Shear-induced phase changes in polymer blends

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The phase behaviour of polymer blends exposed to shear is analysed in terms of a mean-field theory. One result of the theory is that shear-induced phase changes depend on the stored elastic excess energy. For a negative stored excess energy the miscibility region of the system is enlarged. The shift of the binodal for blends for poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile) undergoing shearing flow is determined by light-scattering experiments. It has been found for these blends that shear flow elevates phase-separation temperatures.

(Keywords: polymer blends; shear-induced phase changes; copolymers; binodals; interaction parameters; elastic free energy)

INTRODUCTION

Shear-induced phase transitions in polymer solutions[1–4] as well as in polymer blends[5,6] have been studied to some extent. The phase behaviour of polymer mixtures is influenced by shear. However, different studies result in apparently conflicting observations. For example, investigations of dilute polymer solutions exhibiting upper critical solution temperatures (*UCST*) indicate that the *UCST* is shifted to higher temperatures by stress or, in other words, phase separation is triggered by flow[3,4]. In contrast, the results submitted in refs. 1 and 2 demonstrate a shear-dependent *UCST* depression in polymer solutions. For miscible polymer blends with a lower critical solution temperature (*LCST*) the system subjected to shear remains homogeneous above the *LCST*, i.e. the critical temperature ascends under flow.

So far as the authors are aware, there have been a number of attempts based chiefly on thermodynamics to explain theoretically the effect of shear on the phase behaviour of mixtures[7,8]. In principle, the explanation of shear-dependent phase behaviour is straightforward. If a system exposed to shear can store energy, then an additional contribution to the free energy results. For mixtures one may distinguish different situations depending on the variation of the stored energy as a function of composition:

(i) The stored energy of the mixture is the sum of the stored energies of the respective components (additivity); then there is no additional contribution to the free energy of mixing, i.e. the phase behaviour is unchanged.

(ii) The mixture exhibits negative (positive) deviation of the stored energy from additivity; then a negative (positive) contribution to the free energy results leading to an extended (reduced) region of miscibility.

(iii) For an S-shaped dependence of the stored energy on concentration, flow induces miscibility in a certain range of concentration and phase separation in the remaining range.

It should be noticed here that the influence of shear on the phase behaviour is especially relevant to miscible polymers, which in the vast majority exhibit a *LCST*. As discussed above, the binodal is then shifted a few degrees to higher or lower temperatures, respectively. This effect of shear may also be of practical importance for the processing of some polymer blends. However, it should be mentioned that completely immiscible polymers remain vastly immiscible also under shear. Deviations could be only observed in systems exposed to extreme shearing conditions[9].

In the present paper, the mean-field theory[10] describing the phase behaviour of polymer blends will be extended to account for the effect of shear flow on the phase behaviour. We then report a shear-flow experiment on the system poly(methyl methacrylate) (PMMA) blended with poly(styrene-*co*-acrylonitrile) (SAN), which gives as a result the variation of the binodal as a function of shear rate.

THEORY

In polymer systems shear flow leads to changes of the chain conformation. This rearrangement of chain molecules affects the Gibbs free energy of mixing and hence the phase behaviour. After the flow ceases, this effect disappears; therefore, it is an elastic free-energy contribution. As is well known, in a viscoelastic fluid differences develop in the normal stress components parallel and perpendicular to the flow. Only the differences in the normal stresses have rheological significance. Chain molecules are deformed under flow, which corresponds to an entropy change. This entropy reduction is produced by the difference in the normal stresses. As a result, the additional term to the Gibbs free energy caused by flow under steady-state conditions can be related in a good approximation to the first normal stress difference N_1 of the polymer system[11,12]:

$$G_{\mathrm{el}}=\frac{1}{2}VN_1 \qquad (1)$$

where V is the molar volume of the system. Introducing

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into equation (1) the reduced state variables $\tilde{T}$, $\tilde{P}$ and $\tilde{V}$ defined by:

$$\tilde{T} \equiv T/T^* \qquad \tilde{V} \equiv V/V^* \qquad \tilde{P} \equiv P/P^* \tag{2}$$

where the starred quantities are constant reference parameters, it follows that:

$$\frac{G_{\mathrm{el}}}{RT} = \frac{1}{2}\frac{V^*P^*}{RT^*}\frac{\tilde{V}\tilde{N}_1}{\tilde{T}} \tag{3}$$

Here $\tilde{N}_1 \equiv N_1/P^*$ is the reduced normal stress difference. For a polymer mixture one has to take into account that the normal stress difference is a function of composition. It is appropriate to assume here that N_1 of the mixture follows the simple but adequate relationship:

$$\tilde{N}_1 = \tilde{N}_{1\mathrm{A}}\phi_{\mathrm{A}} + \tilde{N}_{1\mathrm{B}}\phi_{\mathrm{B}} + \Delta\tilde{N}_1\phi_{\mathrm{A}}\phi_{\mathrm{B}} \tag{4}$$

where $\tilde{N}_{1i}$ and ϕ_i represent the (reduced) normal stress difference and the volume fraction of pure component i, respectively, $\Delta\tilde{N}_1$ describes the deviation of the normal stress difference of the mixture from additivity and depends on the rate of shear.

In steady shearing flow the first normal stress difference can be correlated to the shear rate $\dot{\gamma}$:

$$N_1 = \Psi_1(\dot{\gamma})\dot{\gamma}^2$$

where the 'material function' $\Psi_1(\dot{\gamma})$ is called the first normal stress function.

According to the Rouse–Zimm model[13,14] the first normal stress difference may be related to the storage modulus G'. Taking into account only the longest relaxation time τ_{t} one gets:

$$G' = G_{\mathrm{N}}^0\frac{(\dot{\gamma}\tau_{\mathrm{t}})^2}{1+(\dot{\gamma}\tau_{\mathrm{t}})^2} \qquad N_1 = 2G_{\mathrm{N}}^0(\dot{\gamma}\tau_{\mathrm{t}})^2$$

where G_{N}^0 is the plateau modulus. The relation between N_1 and G' depends on the magnitude of the quantity $\dot{\gamma}\tau_{\mathrm{t}}$:

$$N_1 = 4G' = 2G_{\mathrm{N}}^0 \qquad \text{for} \qquad \dot{\gamma}\tau_{\mathrm{t}} = 0(1)$$

$$N_1 = 2G' \qquad \text{for} \qquad \dot{\gamma}\tau_{\mathrm{t}} \ll 1$$

As can be seen, determination of the plateau modulus as a function of the blend composition yields ΔG_{N}^0, which is closely related to ΔN_1.

Using equations (3) and (4) to calculate the elastic free energy of mixing caused by shear, it follows that:

$$\frac{\Delta G_{\mathrm{el}}^{\mathrm{M}}}{RT} = \frac{1}{2}\frac{V_{\mathrm{A}}^*P_{\mathrm{A}}^*}{RT_{\mathrm{A}}^*}\frac{\tilde{V}_{\mathrm{A}}}{\tilde{T}_{\mathrm{A}}}\Delta\tilde{N}_1\phi_{\mathrm{A}}\phi_{\mathrm{B}} \tag{5}$$

Employing[10]:

$$-\frac{U}{RT} = \frac{P^*V^*}{RT^*}\frac{1}{\tilde{T}\tilde{V}} \tag{6}$$

one obtains for equation (5):

$$\frac{\Delta G_{\mathrm{el}}^{\mathrm{M}}}{RT} = -\frac{1}{2}\frac{U_{\mathrm{A}}}{RT}\tilde{V}_{\mathrm{A}}^2\Delta\tilde{N}_1\phi_{\mathrm{A}}\phi_{\mathrm{B}} \tag{5a}$$

where U_{A} is the molar configurational energy of component A.

The Gibbs free energy of mixing for a binary polymer blend in the absence of flow may be expressed as:

$$\frac{\Delta G^{\mathrm{M}}}{RT} = \frac{\phi_{\mathrm{A}}}{r_{\mathrm{A}}}\ln\phi_{\mathrm{A}} + \frac{\phi_{\mathrm{B}}}{r_{\mathrm{B}}}\ln\phi_{\mathrm{B}} + X\phi_{\mathrm{A}}\phi_{\mathrm{B}} \tag{7}$$

where r_i is the degree of polymerization of component i. The free-energy parameter X is given according to the mean-field theory by[10,15]:

$$X = -\frac{U_{\mathrm{A}}}{RT}2X_{\mathrm{AB}} + \frac{C_{V\mathrm{A}}}{R}\frac{7}{8}\Gamma^2 \tag{8}$$

($C_{V\mathrm{A}}$ being the molar heat capacity.) The parameters X_{AB} and Γ represent the interaction and free-volume contribution, respectively, to the free-energy parameter X, whereas the prefactors govern the temperature dependence of these effects as can be seen already from equation (6). Applying Flory's equation of state[16]:

$$\tilde{T} = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \tag{9}$$

where $\tilde{V}^{1/3}$ varies in the range 1 to $\frac{4}{3}$, analogously to equation (6) one can also replace the heat capacity by the reduced volume:

$$\frac{C_{V\mathrm{A}}}{R} = \frac{\tilde{V}_{\mathrm{A}}^{1/3}}{\frac{4}{3} - \tilde{V}_{\mathrm{A}}^{1/3}} \tag{6a}$$

Adding the elastic energy (5a) to equation (7), for X, instead of (8), it follows that:

$$X = -\frac{U_{\mathrm{A}}}{RT}(2X_{\mathrm{AB}} + \tfrac{1}{2}\Delta\tilde{N}_1\tilde{V}_{\mathrm{A}}^2) + \frac{C_{V\mathrm{A}}}{R}\frac{7}{8}\Gamma^2 \tag{10}$$

For high-molar-mass polymers to be miscible the free-energy parameter X must be negative. As can be seen from equation (8) the second term, the free-volume term, is always positive. Therefore, polymer miscibility can only occur if the interaction term or X_{AB} is negative. In the approximation represented by equation (10) the stress term is associated solely with the interaction contribution to the parameter X. Shear does not in that approximation cause any change of the free-volume term. Therefore, equation (10) indicates that flow corresponds to an additional (shear-rate-dependent) interaction. For negative deviations of N_1 from additivity, i.e. $\Delta\tilde{N}_1 < 0$, a polymer blend exposed to shear feels a stronger attraction between the different segments leading to enhanced miscibility between the two components. This shear homogenization originates from an additional ordering in the system leading to favourable interchain interactions, which for an *LCST* are counterbalanced by a corresponding entropy reduction.

The shift of the spinodal temperature caused by flow can be estimated in the following way. The spinodal is given as in the case of a quiescent system:

$$\left(\frac{\partial^2\Delta G^{\mathrm{M}}}{\partial\phi^2}\right)_{P,T} \equiv \Delta G^{\mathrm{M}''} = 0 \tag{11}$$

where ΔG^{M} is the sum of equations (5) and (7). The Gibbs free energy and the spinodal temperature in the absence of flow will be labelled by the index 0. It follows that:

$$\Delta G^{\mathrm{M}} = \Delta G_0^{\mathrm{M}} + \Delta G_{\mathrm{el}}^{\mathrm{M}} \tag{12}$$

Now expanding $\Delta G^{\mathrm{M}''}$ around the spinodal temperature T_0 for the quiescent blend one gets:

$$\Delta G^{\mathrm{M}''}(T) = \Delta G_0^{\mathrm{M}''}(T_0) + \Delta G_{\mathrm{el}}^{\mathrm{M}}(T_0) + (T - T_0)\left(\frac{\partial\Delta G^{\mathrm{M}''}}{\partial T}\right)_{T_0} = 0 \tag{13}$$

The first term on the right-hand side vanishes according to equation (11); $-\partial(\Delta G^{\mathrm{M}''})/\partial T$ equals the second derivative of the entropy of mixing with respect to concentration, $\Delta S^{\mathrm{M}''}$. Putting $\Delta T \equiv (T - T_0)$ it follows from equation (13) for the temperature shift:

$$\Delta T = \Delta G^{\mathrm{M}''}_{\mathrm{el}}(T_0)/\Delta S^{\mathrm{M}''}(T_0) \tag{14}$$

Employing equations (5) and (7) one can calculate the quantities determining ΔT. After some straightforward calculations one arrives at:

$$\Delta G^{\mathrm{M}''}_{\mathrm{el}} = -P^*_{\mathrm{A}} V^*_{\mathrm{A}} \tilde{V}_{\mathrm{A}} \Delta\tilde{N}_1$$
$$\Delta S^{\mathrm{M}''} = 2R\tilde{T}_0 \left(\frac{\partial X}{\partial \tilde{T}}\right)_{T_0} \tag{15}$$

For miscible polymers with an *LCST* the free-energy parameter X increases with temperature, hence $\partial X/\partial T > 0$. Therefore, the sign of ΔT will be determined solely by the sign of $\Delta\tilde{N}_1$. For $\Delta\tilde{N}_1 < 0$ this results in $\Delta T > 0$, and vice versa. One sees that for an *LCST* the shear homogenization is directed by the balance of a negative elastic energy contribution and a negative entropy term to the Gibbs free energy of mixing. The opposite is true for an *UCST*. In that case the parameter X descends with increasing temperature, and therefore $\partial X/\partial T < 0$. Hence, for $\Delta\tilde{N}_1 < 0$ it follows, contrary to an *LCST*, that $\Delta T < 0$.

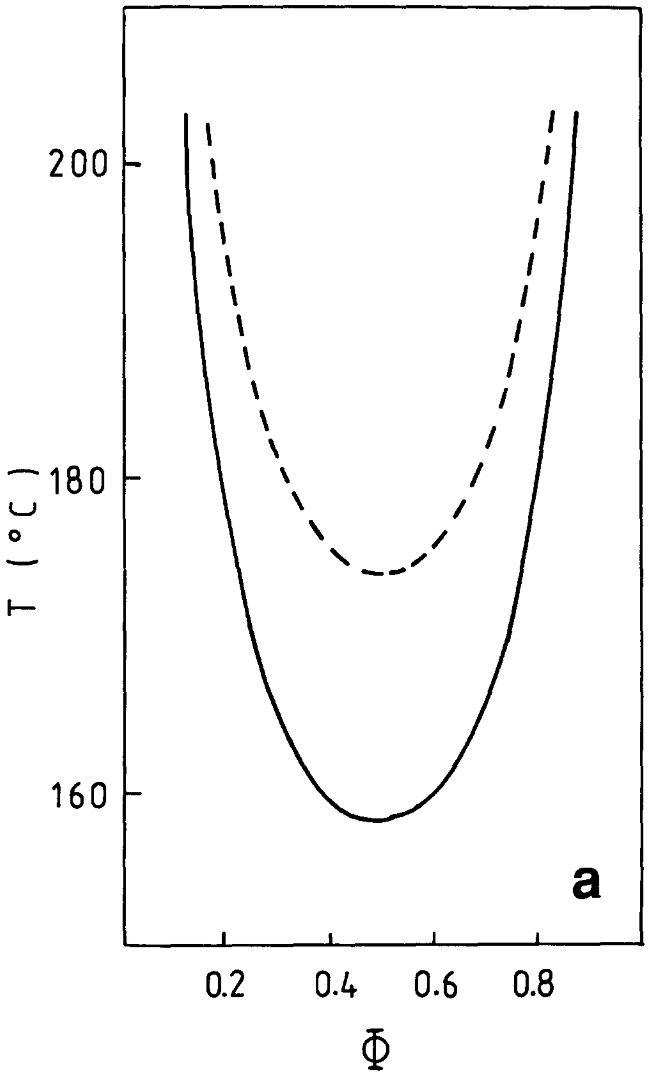
Employing equation (7) with (10) one can easily calculate binodals for a quiescent blend and a blend subjected to shear, respectively. The results are depicted in *Figure 1a* for the parameters as indicated in the legend. Additionally, the corresponding parameters X and their interaction and free-volume parts as functions of temperature are plotted in *Figure 1b*, again for the blend at rest and under shear, respectively.

EXPERIMENTAL MATERIALS AND METHODS

The SAN sample ($M_w = 225\,000$, $M_w/M_n = 1.8$) containing 31.5 wt% acrylonitrile was supplied by Chemisches Kombinat Buna. The PMMA sample ($M_w = 40\,000$, $M_w/M_n = 1.7$) was prepared as described elsewhere[17]. The molecular weights were estimated by g.p.c. calibrated with polystyrene standards.

For blend preparation the SAN and PMMA samples were dissolved in different proportions at 3 wt% of total polymer in 1,2-dichloroethane as a common solvent. The solutions were cast on glass substrates and dried at 80°C for 2 weeks. The film specimens with a diameter of 5 mm and a thickness of approximately 20 μm were transparent and showed a single glass transition temperature.

We measured the cloud-point curve in the polymer blend subjected to Couette-type shear flow by light scattering. The film specimens were inserted between two quartz-glass plates of the rheometer in such a way that the centres of the plates and the sample coincided. The plate–plate system is installed in an oven to regulate the temperature. The heating rate for all experiments was chosen as 2 K min^{-1}. The rheometer is equipped with an optical microscope. The light intensity transmitted through the sample was recorded by a photocell at a



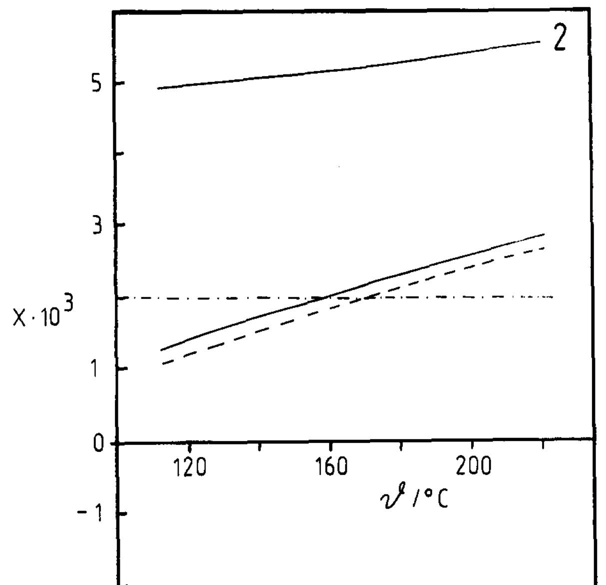


Figure 1 (a) The binodals of a blend as calculated from equations (7) and (10). The parameters used are: $X_{\mathrm{AB}} = -10^{-4}$, $\Gamma = 0.038$, $r_{\mathrm{A}} = r_{\mathrm{B}} = 1000$, $T^*_{\mathrm{A}} = 8100$ K, $P^*V^*/RT^* = 1$. The full and broken curves result from $\Delta\tilde{N}_1 = 0$ and $\Delta\tilde{N}_1 = -2\times10^{-5}$, respectively. (b) Representation of the interaction (1) and the free-volume contribution (2) to the parameter X against temperature as calculated from equation (10). The combinatorial entropy of mixing at $\phi = 0.5$ and $r = 1000$ is indicated by the chain line. Other parameters and symbols are chosen as in (a)

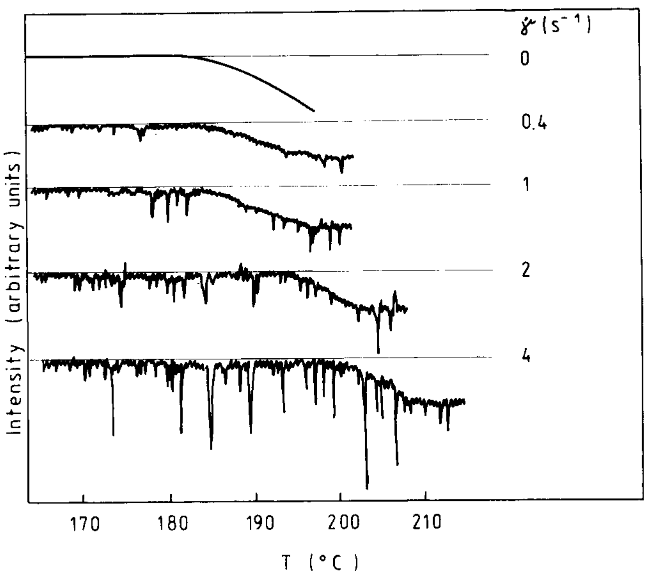


Figure 2 Light intensity traces *versus* temperature for the PMMA/SAN 60/40 blend subjected to different rates of shear

distance of 2.35 mm from the centre. The cloud point was chosen as the temperature at which the measured intensity started to drop from a baseline level (*Figure 2*). The shear rates varied in the range from 0.4 to 4.0 s^{-1}. The uncertainty in the determination of the cloud points could be estimated to be about $\leqslant 2°C$.

RESULTS AND DISCUSSION

Typical unmixing patterns of the PMMA/SAN 60/40 blend at a temperature just above the binodal are shown in *Figures 3* to *5*. In *Figure 3* the morphology of the quiescent blend can be seen. The spinodal decomposition leads to a regular bicontinuous two-phase structure with a periodic distance of about 2 μm. *Figure 4* reveals in a qualitative way the influence of shear on the phase-separated sample. The pattern in the steady-state shear flow is circularly symmetric around the centre of the sample in the plate–plate system. At very low rates of shear, i.e. at very low distances from the centre, the pattern is only slightly elongated parallel to the flow direction. With increasing distance from the centre, however, the pattern is increasingly elongated. *Figure 5* presents the region of the sample at a distance of 2.35 mm from the centre. It indicates that the originally bicontinuous structure is highly elongated parallel to the flow direction, resulting in a stratified structure. These results suggest qualitatively that shear can counteract the unmixing of the blend into two phases, giving rise to highly deformed patterns or, in other words, to shear-induced homogenization.

As predicted above, sufficient shear can significantly affect the phase behaviour of blends. In a more quantitative way, this is demonstrated in *Figures 6* and *7*. As can be concluded from *Figure 6*, shear suppresses phase separation and enlarges the homogeneous region of the PMMA/SAN mixture. The binodals for blends exposed to shear could be detected only for SAN-rich systems. In the opposite range of PMMA-rich blends, 'melt fracture' made reliable measurements of cloud points impossible. *Figure 7* shows the temperature of phase separation as a function of shear rate at different blend compositions. Again, it is demonstrated that the flow field elevates the binodal points. In terms of the theory developed above, this effect becomes operative if the stored energy is of the same order as the free-energy gain the quiescent blend could realize by phase separation.

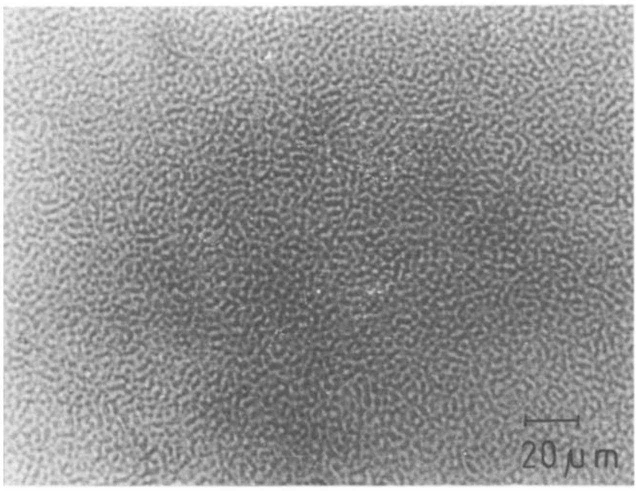


Figure 3 Light micrograph of the regular two-phase morphology above the binodal; PMMA/SAN 60/40

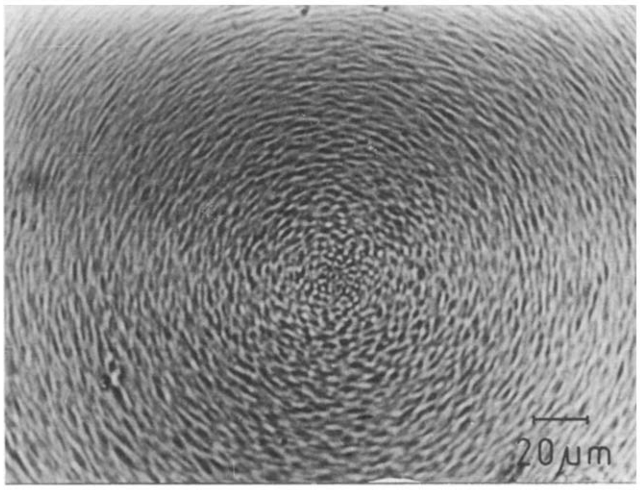


Figure 4 The same blend as in *Figure 3* subjected to shear in a plate–plate geometry

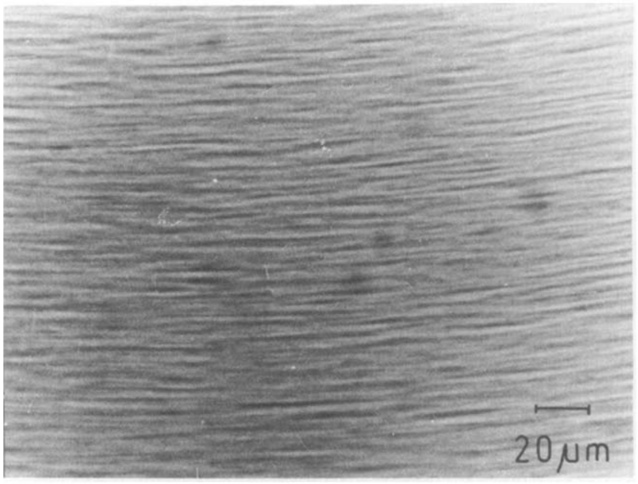


Figure 5 The region of the sample as in *Figure 4* at a distance of 2.35 mm from the centre. This is the distance where the light intensity was recorded

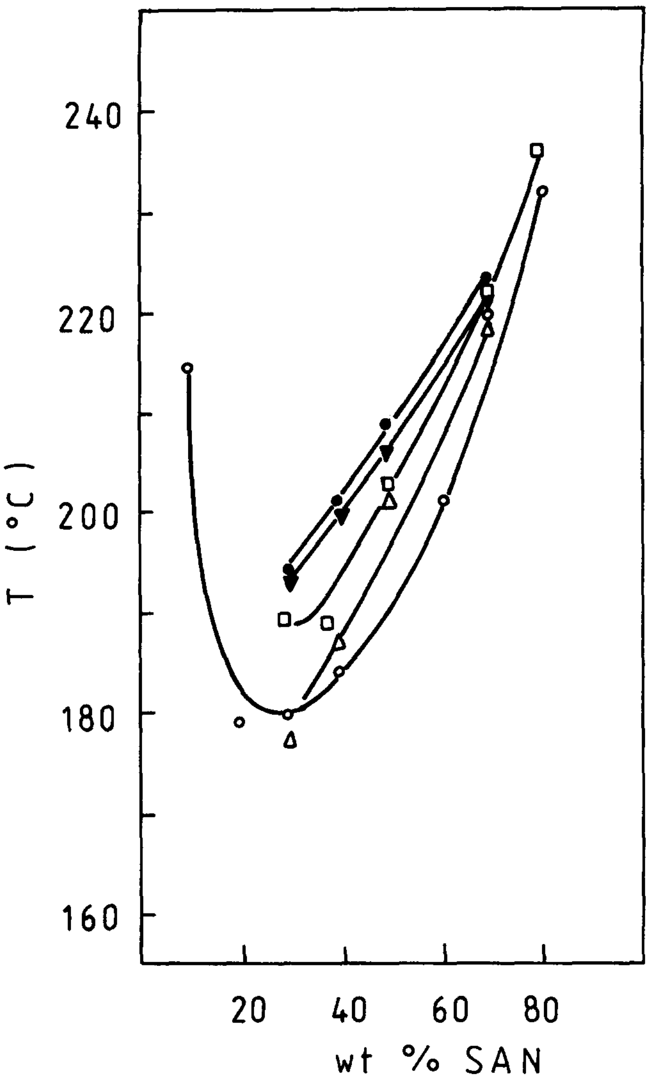


Figure 6 Cloud-point curves of the system PMMA/SAN demonstrating flow-induced miscibility. Rates of shear: 0 (○), 0.4 (△), 1.0 (□), 2.0 (▼) and 4.0 s^{-1} (●)

For the system PMMA/SAN 31.5 studied here all parameters occurring in equations (14) and (15) are known with the exception of $\Delta\tilde{N}_1$. Therefore, we can estimate this quantity. The parameters X_{AB} and Γ are given by[10]:

$$X_{AB} = \beta\chi_{MMA/S} + (1-\beta)\chi_{MMA/AN} - \beta(1-\beta)\chi_{S/AN}$$
$$\Gamma = \beta\delta_S + (1-\beta)\delta_{AN} - 2\beta(1-\beta)\chi_{S/AN} \qquad (16)$$

where β is the mole fraction of styrene (S) in SAN. The individual segmental interaction parameters determining X_{AB} and Γ were estimated for PMMA/SAN in ref. 15. It follows that:

$$\chi_{MMA/S} = 0.01 \qquad \chi_{MMA/AN} = 0.05 \qquad \chi_{S/AN} = 0.12$$
$$\delta_S = 0.02 \qquad \delta_{AN} = 0.13 \qquad (17)$$

Using these values in (16) one gets for the blend

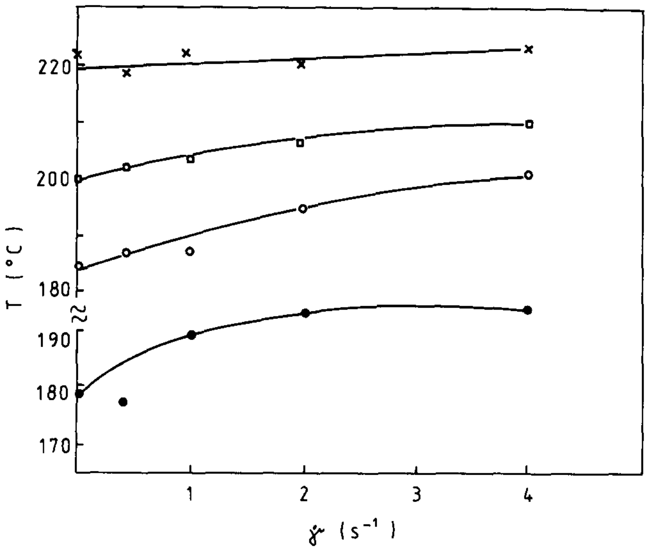


Figure 7 Temperature of phase separation *versus* shear rate at different blend compositions of PMMA/SAN: 70/30 (●), 60/40 (○), 50/50 (□), 30/70 (×)

PMMA/SAN 31.5:

$$X_{AB} = -9.6 \times 10^{-4} \qquad \Gamma = 0.0123$$

From *Figures 6* and *7* we can extract a phase-separation temperature of 184°C for the quiescent 60/40 blend and one may assume as reliable $\Delta T = 10$ K. Employing equation (9) and $T_A^* = 8100$ K[15], the phase-separation temperature corresponds to $\tilde{V}_A^{1/3} = 1.0755$. From equations (14) and (15) it then follows immediately that $\Delta\tilde{N}_1 = -7 \times 10^{-5}$. For the reduced pressure an adequate value[18] is $P_A^* = 5 \times 10^8$ Pa. Therefrom, one gets for the estimated stored (specific) excess energy: $\Delta N_1 = -3.5 \times 10^4$ Pa.

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