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Miscibility of Poly(vinyl methyl ether) with Styrene-*co*-Methyl Methacrylate Random Copolymers Reexplored by Fluorescence Quenching Experiments

J. L. Halary* and M. H. Leviet

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

T. K. Kwei and E. M. Pearce

Department of Chemistry, Polytechnic University, Brooklyn, New York 11201

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ABSTRACT: The miscibility of poly(vinyl methyl ether) (PVME) with a series of styrene-*co*-methyl methacrylate random copolymers (ScoMMA) was examined by using the fluorescence quenching technique previously developed for the study of PVME–polystyrene (PS) blends. These observations on the molecular scale yield results at variance with previous cloud-point measurements, which have led to the conclusion that the maximum value of LCST of the pair PVME–ScoMMA exceeds that of the pair PVME–PS. Equilibrium phase diagram determinations suggest that the presence of MMA units does not generate any noticeable synergy property. It is shown to provoke only a pronounced slowing down of the phase-separation rate, as the result of the corresponding change in the friction coefficient.

Introduction

In contrast with the pair poly(vinyl methyl ether) (PVME)–polystyrene (PS), which is miscible at room temperature and exhibits a thermally induced phase separation of LCST type at higher temperature, the pair PVME–poly(methyl methacrylate) (PMMA) is fully incompatible. As a consequence, the study of the miscibility of PVME with random copolymers of styrene and methyl methacrylate (ScoMMA), initiated by Chien et al.,[1] is of special interest. From cloud-point measurements, these authors have observed that, at nearly the same molecular weights, the maximum value of LCST of the pair PVME–ScoMMA exceeds that of the pair PVME–PS for the methyl methacrylate copolymer mole fraction in the range 0.05–0.30. This synergy effect is maximum for a mole fraction of methyl methacrylate units of about 0.16–0.20. Similar observations have also been reported for other blends of homopolymer A with random copolymer B_yC_{1-y}.[2] They are compatible with an expression of the interaction parameter χ_{blend} of the form:[3-6]

$$\chi_{\text{blend}} = y\chi_{AB} + (1-y)\chi_{AC} - y(1-y)\chi_{BC}$$

At the same time, the use of anthracene-labeled polystyrene (PS*) as a fluorescent probe has proven to be suitable for the study, on a molecular scale, of phase-separation phenomena in the model blend PS–PVME. Quenching of the fluorescence emission of PS* occurs in the homogeneous blends as a consequence of specific interactions between the components but tends to cease when phase separation develops.[7,8] LCST phase diagrams have been determined with confidence, allowing the precise determination of the influence on the miscibility of chain characteristics such as molecular weight, polydispersity, and isotope effects.[8] In addition, the kinetics of phase separation have been analyzed in both spinodal decomposition and nucleation and growth regimes and compared with the relevant theoretical predictions.[9,10]

The purpose of the present paper is to reexplore the miscibility of PVME with ScoMMA by taking advantage of the sensitivity of the fluorescence quenching method. Obviously, the ideal fluorescent probe for such a study would be an anthracenic group labeled to the ScoMMA copolymer. Since this material was neither available nor easy to synthesize, the study was undertaken with the probe PS* by postulating that the ternary systems PVME–ScoMMA–PS* behave in all respects like PVME–ScoMMA, in spite of the presence of small amounts (usually around 0.5 wt %) of polystyrene chains. As discussed later on in this paper, this assumption seems to be reasonable.

Experimental Section

Materials. Characteristics of the materials under study are given in Table I. For the sake of simplicity, the copolymers ScoMMA are coded with the initials SM followed by a number that indicates their mole fraction in methyl methacrylate units. Their preparation and purification conditions were described in a previous paper.[1] The fluorescent probe PS*, including one anthracenic group covalently bound in the middle of an anionic PS chain, was prepared according to the procedure detailed previously.[8]

Film Preparation. Solutions of PVME–ScoMMA (or PS)–PS* were prepared by dissolving under stirring appropriate amounts of dried PVME and ScoMMA (or PS) in a solution of PS* in toluene. Next, films were cast on glass plates from the solutions and then dried in an oven under nitrogen at room temperature for 24 h followed by 24 h at 60 °C and finally under vacuum in order to remove all the solvent. The PS* concentration in the solution was adjusted in order to label the films with around 6 ppm of anthracene groups.

Fluorescence Measurements. Measurements were carried out under continuous illumination by using a fluorescence microscope with excitation and fluorescence emission wavelengths around 365 and 440 nm, respectively. As detailed in the previous papers of the series[7-10] insight in the two-phase domain is detected as the temperature at which fluorescence intensity, I_F, increases suddenly. This is achieved by using a Mettler hot stage attached to the microscope, either under continuous heating at a constant rate (in the range 1–16 °C/min) or in isothermal conditions by recording I_F as a function of time. Ramp experiments yield an apparent, nonequilibrium, phase-separation temperature, whereas the isothermal experiments permit determination of the true phase coexistence temperature, *T*(iso).

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* To whom correspondence should be addressed.

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Table I
Polymer Characteristics

sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
PVME[a]	18 400	35 200	1.9
PS[a]	71 400	116 400	1.6
SM0.10[a]	93 100	143 200	1.5
SM0.20[a]	81 800	129 000	1.6
SM0.25	62 500	137 000	2.2
SM0.30[a]	86 800	139 000	1.6
SM0.35[a]	76 200	119 000	1.6
SM0.40[a]	98 000	152 700	1.6
SM0.50	69 000	139 000	2.0
SM0.75	98 500	193 000	1.9
PS*	127 000	140 000	1.1

[a] Data taken from ref 1.

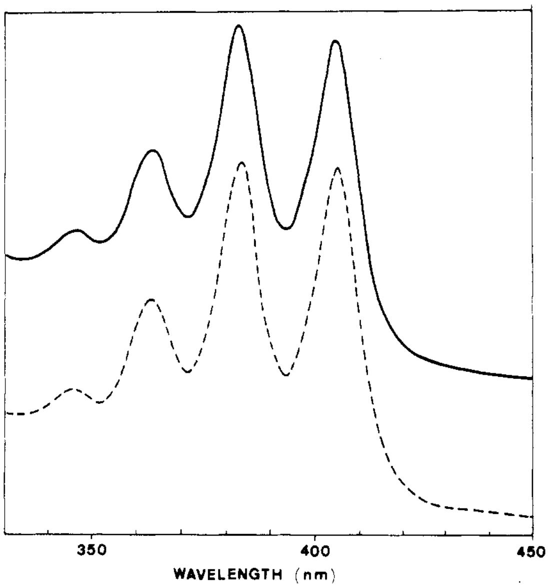

Figure 1. UV absorbance spectra of dilute mixtures of PS*–ScoMMA in toluene: solid line, SM0.75; dashed line, SM0.25.

The following procedure was used to determine the phase-separation kinetics. Samples of thickness around 60 μm were placed in a hot stage attached to the microscope, then heated very rapidly up to the temperature $T = T(\text{iso}) + \Delta T_Q$, and finally held in isothermal conditions. ΔT_Q values ranged from 0.5 to 10 °C. Fluorescence intensity I_F was recorded continuously over the duration of the experiments. Since we were not interested in the absolute values of I_F (which should depend on film thickness and blend composition) but rather in the evolution of I_F as a function of the phase-separation time, the data have been replotted by normalizing I_F to an arbitrary value of 100 at zero time, whatever the sample under study may be.

Check of the Suitability of the Fluorescence Quenching Technique for Studying the System PVME–ScoMMA–PS*. In spite of the success of the fluorescence quenching method for the study of the blends PS–PVME–PS*,[7-10] some additional questions arise about the suitability of this technique in the presence of polar methyl methacrylate units.

The UV absorption spectra of PS* in 5 wt % solutions of various ScoMMA in toluene were recorded by a Uvikon 810 Kontron double-beam spectrophotometer. As shown in Figure 1, the maxima of the absorption band of the dimethylanthracene unit fall at the same wavelengths (namely, 345.3, 362.8, 383.2, and 405.0 nm) whatever the copolymer MMA content may be. Similarly, the fluorescence emission spectra recorded on a Fica 55 fluorimeter do not reveal any marked difference in band position and intensity (Figure 2). Within the limits of the experimental errors, the lifetime of the fluorescent probe in the excited state, about 7 ns at room temperature,[7] does seem to be affected by the presence of MMA units. The same conclusions hold in the solid state for films of ScoMMA–PS* containing 100 ppm of anthracene rings and prepared by evaporation from 15 wt % solutions in toluene. Thus, one can conclude that the COO groups of the MMA units do not modify the fluorescence behavior of PS* in a significant manner.

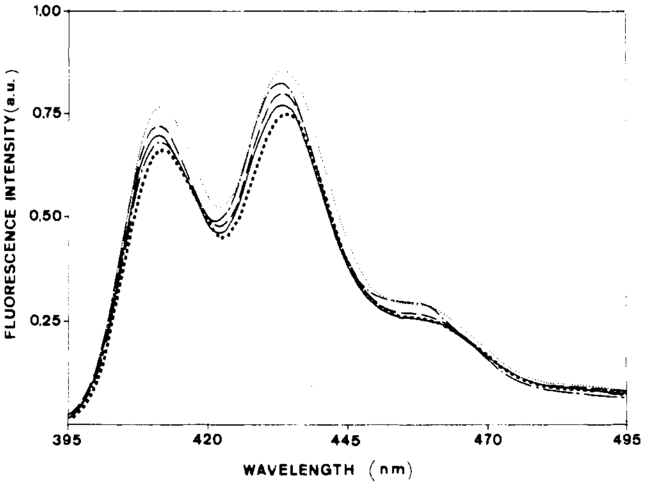

Figure 2. Fluorescence emission spectra of dilute mixtures of PS*–ScoMMA in toluene: (···) SM0.25; (– –) SM0.50; (—) SM0.75. Mixtures including parent homopolymers are given for comparison: (- - -) pure PS; (·-·) pure PMMA.

Table II
Values (in Arbitrary Units) of I_1 and I_2 Deduced from Fluorescence Measurements on Various Films at the Same Thickness and the Same PS* Content

film code	PVME, wt %	nature of 2nd polym	I_1	I_2
A	33	PS	72	790
B	50	PS	67	750
C	33	SM0.25	81	640
D	50	SM0.25	85	550

The next step was to check whether quenching of the fluorescence intensity actually occurs in the homogeneous blends PVME–ScoMMA–PS* and tends to disappear in the two-phase state, as expected. Table II gives fluorescence data relative to blends of PVME with either pure PS or SM0.25. All these systems, which are miscible at room temperature, exhibit similar fluorescence intensities I_1 in the presence of the same PS* content (adjusted to 10 ppm of the anthracene rings). Intensities I_2, corresponding to the maximum signal recorded in the two-phase state, reveal the occurrence of a great upturn of fluorescence emission (by a factor from 5.5 to 10) upon phase separation. Although this effect is systematically less pronounced with ScoMMA than with PS, it clearly validates the extension of the fluorescence quenching technique to the present study.

Results and Discussion

Phase Diagram Determination. In agreement with the previous statements,[1] copolymers ScoMMA containing a mole fraction of MMA units in the range 0.05–0.35 are miscible in all proportions with PVME at ambient temperature. In contrast, copolymers containing a mole fraction of MMA units as small as 0.40 are immiscible with PVME.

The fluorimetric study of a series of blends at different compositions yields boundary curves similar to those shown in Figure 3 on the particular example of the pair PVME–SM0.2. Systematically, curves deduced from continuous heating experiments deviate from the true phase coexistence curve obtained in isothermal conditions. The higher the heating rate, the larger the deviation is, owing to increased nonequilibrium effects.

Let us focus on the minima of the different curves, each being characterized by a temperature $T_{\min}$. All the blends PVME–ScoMMA exhibit $T_{\min}$'s, which are a function of heating rate (Table III). This behavior is in contrast with that of PS–PVME blends of comparable molecular weights for which $T_{\min}$ was shown to remain constant.[7] However, the heating rate dependence of $T_{\min}$ has already been

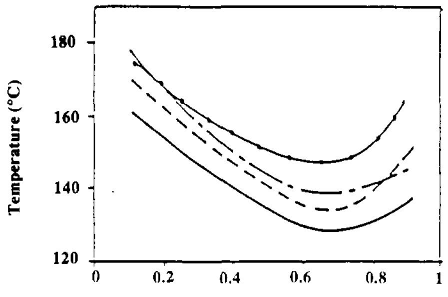

Figure 3. Fluorimetric detection of phase separation of the pair PVME–SM0.20 (from top to bottom: at 16 °C/min; at 5 °C/min; at 1 °C/min; and in isothermal conditions.

Table III
Values of T_{min} (°C) Deduced from Isothermal and Ramp Fluorimetric Measurements[a]

	fluorimetric measurements				
system	isothermal	2 °C/min	5 °C/min	16 °C/min	cloud pt: 2 °C/min
PS	127				121
SM0.10	130	133	136	141	145
SM0.20	124	129	135	149	151
SM0.30	113	116	119	130	126
SM0.35	85	92	96	105	98

[a] Cloud-point data, taken from ref 1, are given for comparison.

reported in the case of high molecular weight PS–PVME blends.[11] As a general rule, the origin of such a phenomenon is the consequence of a substantial slowing down of the rate of phase separation, whatever its physical origin may be: it just means that the heating rate of the sample is faster than the phase-separation rate.

Measurements performed on the different copolymers under continuous heating at 16 °C/min yield values of T_{min}, called T^{16}_{min}, that are in good agreement (Figure 4) with the minima T^{cp}_{min} derived from cloud-point measurements under continuous heating at 2 °C/min.[1] This suggests that the maximum of miscibility observed for the MMA mole fraction equal to 0.20 has no thermodynamic meaning, since T^{16}_{min} is actually characteristic of a nonequilibrium curve.

As shown in Figure 4, isothermal experiments yield values of T_{min}, called T^{iso}_{min}, that are, in the presence of copolymers, markedly lower than the T_{min}'s deduced from the usual cloud-point measurements. It is also apparent from Figure 4 that the dependence of T^{iso}_{min} on the MMA mole fraction is quite different from that of T^{cp}_{min}. T^{iso}_{min} remains constant within the experimental error up to a MMA mole fraction of close to 0.15 and then decreases more and more rapidly until the limit of compatibility is reached, at about 0.4. Thus, the origin of the gap observed between the plots T^{cp}_{min} and T^{iso}_{min} versus the MMA content (Figure 4) has to be searched for in kinetic effects.

All these observations support the assumption that the presence of the probe PS* does not affect the compatibility of the pair PVME–ScoMMA. Indeed, if PS* did play any role, it should not be to generate a decrease of the phase-separation rate, as observed.

Influence of the Copolymer MMA Content on Phase-Separation Kinetics. The heating rate influence on the phase diagram location can be estimated by the quantity $\Delta T_{min} = T^{16}_{min} - T^{iso}_{min}$. The ΔT_{min}'s are indicative in a semiquantitative way of the kinetics of the processes, since these quantities vary in inverse proportion to the rate of phase separation v. Figure 5 shows that v decreases strongly with an increase in the MMA mole fraction in the copolymer up to 0.20, where it reaches a minimum and then increases weakly. Since T^{iso}_{min} does not depend on the copolymer MMA content in the range 0–0.20, then the blend interaction parameter χ_{blend} is almost invariant in this composition range. By the way, one may notice that this result is not incompatible with the theoretical calculations:[3–6] owing to the weakness of the interaction parameters under consideration here,[1] a very small change in their values is sufficient to justify a constant value of χ_{blend} or a decrease of this quantity, as suggested previously.[1] As a consequence of the invariance of χ_{blend} in the range 0–0.20, the observed decrease of v cannot result from a change in the thermodynamic driving force. It results from a slowing down of the molecular motions involved in the phase-decomposition process, because of the change in the friction coefficients[12] associated with the presence of rigid MMA units. On the other hand, in the range 0.20–0.35, both effects occur: the increase in parameter χ_{blend}, accompanying the decrease of T^{iso}_{min}, favors an increase in v, whereas the progressive increase in the copolymer chain rigidity has an opposite effect. The weak increase in v that is observed is the result of this competition.

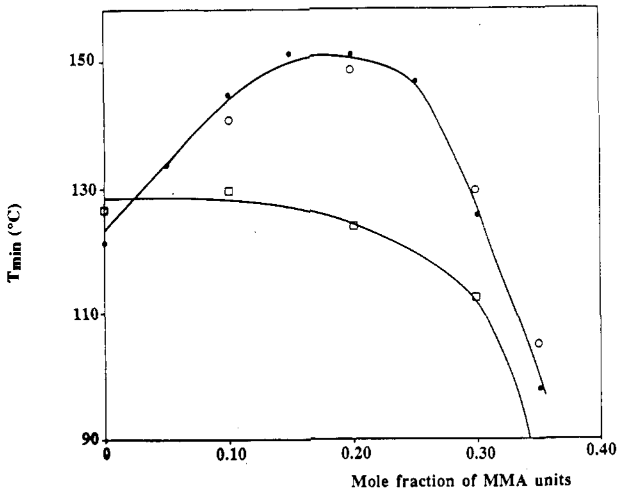

Figure 4. T^{iso}_{min}(□), T^{16}_{min}(○), and T^{cp}_{min} (●) versus the mole fraction MMA units in the copolymers ScoMMA. (Values of T^{cp}_{min} are taken from ref 1).

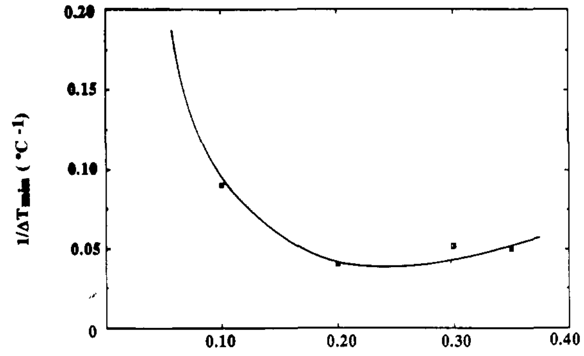

Figure 5. $1/\Delta T_{min}$ versus the mole fraction of MMA units in the copolymers ScoMMA.

Initial Rates of Phase Separation. The earliest stages of phase separation can also be followed in isothermal conditions, when the system is subjected to small quenches, ΔT_Q, inside the two-phase domain. As shown in Figure 6 on the example of the blend PVME–SM0.30 containing 71 wt % of PVME, the increase in fluorescence intensity as a function of time exhibits a logarithmic profile, whatever ΔT_Q may be. The limit observed corresponds to the situation where the system has reached the late

Table IV
Initial Phase Separation Rate v_0 versus ΔT_Q

	ΔT_Q (°C) for v_0[b] =						
blend	1	2	3	4	5	6	7
PVME-SM0.30	1.3	1.4	2.6	3.9	17.1	36.6	73.7
PVME-PS[a]	26.5	31.1	44.1	78.7			

[a] Data taken from ref 10. [b] In percent of phase separation per minute.

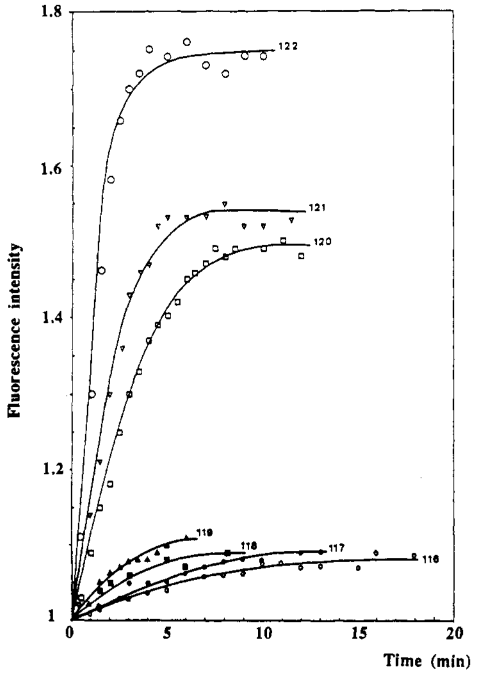

Figure 6. Normalized fluorescence intensity versus time at different ΔT_Q for the blend of PVME (71 wt %) with SM0.30. (Numbers indicate the experimental phase-separation temperatures in degrees Celsius).

stage of phase decomposition: the compositions of each phase are still the equilibrium compositions, and only the size of the domains is allowed to grow further with time.[10] Analysis of such curves[9,10] yields the initial rates of phase separation v_0, which represent the percentage of the overall phase decomposition per minute. As shown in Figure 7, two regimes are observed: phase-separation rates are very low for $\Delta T_Q \leq 4$ °C, whereas an important increase in the initial rate is observed for $\Delta T_Q \geq 5$ °C. Similar observations have already been reported for the pair PVME–PS and explained by a change from nucleation and growth to the spinodal decomposition mechanism.[10] In the case of the pair PVME–ScoMMA, the same explanation might hold but remains purely speculative since the positions of both the spinodal curve and critical point have not been determined. Table IV permits direct comparison of the order of magnitude of these initial rates with those observed at the same depths of quench ΔT_Q with a PS–PVME blend of similar composition (69.2 wt % PVME), phase coexistence temperature (113 °C), and polymer molecular weights. It is clearly confirmed that the presence of MMA units in the copolymer is responsible for a decrease of the phase-separation rate by a factor of about 20. An even more pronounced rate reduction (by a factor of about 50) was observed with the copolymer SM0.20.

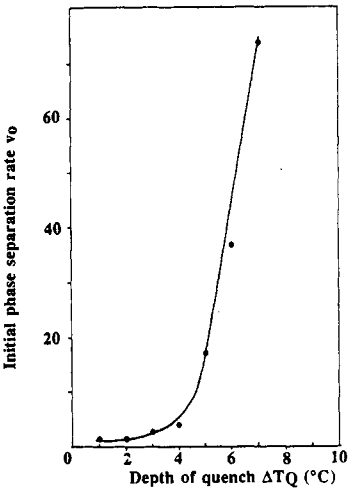

Figure 7. Initial phase-separation rate, v_0, versus the depth of quench, ΔT_Q, for the blend of PVME (71 wt %) with SM0.30.

It appears from these results that the rate effect needs to be assessed carefully in future studies of the phase separation of copolymer blends. This conclusion does not necessarily stand in the way of cloud-point determinations by the light-scattering technique. It just stresses the risk of the artifact associated with the temperature scan approach, which may yield nonequilibrium data.

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Registry No. PVME (homopolymer), 9003-09-2; ScoMMA (copolymer), 25034-86-0.