

Phase separation in polystyrene–poly(vinylmethylether) blends: a fluorescence emission analysis

J. L. Halary*, J. M. Ubrich, J. M. Nunzi and L. Monnerie

Laboratoire de Physicochimie Structurale et Macromoléculaire, Ecole Supérieure de Physique et Chimie Industrielles de Paris, 10, rue Vauquelin, 75231 Paris Cedex 05, France

and R. S. Stein

Polymer Research Institute and Materials Research Laboratory, University of Massachusetts, Amherst, Mass 01003, USA

(Received 14 July 1983)

Fluorescence emission of labels appears to be a new technique for the investigation of the *LCST* behaviour of polystyrene–poly(vinylmethylether) (PS–PVME) blends. Indeed, heating ternary blends of PVME/PS/labelled PS results in sharp increases in the fluorescence intensity, which occur simultaneously with their phase separation. Specific interactions between the anthracenic units of the labelled PS and the ether functions of PVME, are responsible for the fluorescence quenching, which occurs in the compatible blends. Quenching drops as phase separation proceeds, because of the lowering of the probability for label–PVME interactions in the two-phase state. By relating the phase separation curves obtained in this way to those acquired by the classical light scattering method, it is shown that fluorescence experiments may allow determination of both spinodal and binodal curves, provided that heating rate is appropriate.

(Keywords: polystyrene; poly(vinylmethylether); polymer blends; fluorescence; spinodal decomposition; nucleation; growth)

INTRODUCTION

During the past decade, an increasing number of publications have been devoted to the compatibility of polymer blends, both from an experimental and a theoretical viewpoint^{1–3}. A few amorphous polymer mixtures have been shown to be compatible pairs at ordinary temperatures, but to exhibit lower critical solution temperature (*LCST*) phase diagrams at higher temperatures. Binary mixtures of polystyrene (PS) and poly(vinylmethylether) (PVME) were among the first to be used^{4–9}, and they were investigated using a number of techniques, including optical and electron microscopy, differential scanning calorimetry, light and neutron scattering, n.m.r. spectroscopy and recently excimer fluorescence¹⁰. After investigating the phase separation characteristics of blends, it was found that nucleation and growth occurs for metastable one-phase compositions, while spinodal decomposition occurs for unstable one phase compositions³. Cahn's concepts on spinodal decomposition in metallic alloys¹¹ were applied to polymeric solid solutions^{5,12}. This theoretical background was extended by studies on the growth process of the unstable concentration fluctuations, involved in the spinodal decomposition mechanism^{13,14}.

In this work, we have studied these phenomena by means of fluorescence microscopy. This new approach

shows promise, because it may be possible: (i) to determine experimentally the boundaries in the phase diagrams from fluorescence intensity measurements and (ii) to obtain information on the earlier stages of phase separation from fluorescence depolarization experiments.

In this paper, we report on the first application of this technique. The system studied was the PS–PVME pair, which was chosen because of the extensive data available and because of the ease of labelling PS with fluorescent anthracenic units. First it is necessary to show how fluorescence of the blend is sensitive to phase separation and to demonstrate why this occurs. The phase diagrams from the fluorescence studies will be compared with those from the classical light scattering method⁸. Finally, the influence of the heating rate on the location of the boundary will be investigated, in order to attempt to distinguish between spinodal and binodal curves.

EXPERIMENTAL

Materials

Different PS samples with narrow molecular weight distributions and a polydisperse PVME sample have been used without further purification or fractionation. These materials were dried for 24 h at 80°C under reduced pressure with a residual atmosphere of nitrogen before film preparation. The origin and molecular weight of PS and PVME samples are given in *Table 1*.

Labelled PS (PS*) samples were synthesized, as previously reported¹⁵. Anionic monofunctional chains of

* Research Associate in the Polymer Research Institute, University of Massachusetts: July–September, 1981, and July–September, 1982.

molecular weight 15 000 (or 150 000) were deactivated by 9,10-bis(bromomethyl)anthracene; the resultant chains of molecular weight 30 000 (or 300 000) contain dimethyl-anthracene fluorescent groups in their middle, as shown in Figure 1.

Isobutylbenzene (IBB), and butylmethylether (BME), used as model compounds for PS and PVME, were purchased from EGA Chemie and Fluka AG, respectively. Before use, these chemicals were shaken in the presence of activated carbon in order to remove any fluorescence.

Blend preparation

Films of PS/PS*/PVME mixtures were cast at room temperature from 10% benzene solutions. The PS* chain concentration was adjusted to be around 6 ppm of anthracenic units (i.e. less than 0.1 wt % of PS* of molecular weight 30 000); in these conditions, the PS/PS*/PVME blends behave chemically like a binary PS/PVME mixture and the label concentration is low enough to prevent undesired intermolecular energy transfer. The films were dried in an oven under nitrogen, first at room temperature for 24 h, then at 60°C for 24 h and finally in vacuum until complete removal of the solvent had occurred. The thickness of the films was about 50 μm .

For comparative measurements, in which the fluorescence intensity was followed at room temperature as a function of PVME content, moulded samples were used. For this purpose, 4% benzene solutions of PS 4/PS*/PVME were freeze-dried, and complete elimination of the solvent was ensured by subsequent drying for 24 h at 60°C. Finally, 0.5 mm thick discs were moulded under argon at 20°C above the glass transition temperature T_g of the blend. The T_g 's (Table 2) were determined using a Dupont 1090 differential scanning calorimeter operating at a heating rate of 20°C/min.

Table 1 Polymer origin and characteristics

Polymer	Origin	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
PVME	Scientific Polymer Products	46 500	99 000	2.12
PS 0	Polymer Labs Ltd	8 600	9 000	1.05
PS 1	Pressure Chemical Co	19 300	20 400	1.06
PS 2	Polymer Labs Ltd	34 000	35 700	1.05
PS 3	This laboratory (Paris)	62 000	67 000	1.08
PS 4	Pressure Chemical Co	100 000	106 000	1.06
PS 5	Polysciences Inc	220 000	233 000	1.06

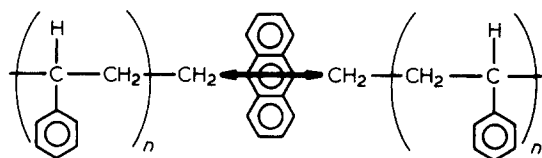


Figure 1 PS* formula. The double arrow symbolizes the transition moment of the anthracenic unit

Table 2 Glass transition temperature of PS 4/PS*/PVME blends with different PVME content

PVME content (wt %)	0	0.35	0.60	0.98	1.64	2.42	3.61	4.28	5.63	7.23	10.83
T_g (°C)	107	104	104	102	100	98	96	94	89	83	74

Fluorescence measurements

Measurements were carried out under continuous illumination using a Nchet NS 400 microscope, which had been modified with a view to performing fluorescence depolarization experiments¹⁶. In this machine, excitation and fluorescence wavelengths (around 365 nm and 440 nm, respectively) are selected by appropriate filters. The equipment is operated with polarized excitation light and provides both fluorescence intensities, I_v and I_H , corresponding to parallel and perpendicular directions. Therefore, two separate measurements of fluorescence evolution with increasing temperature were simultaneously performed on each blend. Similar behaviour was observed for I_v and I_H . The intensity of the fluorescence emission, I_F , is given by the sum $I_v + 2I_H$. The sample holder of the microscope was replaced by a Mettler FP 4 hot stage, and samples were subjected to heating rates ranging from 0.2 to 1, 5, 10 and 16°C/min.

Measurements in solution were carried out using a spectrofluorimeter Fica 55. Fluorescence intensities, I_n were determined from the height of the emission peak at its maximum. The position of this maximum was found to be independent of the nature of the solvent (IBB or BME). Label lifetimes were obtained from fluorescence decay experiments using equipment and methods reported in a previous paper¹⁷.

Light scattering experiments

Phase diagrams were obtained from photometric light scattering experiments by following a procedure reported elsewhere⁸. Samples were heated in a Mettler FP 4 hot stage at a rate of 0.2°C/min and light intensities scattered at an angle of 20 degrees were recorded as a function of temperature. Phase separation is characterized in such experiments by an upturn in the scattered intensity.

RESULTS AND DISCUSSION

Relationship between phase separation and fluorescence emission

Heating of ternary blends of PVME/PS/PS* results in a sharp increase in the fluorescence intensity ' I_F ' at a temperature, T_C , which depends on both the PS content and the molecular weight. This phenomenon (a typical example of which is given in Figure 2), occurs irrespective of the molecular weight of PS, with the exception of the mixtures involving PS 0. In the case of this low molecular weight sample, the films are transparent but very fluid at 210°C but it becomes experimentally impossible to heat any further. As discussed later in this paper, the observed T_C is found in the same temperature range, where the cloud points are observed from light scattering measurements. Also, the T_C 's are observed prior to the appearance of two separate T_g 's in the materials.

Because phase separation is a reversible process (at least in the early stages⁵), one may check the hysteresis behaviour of I_F . Repeated heating and cooling near T_C (while monitoring the variation of I_F with time) shows that I_F regains the initial value during several cycles (Figure 3).

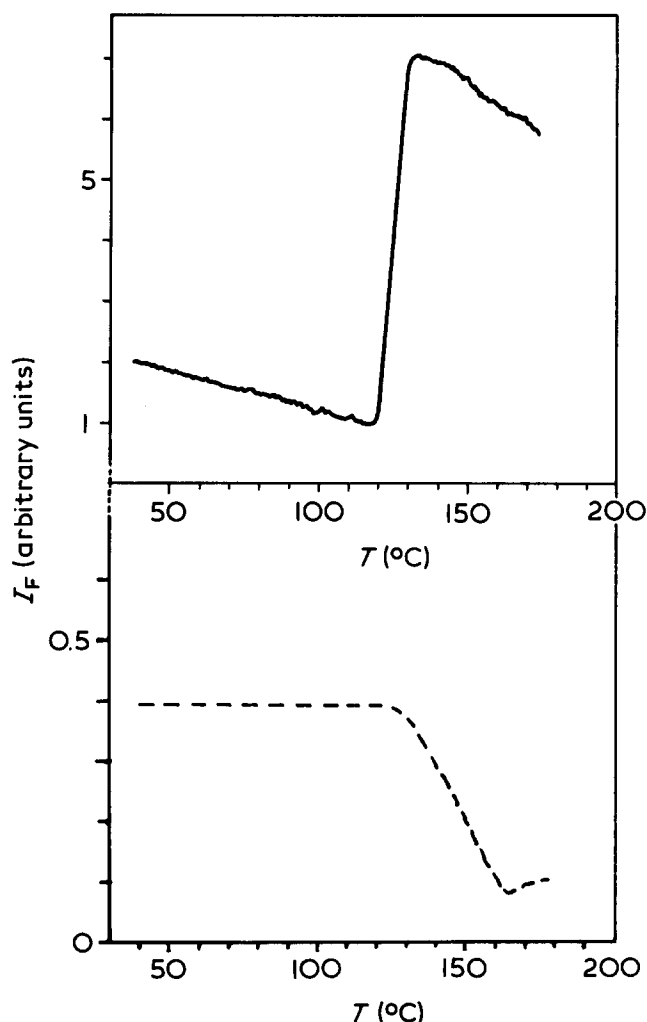


Figure 2 Typical recording of fluorescence intensity, I_F , versus temperature for the PVME/PS 5/PS* = 67/32.9/0.1 mixture (Heating rate 10°C/min). The dashed line refers to as the response of a blank sample PVME/PS 5 = 67/33

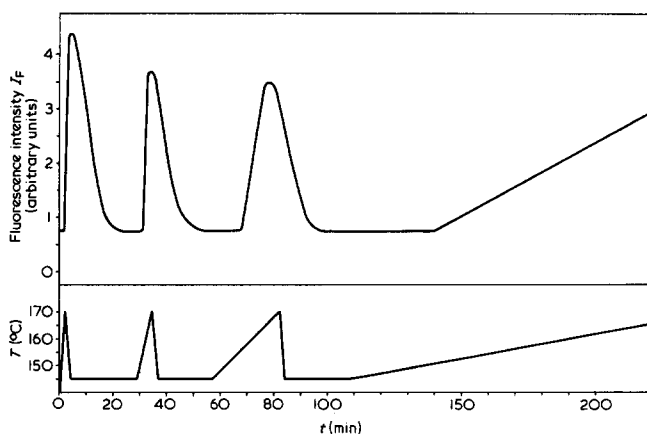


Figure 3 Typical recording of fluorescence intensity, I_F , versus time on repeated heating and cooling near the phase separation temperature of the PVME/PS 2/PS* = 80.3/19.6/0.1 mixture

The speed of this recovery decreases with increasing PS molecular weight, or the temperature difference from T_C .

Two additional observations must be reported in this section. At first, the T_C 's are the same (within the experimental error) regardless of the batch of PS* used for the experiments. This means that the labelled chains in the ternary blends do not clarify their own phase separation

but instead clarify that of PS chains. Otherwise large differences in T_C values should be observed using either PS* of molecular weight 30 000 or PS* 300 000. Secondly, it is worthwhile noting that the increase in fluorescence emission near the cloud point is not an artefact due, for instance, to scattering phenomena. Indeed, experiments on blank mixtures of PVME/PS in the absence of any fluorescent probe are marked by a drop (and not an increase) in residual intensity a few degrees above T_C (Figure 2). The higher the film turbidity, the smaller the residual intensity. As a consequence, the origin of the change in fluorescence emission must be searched for in the fluorescence process itself, i.e. in quenching phenomena.

Evidence for fluorescence quenching by PVME

The nature of the molecules next to the PS* obviously depends on the composition of the blends: in the one-phase state there is a mixture of PS and PVME, but in the two-phase state the molecules are mainly PS. Thus, a simple explanation of the change in fluorescence intensity at the phase separation would be that PS* emission is greater in PS than in PS-PVME mixtures; in other words, PVME quenches the fluorescence emission of PS*.

It is easy (though naïve) to argue from spectrofluorimetric experiments in solution (using isobutylbenzene and butylmethylether as model compounds for PS and PVME, respectively) that the fluorescence emission of PS*, I_{fl} , decreases uniformly in mixtures ranging from pure IBB to pure BME (as shown in Figure 4). This means that BME, the model compound for PVME, produces quenching in the presence of PS*. Let us now consider IBB solutions of PS* (in which up to 15% of the polymers were added, while the PS* concentration remained constant). In Figure 5, the addition of PS leads to an increase in the fluorescence intensity I_{fl} , which is a consequence of the increase in solution viscosity. However, the addition of PVME results in a decrease of I_{fl} , as the viscosity effect is counteracted by the greater quenching effect.

Comparative intensity measurements are difficult to carry out in the solid state. This is because of the large

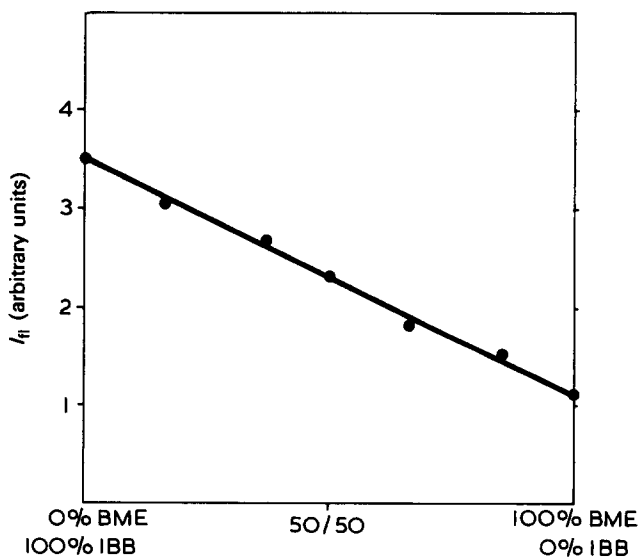


Figure 4 Plot of fluorescence intensity, I_{fl} , versus composition of the IBB-BME solvent mixture (label concentration: 4.10^{-2} mol l $^{-1}$)

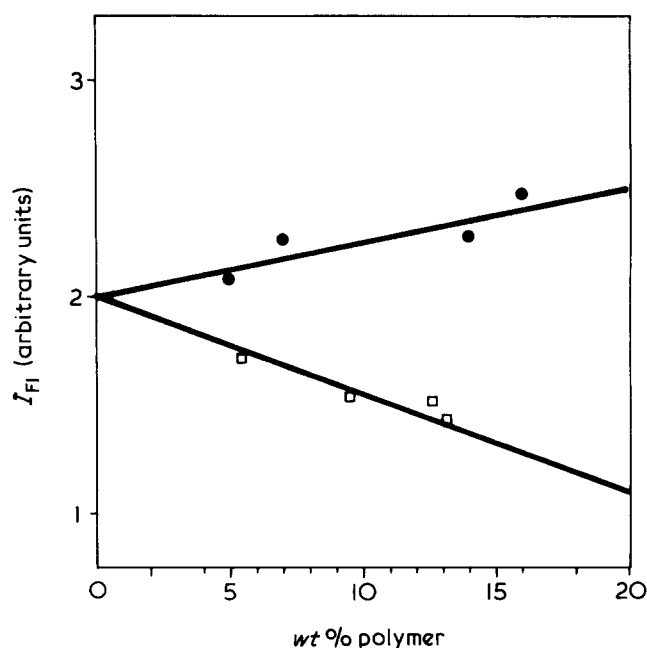


Figure 5 Plot of fluorescence intensity, I_F , versus polymer concentration in IBB solutions: (●) PS 4; (□) PVME (Label concentration: $4.10^{-2} \text{ mol l}^{-1}$)

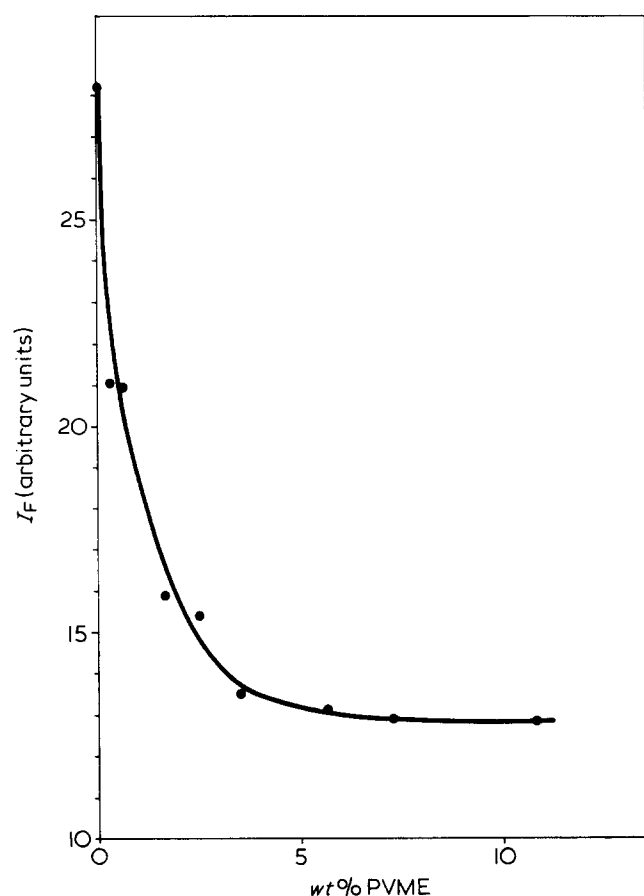


Figure 6 Plot of fluorescence intensity, I_F , versus PVME content in PS 4-PVME mixtures

confidence range which results mainly from non-reproducibility in the cast-film thickness and surface shape. However, resolution may be possible using moulded samples of controlled thickness. In *Figure 6*, I_F drops drastically at room temperature in the presence of small amounts of PVME in PS matrices. No significant

change in this behaviour is detected by performing the I_F measurements at temperatures above the glass transition of these blends, but below phase separation.

Although this set of experiments provides evidence for fluorescence quenching by PVME, the origin of this quenching is not known. Two types of fluorescence quenching may occur which are dynamic¹⁸ and static¹⁹ quenching. Dynamic quenching is characterized by a fluorescence intensity which is proportional to the lifetime of the probe in its excited state. On the other hand, in static quenching, which results from specific interactions between a probe and the quenching molecules, the lifetime remains constant whatever the fluorescence emission. Lifetime measurements for PVME-PS 5-PS* mixtures of various compositions are given in *Figure 7*. Results obtained at high temperatures (more than 120°C) may be ignored because of the lack in transparency of the films due to phase separation. Taking into account the large standard deviation ($\pm 0.2 \text{ ns}$), the major observation from these results is that the lifetimes decrease slightly with increasing temperature, in the same way, whatever the PVME content. Such behaviour is contradictory to the large increase in fluorescence intensity, which occurs with phase separation. This indicates that static quenching occurs in the one-phase PS/PVME blends, and then ceases in the phase separated mixtures.

It is only reasonable to place the relevant specific interactions between the anthracenic units of PS* and the ether functions of PVME. Indeed, similar interactions, although weaker, exist between PVME and the phenyl rings of PS and are responsible for the compatibility of both polymers²⁰. Besides, similar quenching effects have been recently shown to occur between poly(dimethyl-phenylene oxide) and PS* and will be reported in a subsequent communication²¹.

From the data presented in this paper, it is possible to infer that static fluorescence quenching occurs in compatible blends, but decreases as phase separation proceeds (because of lowering of the probability for PVME-label interactions in the two-phase state).

Phase separation diagrams

Phase diagrams from fluorescence experiments performed at heating rates of 0.2 and 16°C/min are given in *Figures 8* and *9*. These diagrams show similar

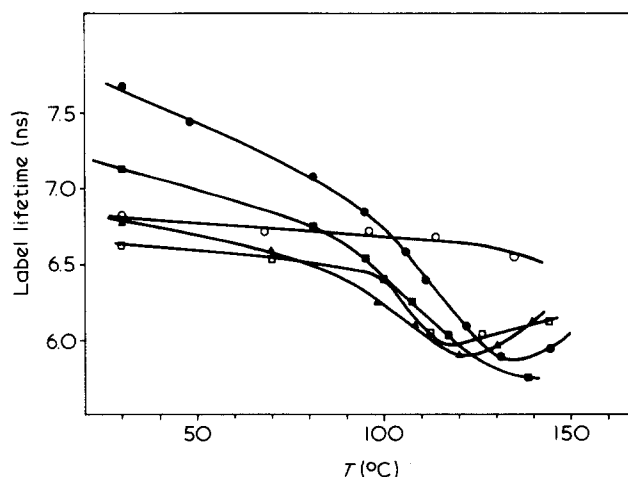


Figure 7 Temperature dependence of PS* lifetimes for various compositions of PS 5-PVME blends: (●) 0% PS; (▲) 60% PS; (■) 20% PS; (□) 80% PS; (○) 100% PS

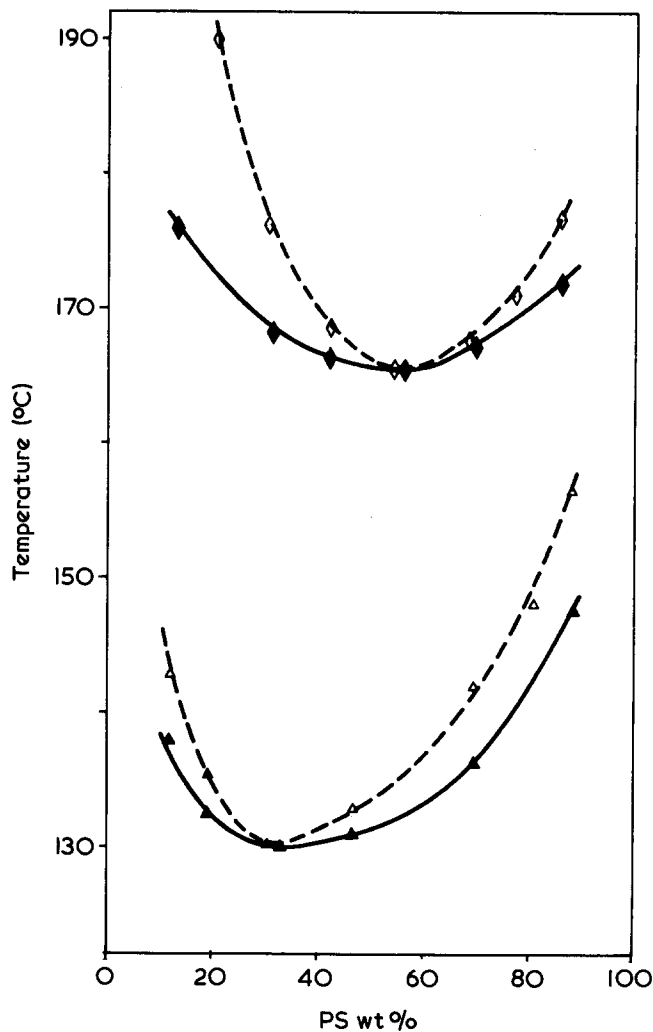
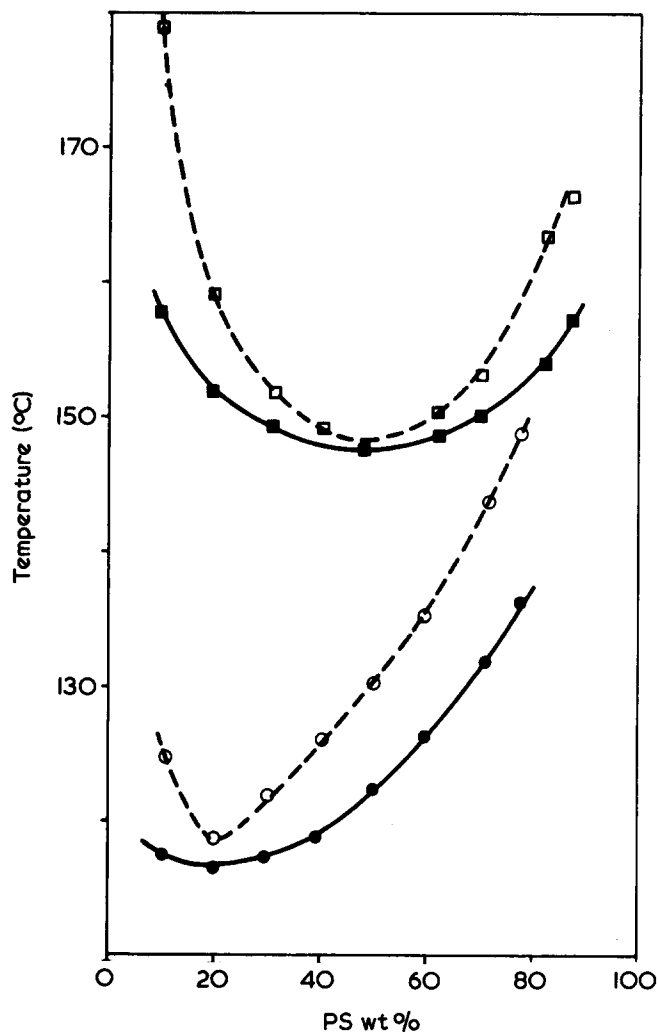


Figure 8 PS-PVME phase diagrams as obtained from fluorescence experiments. Solid and dashed curves refer to heating rates of 0.2 and 16°C/min, respectively. ((●) = PS 5; (■) = PS 2; (▲) = PS 3; (◆) = PS 1)

features, regardless of the PS molecular weight in the range 19 300–220 000.

The heating rate is unimportant around the minimum of the curves (the two curves are identical within the confidence range). However, for PVME or PS-rich blends, modifying the heating rate from 0.2 to 16°C/min allows the boundary temperature to rise by about 20°C. Moreover, the light scattering data agree with the phase diagrams obtained from fluorescence experiments carried out at 16°C/min. A typical example is shown in Figure 9, but checks were made on all the mixtures under study. Thermodynamic analysis of such phase diagrams is critical because of the polydispersity of PVME. According to McMaster¹², the critical point may differ in location from the minimum of the temperature-composition curve. Consequently, it should be *a priori* open to criticism to use Scott's treatment of polymer mixtures²² to calculate spinodal and binodal curves, and compare them with our experimental data. For this reason, we prefer to limit our analysis to qualitative comments.

Let us firstly look at the behaviour around the minimum of the phase separation curve. In this region it is now quite well established that phase separation occurs by spinodal decomposition. The most straightforward feature obtained from fluorescence emission measurements is that there is no evidence for heating rate dependence. This means that the concentration fluctuations required to be detected in such experiments should be sufficiently small

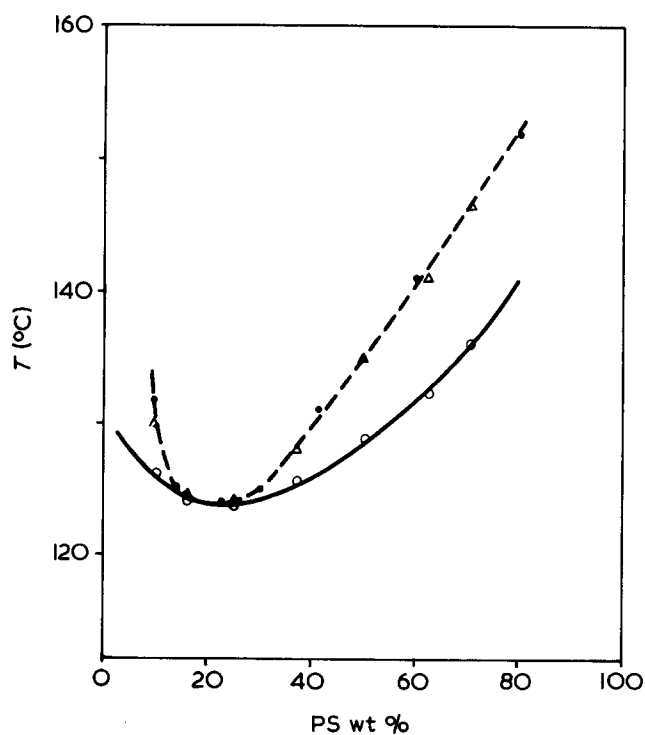


Figure 9 PS 4-PVME phase diagrams. Solid line: from fluorescence experiments [○] (heating rate: 0.2°C/min). Broken line: either from fluorescence experiments [△] (heating rate: 16°C/min) or from light scattering [●] (heating rate: 0.2°C/min)

in amplitude and should develop fast enough not to lead to any noticeable effect in the heating rate range studied. The origin of the sensitivity of fluorescence measurements is due to the fact that fluorescence acts as a molecular probe of thermodynamic compatibility. Such a conclusion was previously obtained in other fluorescence studies, based either on excimer fluorescence¹⁰ or on energy transfer between labelled blend components²³. However, in the region around the minimum of the phase separation curves, light scattering experiments at an angle of 20 degrees yield a heating rate dependence of the temperature at which an upturn in scattered intensity occurs. Such an upturn is associated with the occurrence of some concentration and refractive index fluctuations at a spatial size in the range of the excitation wavelength. In this way, the heating rate is a critical parameter in light scattering experiments because concentration fluctuations have to develop to a sufficiently large size in order to be detected. Considering the light scattering experiments, only those monitored at sufficiently low heating rate (i.e., 0.2°C/min in our experiments) lead to detected phase separation temperatures in agreement with our fluorescence data.

Let us consider the behaviour in the composition regions far from the minimum of phase separations curves (either PS-rich or PVME-rich blends), in which the two phase separation processes are known to occur. The first process, at the lower temperature, corresponds to binodal phase separation and results from a nucleation and growth mechanism. The second process, at a higher temperature, corresponds to spinodal decomposition, and involves a concentration fluctuation mechanism. As reported above, a large heating rate dependence is observed in the case of PS or PVME-rich mixtures for the phase separation temperatures obtained from fluorescence emission measurements. This effect is illustrated in

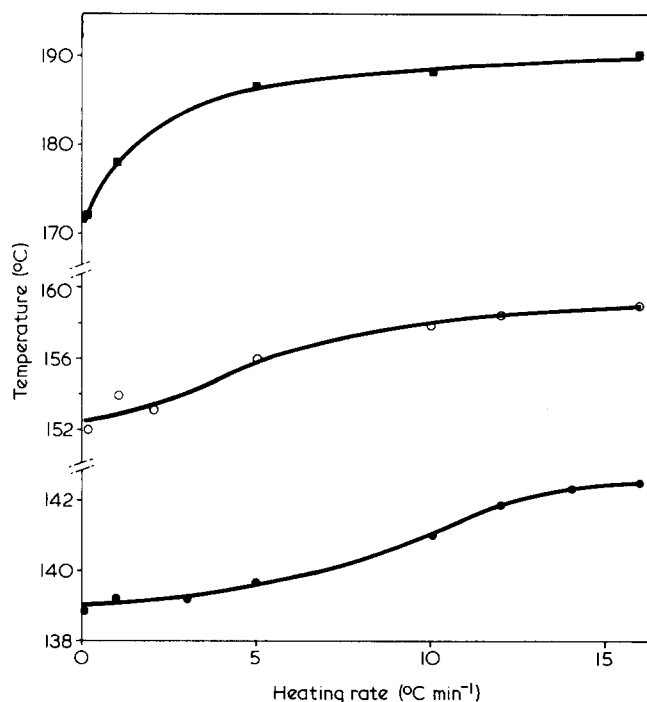


Figure 10 Plot of the observed phase separation temperature versus heating rate during fluorescence experiments: (●) PVME/PS 3/PS*: 88/11.9/0.2 mixture; (○) PVME/PS 2/PS*: 80/19.9/0.1 mixture; (■) PVME/PS 1/PS*: 79/20.9/0.1 mixture

Figure 10, in which data relative to three PS molecular weights are shown. In each case, at high heating rates a high temperature plateau is obtained; however, in the low heating rate range, the behaviour depends on the molecular weight of PS. A sufficiently high molecular weight (62 000) in our experiments is required to get a temperature plateau. The occurrence of such asymptotic temperatures suggest that they would correspond to thermodynamic temperatures. The extent of the gap between low and high plateau temperatures depends on the mixture composition: the greater the departure from the minimum, the larger the gap (Figures 8 and 9). Such behaviour cannot originate from a decrease in mobility of the polymer chains (due to a rise of glass transition temperature of the compatible mixture), as it could be possible in the PS-rich region. Indeed the same effect, is found in changing to PVME-rich compositions for which an increase in chain mobility would be expected as a consequence of the drop in glass transition temperature. Taking into account, first that occurrence of a high-temperature plateau is independent of PS molecular weight, and secondly that the extent of the gap largely increases at extreme compositions; one may associate the corresponding asymptotic temperature with spinodal decomposition. Such an assignment is additionally supported by the observation that no heating rate dependence on fluorescence data is found around the minimum (where no other process than spinodal decomposition can occur). In the case of high molecular weight PS, for which a low-temperature plateau is observed, the corresponding asymptotic temperature can be ascribed to the second type of phase separation, i.e., the binodal one. The low-temperature plateau is not reached for low molecular weight PS's (PS 1 in Figure 10) because the speed of the nucleation and growth process is too fast with respect to the heating rate used. Polymer chain diffusion greatly increases in this special case for two main reasons. The first one is concerned with the general molecular weight dependence of diffusion coefficients. The second one results from a peculiarity of LCST phenomena and corresponds to the increase in phase separation temperature when lowering the molecular weight. As a consequence, diffusion phenomena leading to phase separation occur farther and farther from the glass transition temperature, which results in higher and higher chain mobility. Thus, it is clear that for low molecular weight PS, the asymptotic temperature associated with binodal decomposition is difficult to reach by performing heating experiments. For such cases, the best way for determining an accurate binodal phase separation temperature would be to heat the samples step by step, starting a few degrees below the temperature given by low heating rate experiments.

The above reported agreement between results obtained from fluorescence emission at 16°C/min and light scattering at 0.2°C/min suggests that, for the investigated systems, light scattering experiments performed in such conditions correspond to spinodal decomposition.

A final comment about the phase diagrams given in Figures 8 and 9 deals with the effect of PS molecular weight. As reported earlier²⁴, phase separation temperature decreases with increasing PS molecular weight. From a quantitative point of view, one can deduce from our data, as shown in Figure 11, that the temperatures relative to the minimum of the phase separation curve varies linearly with the inverse of PS molecular weight. An

additional argument in favour of such a relationship is that the PVME-PS0 mixture should present a minimum temperature at about 220°C (as an experimental result). This mixture presents a single phase at 210°C, which is the upper temperature that can effectively be reached in such experiments. Finally, a linear relationship also exists between temperatures and blend compositions, both

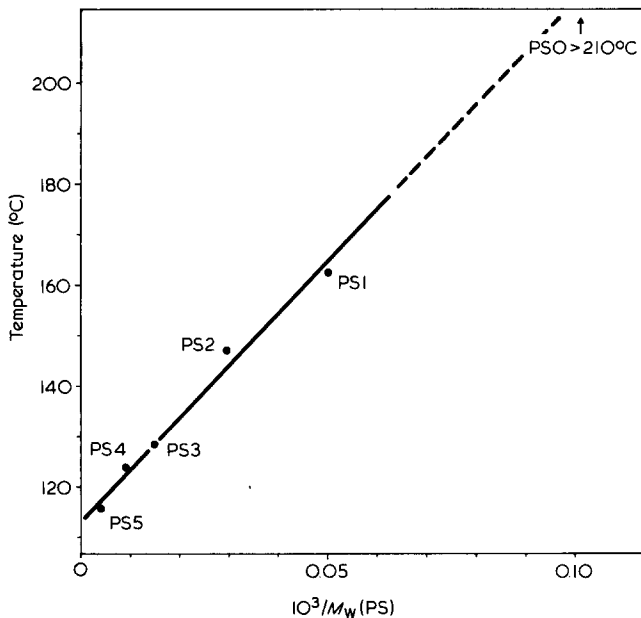


Figure 11 Plot of minimum temperatures of phase separation curves versus the inverse of PS molecular weights

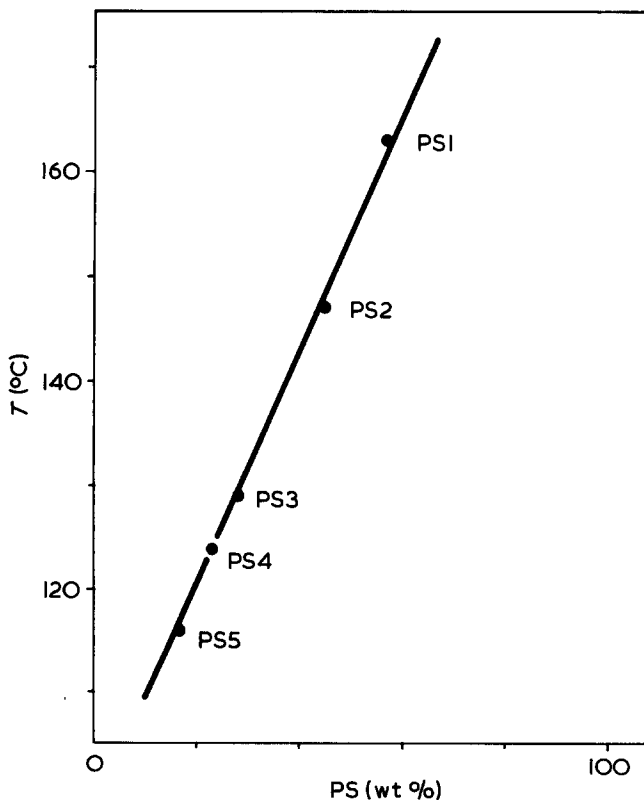


Figure 12 Plot of minimum temperatures of phase separations curves versus blend compositions at the minimum temperatures for various PS molecular weights

relative to the minima of the phase separation curves (Figure 12).

CONCLUSION

Sensitivity of the fluorescence emission of PS* for the determination of phase separation in PS-PVME blends permits exploration of a large range of heating rates (from 0.2 to 16°C/min in this study). Therefore, this technique may provide both spinodal and binodal phase separation curves: the spinodal curves are obtained using high heating rates, whereas the binodal curves are either generated (in the case of high molecular weight PS's) or roughly approached (in the case of low molecular weight PS's) at low heating rates. An unquestionable proof of the merits of such ascriptions would be given by a comparison with the binodal and spinodal curves calculated from the thermodynamics of polymer mixtures. Before, the polydispersity of PVME stood in the way of this check, but the experimental results are now encouraging enough to justify the time-consuming fractionation of PVME. Studies are currently in progress in our laboratories with the aim of confirming the findings of the present paper by only using polymers with a narrow molecular weight distribution.

ACKNOWLEDGEMENTS

We thank the Scientific Affairs Division of NATO for a grant to one of us (J.L.H.). Thanks are also due to Dr C. W. Frank for his comments of this paper.

REFERENCES

- 1 Krause, S. J. *Macromol. Sci., Revs. Macromol. Chem.* 1972, C7 (2), 251
- 2 Paul, D. R. and Newman, S. 'Polymer Blends', Academic Press, New-York, 1978
- 3 Olabisi, O., Robeson, L. and Shaw, M. T. 'Polymer-Polymer Miscibility', Academic Press, New-York, 1979
- 4 Bank, M., Leffingwell and Thies, C. J. *Polym. Sci.* 1972, A-2, 1097
- 5 Nishi, T. Wang, T. T. and Kwei, T. K. *Macromolecules* 1975, 8, 227
- 6 Davis, D. D. and Kwei, T. K. *J. Polym. Sci., Polym. Phys. Edn.* 1980, 18, 2337
- 7 Kwei, T. K., Nishi, T. and Roberts, R. G. *Macromolecules*, 1974, 7, 667
- 8 Yang, H., Hadziiodannou, G. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1983, 21, 159
- 9 Jelenic, J., Kirste, R. G., Oberthür, R. C., Schmitt-Strecker, S. and Schmitt, B. J. *Makromol. Chem.* 1984, 185, 129
- 10 Gelles, R. and Frank, C. W. *Macromolecules* 1983, 16, 1448
- 11 Cahn, R. W., *J. Chem. Phys.* 1965, 42, 93
- 12 McMaster, L. P. *Macromolecules*, 1973, 6, 760
- 13 De Gennes, P. G. *J. Chem. Phys.* 1980, 72, 4756
- 14 Pincus, P. *J. Chem. Phys.* 1981, 75, 1996
- 15 Valeur, B., Rempp, P. and Monnerie, L. *C. R. Acad. Sci.* 1974, 279 C, 1009
- 16 Pinaud, F., Jarry, J. P., Sergot, P. and Monnerie, L. *Polymer* 1982, 23, 1575
- 17 Valeur, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn.* 1976, 14, 11
- 18 Stern, O. and Volmer, H. *Physik Z.* 1919, 20, 184
- 19 Perrin, F. *C. R. Acad. Sci.* 1924, 178, 1978
- 20 Lu, F. J., Benedettic, E. and Hsu, S. L. *Macromolecules* 1983, 16, 1525
- 21 Takahashi, N., Tissin, J. F. and Monnerie, L. to be published
- 22 Nishi, T. *J. Macromol. Sci., Phys.* 1980, B17, 517
- 23 Mikes, F., Morawetz, H. and Dennis, K. S. *Macromolecules* 1980, 13, 969
- 24 Nishi, T. and Kwei, T. K. *Polymer*, 1975, 16, 285