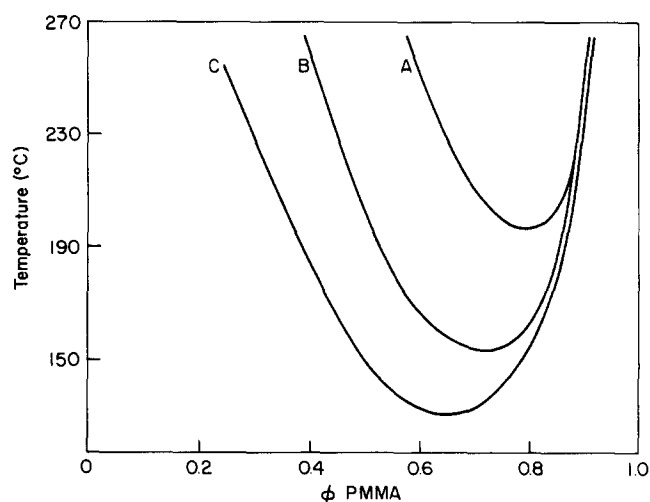
Figure 10 Simulated spinodals for blends of PVC and it-PMMA, for various molar masses and thermal expansion coefficients of the latter. Curve A: $M_w = 3000$ and $\alpha = 0.650 \times 10^{-3}$ K^{-1}. Curve B: $M_w = 8000$ and $\alpha = 0.615 \times 10^{-3}$ K^{-1}. Curve C: $M_w = 17\,500$ and $\alpha = 0.600 \times 10^{-3}$ K^{-1}

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