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Miscibility in blends of PVME with styrene-based block copolymers

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The phase behaviours in binary blends of styrene–isoprene diblock copolymer and poly(vinyl methyl ether) (PVME) were investigated by using small-angle X-ray and light scattering techniques. It was observed that the added homopolymer molecules were dissolved into the microdomains of the styrene blocks of the copolymer. The blends exhibited a lower critical solution temperature as seen in the blends of PVME with polystyrene. The experimental results were compared with that of the modified Meier's theory in a semiquantitative way. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: block copolymer; mesophase; lower critical solution temperature)

INTRODUCTION

It is known that binary mixtures of a block copolymer and a homopolymer exhibit complex phase behaviours due to the coupling of the two phase transitions; a microscopic phase separation transition of the block copolymer itself and a macroscopic segregation between the two polymers. Many theoretical and experimental studies[1-18] have been done to describe the phase behaviours of the blend systems containing a block copolymer. However, these studies have focused mainly on the special case in which the monomer of the homopolymer is chemically identical with one of the blocks of the copolymer. Only a relatively few studies[19-22] have dealt with the case of the added homopolymer having an exothermic interaction with one of the blocks of the copolymer.

Recently, Tucker et al.[21] investigated the phase behaviours of blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with styrene-based block copolymers. They found no macrophase separation between PPO and the block copolymers, PPO being completely dissolved into the styrene microdomains. According to their experimental results, it was implied that the favourable energetic interaction between PPO and the styrene blocks has a critical effect on the solubilization of PPO into the styrene domains of the block copolymer.

In previous work[23], we developed a theoretical approach for predicting phase separation behaviours in blend systems having a block copolymer, in which the added homopolymer has a specific interaction with one of the blocks of the copolymer. From the results of that work, it was found that the solubility of the homopolymer into the ordered phase of the block copolymer decreased with increasing temperature and the shapes of the phase diagrams were strongly dependent on the energetic interaction between the two polymers. The purpose of this study is to obtain some experimental evidence for the miscibility behaviours in one of those blend systems, blends of poly(vinyl methyl ether) (PVME) with styrene–isoprene block copolymers (SI), by using small-angle X-ray and light scattering techniques.

EXPERIMENTAL

Materials

PVME was obtained from Aldrich Co. It was dissolved into toluene, filtered with activated carbon powder, and precipitated in a large excess of hexane. Solution intrinsic viscosity was determined at 303 K in benzene using a Cannon–Fenske viscometer. The styrene–isoprene diblock copolymer used in this work was kindly synthesized by Dr T. Chang at Postech. The homopolystyrene was prepared by anionic synthesis and the molecular weight of it was measured by gel permeation chromatography (g.p.c). The preparation of diblock copolymer SI was conducted by subsequent anionic synthesis of the polystyrene with isoprene monomers. The styrene content of the diblock copolymer SI was determined by [1]H n.m.r. Thus, the molecular weight of the diblock copolymer SI was evaluated. The characterizations of samples used in this work are summarized in *Table 1*.

Blends of various fractions were prepared by casting from toluene solution and were dried for 4 days at room temperature. To remove residual solvent, the film specimens were further dried in a vacuum oven for 2 days at 323 K to minimize the chance of bubble formation on subsequent heating.

Methods

Cloud point measurement. The cloud temperature was determined by monitoring the intensity of scattered

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Table 1 Description of polymer samples

	SI block copolymer		PVME
	SI15	SI22	VM89
Molecular weight	14 900	22 400	89 000[b]
Polydispersity	1.10	1.03	1.69
Styrene composition[a]	0.52	0.56	—

[a] N.m.r. analysis, in weight fraction
[b] Viscometry

light at a fixed angle through the blend film located on a heating stage in a vacuum chamber. A He–Ne laser (4 mW) was used as a light source. The scattered intensity was recorded by a photo-diode detector (Newport Corporation 835 Optical Power Meter) with a computer interface. The thickness of the sample was about 0.02 mm. A gasket of aluminium, sandwiched between two cover glasses, was used for a sample holder. The heating rate was 1 K min^{-1}.

Small-angle X-ray scattering (SAXS). X-ray scattering measurements were performed with a Kratky camera fitted with a linear position sensitive detector (M. Braun Co.). All the SAXS profiles were obtained using nickel-filtered CuK_α radiation supplied by a generator (Rigaku Denki Co.) operating at 40 kV and 40 mA. In order to investigate structural changes on heating, the samples were held in an aluminum sample holder which was sealed with a window of 8 μm thick Kapton films on both sides. The samples were heated with two cartridge heaters and the temperature of the samples was monitored by a thermocouple placed close to the sample. To prevent degradation, samples were kept under vacuum during measurement. SAXS profiles were corrected for air scattering and absorption. The correction for slit-length desmearing was applied by means of Strobl's algorithm[24].

RESULTS AND DISCUSSION

It is well known that blends of polystyrene (PS) with PVME exhibit a lower critical solution temperature (LCST) which is one of the characteristic phenomena in miscible blends[25,26]. From spectroscopic analysis[27], it has been suggested that the major driving force for the mutual miscibility is a hydrogen-bonding type interaction between the two polymers. In the case where PVME is mixed with a styrene-based block copolymer having an ordered microdomain structure, the PVME molecules might be preferably dissolved into the styrene-microdomains of the copolymer due to the specific interaction. However, the mixtures are expected to exhibit complex phase behaviours arising from the coupling of the microphase separation transition (MST) of the block copolymer and the LCST-type phase segregation between the two polymers.

Figure 1 shows a calculated phase diagram of SI/PVME blends from our theoretical approach[23]. In this diagram, due to the coupling of the micro- and macrophase separations, there appear many phase regions: mesophase, liquid phase, and mixed phases of them. It should be noted that the diagram exhibits a LCST phenomenon, which takes place across the line between the M and M1 + M2 phase regions. As the temperature
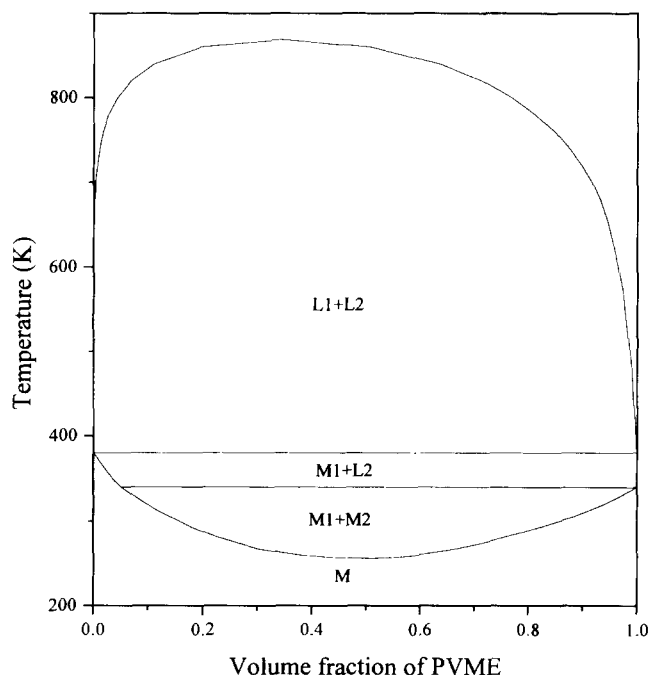

Figure 1 The calculated phase diagram of the SI/PVME blend[23]. Mesophases (M1 and M2) consist of ordered microdomains of the block copolymer swollen with homopolymer. Liquid phases (L1 and L2) consist of disordered block copolymer and homopolymer. The following molecular parameters are assumed: M_{SI} = 25 000 (the volume fraction of styrene block is 0.5), M_{PVME} = 90 000, the interaction energy densities being $B_{PS/PI}$ = 1.6–0.002T (cal cm^{-3}) and $B_{PS/PVME}$ = −0.2 + 0.0005T (cal cm^{-3}). As shown in PS/PVME blends systems, the calculated phase diagram exhibits an LCST phenomenon (see the line under the M1 + M2 region)

is increased, a homogeneous mesophase (M) is separated into two mesophases (M1 + M2) of different PVME fractions, where the mesophases may have the periodic microdomain structures. Therefore, the X-ray scattering technique can be used to determine the transition by monitoring the structural change in the block copolymer, which will be discussed in the following paragraphs with the experimental results.

The light scattering experiments were performed with two blend systems of SI22/VM89 and SI15/VM89, and the results are shown in *Figure 2*. The LCST behaviour is clearly seen, which indicates that the miscibility in the blends of styrene-based block copolymer with PVME is also greatly dependent on the specific interaction between styrene blocks and PVME, just as in binary blends of PS and PVME. It is interesting to note that the blends of higher molecular weight block copolymer exhibit higher cloud temperatures than those of lower molecular weight one. In binary blends of two homopolymers, it is well known that the cloud points are decreased with increasing molecular weight of homopolymers due to the decrease in the favourable combinatorial entropy of mixing. In the blends of a homopolymer with a block copolymer, however, the phase segregation temperature (the cloud point) might be increased with increasing the molecular weight or the volume of the microdomains of the copolymer. The increment of the cloud point with increasing molecular weight of the copolymer can be explained by considering the change in the conformational entropy of the homopolymer (PVME) chains. The added PVME might be preferably dissolved and confined into the
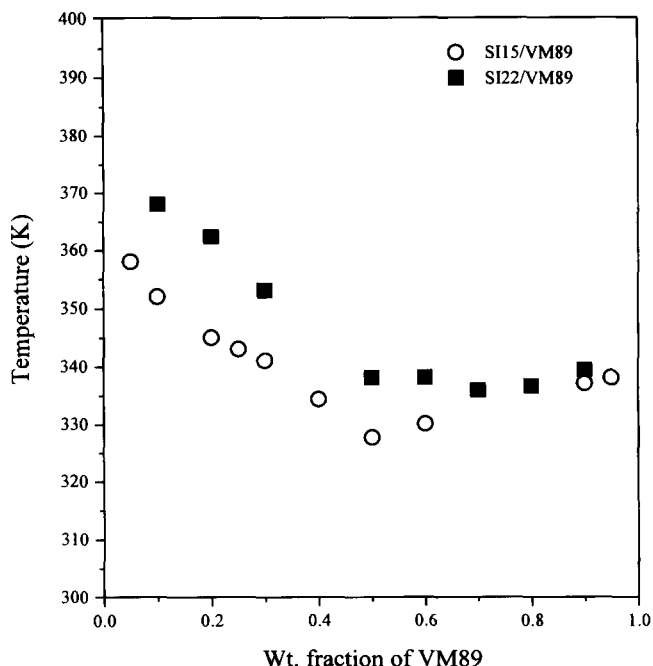
Figure 2 Cloud point results for SI/PVME blends having two different molecular weight block copolymers, where the open circles indicate the cloud points of SI15/VM89 and the square ones the cloud points of SI22/VM89

higher segregation temperatures than the SI15/VM89 blend.

Block copolymers having an ordered microdomain structure may exhibit several diffraction peaks due to the interdomain interference at their SAXS patterns. From the peak positions in the SAXS profiles, the interdomain distance of the block copolymer and its microdomain structure can be determined by using the simple Bragg's relation. The addition of homopolymer molecules into the ordered microdomains gives rise to an increment in the interdomain distance, which will be proved by the shift of the peak positions.

The SAXS profiles obtained from SI22/VM89 blends are shown in *Figure 3*, in which the desmeared intensities, $I(q)$, are plotted against q on a semi-logarithmic plot where q is $4\pi \sin\theta/\lambda$, λ being the wavelength. Here, it is readily found that each of the SAXS curves has a prominent first-order interference peak and the position of the peak shifts slightly toward the smaller q region with increasing VM89 fraction. From these results, it is inferred that the blends, except for the mixture of 3/7 wt% showing no higher order peaks than the first peak, maintain the ordered microdomain structure of the block copolymers and they are swollen with the added homopolymer.

As shown in *Figure 3*, the profile for the pure block copolymer has interdomain interference maxima and shoulders at the scattering vectors with the ratios of 1, 2, and 3, which means that the block copolymer has
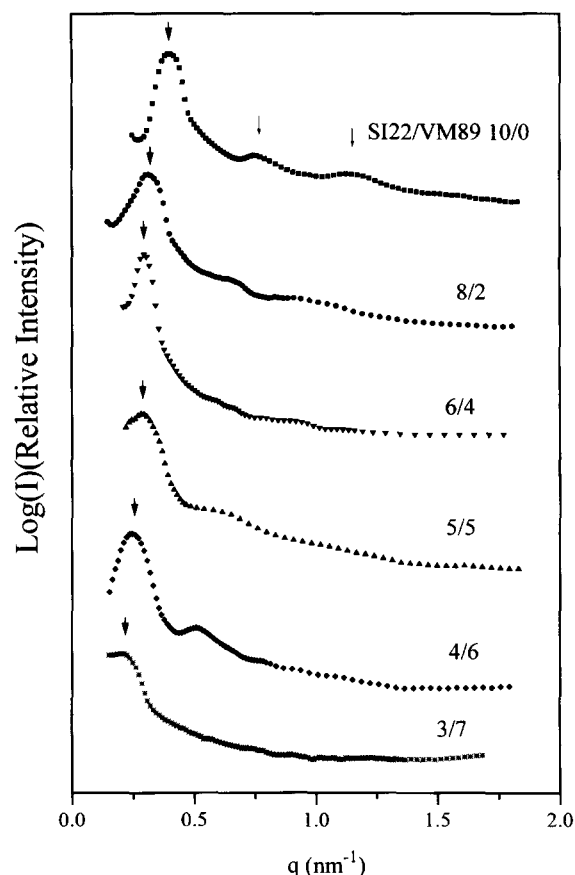
styrene domains owing to the favourable interaction of PVME with styrene blocks of the SI copolymer. The confinement of the added PVME chains into the microdomains gives rise to the loss in the conformational entropy of the PVME chains compared with those in free space, which is unfavourable to the mixing of PVME and the styrene blocks and is reduced with increasing volume of the styrene microdomains[21,23]. According to many experimental results for blends of PS and the styrene-based diblock copolymer, it was found that added PS of molecular weight larger than that of the styrene-blocks cannot be solubilized into the styrene domains. This implies that the PS of the same molecular weight as VM89 used here cannot be solubilized into the styrene domains of SI22 (or SI15) owing to the serious loss in conformational entropy of the PS. The radius of gyration of VM89 is calculated to be about 7.7 nm and, from the results of the SAXS experiments, the interdomain thicknesses of SI22 and SI15 are determined to be about 18 and 13 nm, respectively. From the fact that the volume fraction of the styrene domain is about 0.5, the styrene domain thicknesses of SI22 and SI15 are evaluated to be 9 and 6.5 nm, respectively. Thus, the size of VM89 is compatible with the styrene domain thicknesses. The added VM89 undergoes loss in conformational entropy to squeeze itself into the styrene domains and the amount of the entropy loss is increased with decreasing thickness of the styrene domain. Therefore, the added VM89 within the styrene domains of SI15 loses more conformational entropy than that within the styrene domains of SI22. As the temperature is increased, the favourable interaction energy density between the styrene blocks and VM89 is decreased, and at a certain temperature the conformational entropic contribution exceeds the enthalpic contribution, which provokes the segregation of VM89 from the microdomains of the block copolymer. Thus, the SI22/VM89 blend exhibits

Figure 3 Semi-logarithmic plot of desmeared SAXS patterns for SI22/VM89 blends at room temperature. The weight ratios of SI22 and VM89 in the blends are denoted. The positions of the first peak are indicated by thick arrows and the second and the third ones by thin arrows

lamella-shaped microdomains. As VM89 molecules are added, it is expected that the interdomain distance of the microdomains increases and the morphology of the blend may also change. The morphology is determined from the positions of higher order peaks relative to the first order peak. In this work, however, it is difficult to define the morphology of the blends since the appearance of higher order peaks relative to the first order peak is not clear. As an alternative to examining the morphological change, the interdomain distance could be used as shown in *Figure 4* although it is an indirect evidence for the possible morphological change. The variation of the interdomain distance with VM89 fraction for three representative morphologies, e.g. lamellar, cylindrical, and spherical, is calculated along with the experimental results (*Figure 3*). It should be noted that all the blend samples are visually clear, which indicates that there exists only one mesophase, that is, the added homopolymers are completely dissolved into the microdomain without any macro-segregation of VM89 out of the microdomains. In *Figure 4*, the complete dissolution of VM89 into the microdomains might yield information on the morphological change: the 8/2 wt% mixture may have the lamellar morphology, and the mixtures of 6/4 wt%, 5/5 wt%, and 4/6 wt%, cylindrical morphology. Our discussion, however, is not sufficient to conclude the morphological change since the method used here does not give direct evidence for it, and therefore for decisive proof, it is necessary to examine the microdomain structure by transmission electron microscopy.

According to many experimental studies[18,28], the dissolution of homopolymer A into the A-domains of block copolymer AB might be limited when the

molecular weight of homopolymer is greater than that of the copolymer. In this work, however, the molecular weight of the added homopolymer is about eight times as large as that of the styrene blocks, which means that the specific interaction between VM89 and styrene blocks is one of the most important factors in achieving the complete dissolution of the homopolymer into the copolymer. This explanation is also supported by the experimental results for blends of PPO with styrene-based block copolymers by Tucker *et al.*[21].

Figure 5 shows the temperature dependence of the SAXS pattern for SI22/VM89 of 5/5 wt%, in which only the first-order maximum was highlighted. It can be seen that the peak intensity decreases and its position shifts toward a larger angle (or q) as temperature is increased. For this mixture, the reciprocal of the maximum scattered intensity ($1/I_{max}$) vs the reciprocal of absolute temperature ($1/T$) and the interdomain distance (D) vs $1/T$ are plotted in *Figure 6*. We denote the MST temperature of a block copolymer by a dashed line and the temperature at which the added VM89 begins to be segregated from the styrene-domains of a block copolymer by a solid line. In the high temperature region above 440 K, the correlation length of the block copolymer of a 5/5 mixture is very close to that of the pure block copolymer. This indicates that a block copolymer dominant phase exists in the liquid phase of the mixture. The existence of the block copolymer dominant liquid phase is also suggested by the calculated phase diagram (*Figure 1*). Hence, the linear dependence of $1/I_{max}$ on $1/T$ as suggested by Leibler[29] may be utilized for the determination of the MST temperature of a block copolymer. It should be noted that the segregation of the added VM89 from the block copolymer in the ordered state begins at the same temperature as the cloud point observed in light scattering experiments.
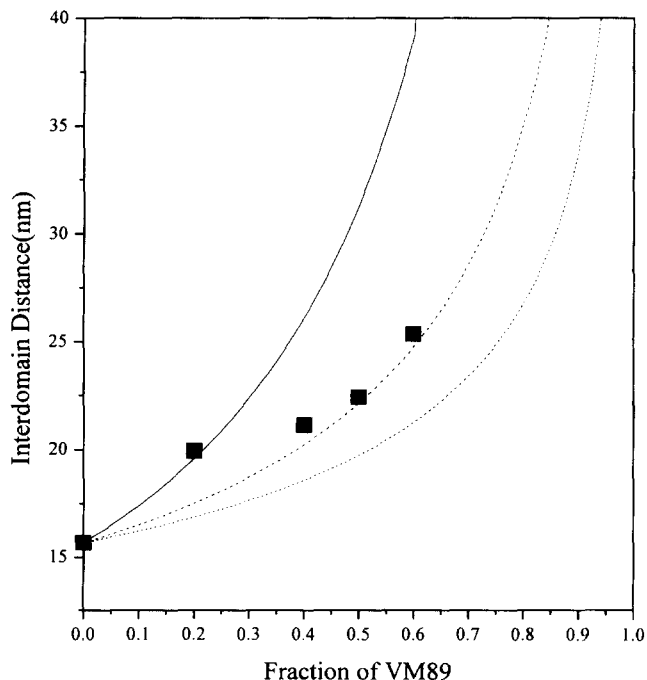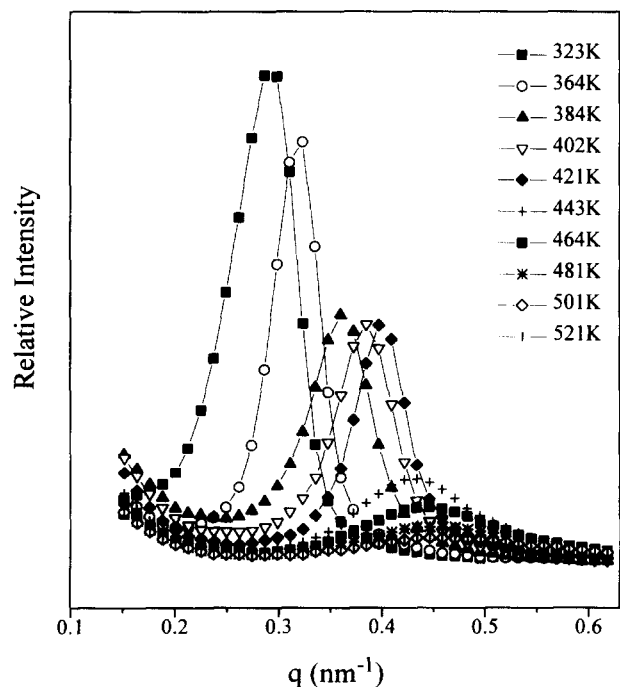
Figure 4 The comparison of experimental results (filled squares) with the calculated ones (for three morphologies, that is, lamellar (solid line), cylindrical (dash line), and spherical (alternating dash and point line) ones) for the variation of the interdomain distance with the VM89 fraction. The mixture of 8/2 wt% shows the lamellar morphology, and the mixtures of 6/4, 5/5, and 4/6 wt% show the cylindrical morphologies

Figure 5 The temperature dependence of the SAXS profile for SI22/VM89 blend of 5/5 wt%. Only the first scattering maxima are highlighted

Figure 7 shows the Bragg spacing of the first-order peak as a function of temperature determined from the SAXS profiles. It can readily be shown that the interdomain distance decreases as the content of VM89 decreases and the temperature increases, and moreover
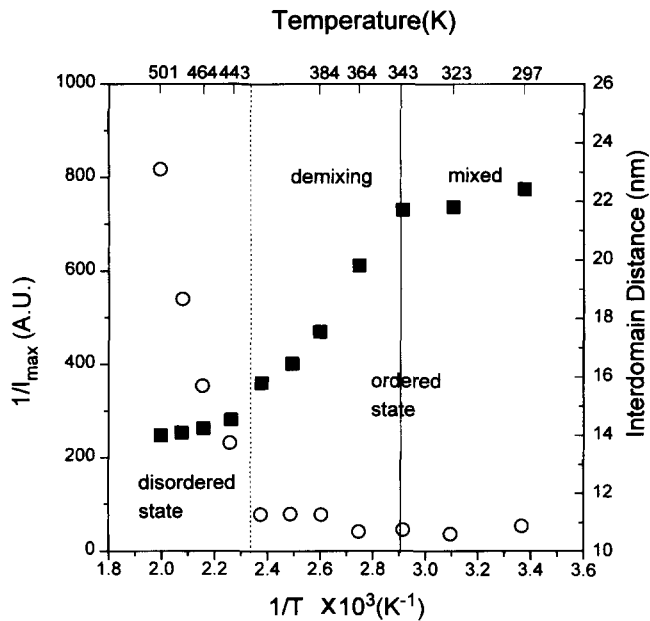
Temperature(K)

Figure 6 A plot of the reciprocal of the maximum scattered intensity $(1/I_{max})$ *versus* the reciprocal of absolute temperature $(1/T)$ ($\bigcirc$) and interdomain distance (D) vs $1/T$ ($\blacksquare$) for SI22/VM89 5/5 wt% blend. The solid line indicates the temperature at which the added VM89 begins to be segregated from the styrene domains of SI22 and the dash line the MST temperature of SI22
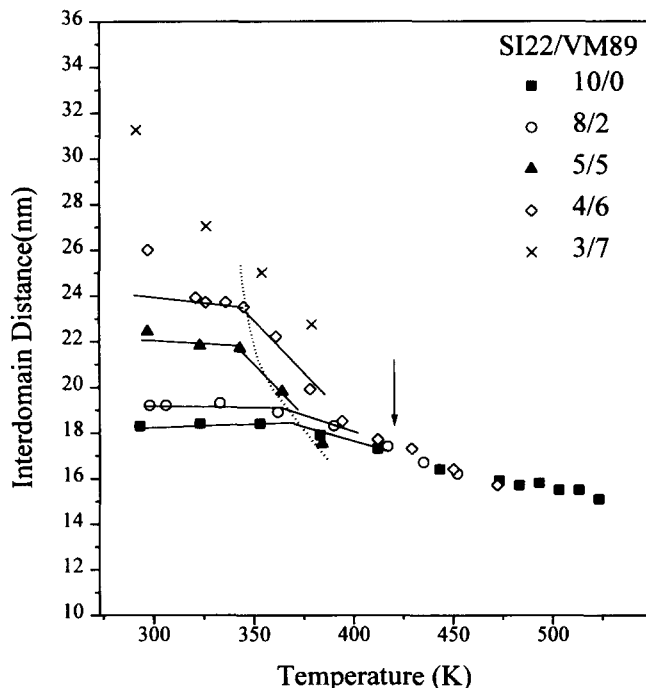
that the interdomain distance for all fractions are collapsed into a single curve at the MST temperature of the copolymer (about 423 K) (denoted by an arrow). The ordered microdomains in the mixture disappear above the MST temperature and only a broad peak due to the intramolecular correlation of block copolymer appears in the SAXS pattern, as shown in *Figure 5*. In addition, it should be noted that each of the curves in *Figure 7* has a certain point where the interdomain distance abruptly decreases with increasing temperature, which indicates that the dissolved homopolymer starts to be segregated out of the microdomains at that point. The dotted line, which connects those points, therefore, denotes the segregation temperatures of the blends. It is found conclusively that the phase separation can also be observed from the temperature dependence of the interdomain distance.

In *Figure 8*, the results of the light scattering experiments of SI22/VM89 are plotted with those of SAXS experiments. There is a good agreement between the cloud points and the demixing temperatures determined by SAXS and, the observed MST temperatures of the block copolymer mixtures are in the region of $420 \, \text{K} < T < 432 \, \text{K}$. It can be seen that the calculated phase diagram in *Figure 1* predicts that the MST takes place at the same temperature for all the blend fractions. As seen in *Figure 8*, the observed MST temperatures for the blends of 10/0, 8/2, 5/5, and 4/6 wt% are almost the same value within a permissible error.

As predicted in *Figure 1*, it is also expected to observe the formation of double peaks in SAXS profiles as the temperature is increased across the transition line, $M \rightarrow M1 + M2$. However, we could not find the double peaks in our SAXS data, for an unknown reason. One possibility not to detect the double peak is that after the transition from M to M1 + M2, the high fraction phase of VM89 (M2) may be short of SI22

Figure 7 A plot of interdomain distance (D) vs temperature of SI22/VM89 blends. All the diagrams have the same pattern; D increases with increasing the fraction of VM89 but decreases with increasing temperature. At about 423 K, all D's of the blends are collapsed into a single curve
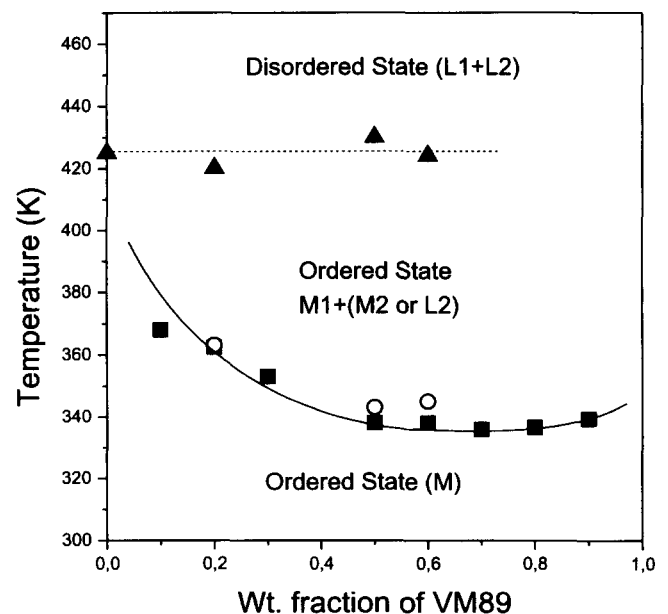

Figure 8 A phase diagram obtained from experimental results for SI22/VM89 blends. As for the macrophase separation temperatures, the open circles denote the results of the SAXS experiments and the filled squares the results of the light scattering experiments. The filled triangles denote the MST temperature evaluated from the SAXS (see *Figure 6*)

molecules that serve to preserve the periodic micro-domain structure in mesophases. Thus, the intensity of SAXS peaks from the high content VM89 phase was so low that we failed to observe it.

CONCLUSIONS

From SAXS experiments, the phase separation temperature could be graphically detected by monitoring the temperature dependence of the interdomain distance. These results had a good agreement with those of light scattering experiment. Both experimental results show that the blends of PVME and SI exhibit an LCST-type phenomenon and that the relatively higher molecular weight of PVME could be dissolved into the micro-domain of the copolymer.

As can be seen in *Figure 1*, the calculated phase diagram predicts the fact that SI/PVME blends exhibit an LCST phenomenon and that there exist mesophases after the transition, M → M1 + M2, with increasing temperature, which could be proved by the scattering experiments. However, there is a large deviation between the observed transition temperatures and the calculated ones, which may arise from our model being over-simplified in order to obtain easily the main feature of the phase diagram for the blends having block copolymers.

In conclusion, the specific interaction between styrene block and PVME has a major role in determining the phase behaviour of styrene–isoprene block copolymer and PVME blends.

ACKNOWLEDGEMENT

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