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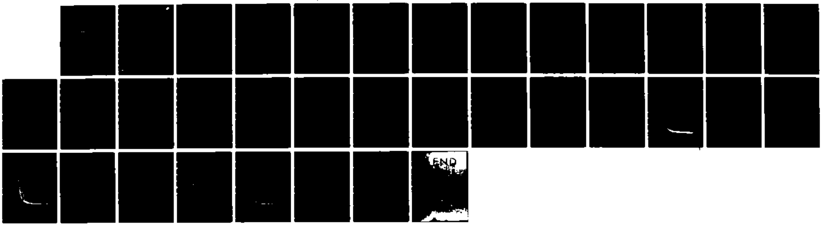

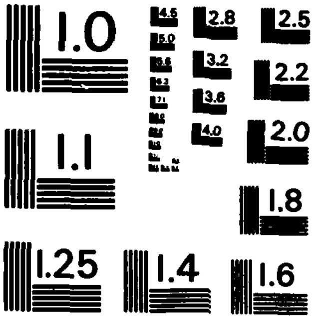

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TECHNICAL REPORT NO. 11

Phase Diagram of Polymer Blends Containing Block Copolymers

by

R. J. Roe

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ABSTRACT

The phase transition and phase separation behavior occurring in mixtures containing an A-B block copolymer and an A homopolymer is discussed. With a pure block copolymer an order-disorder transition can be induced by raising the temperature, whereby the ordered lattice of segregated microdomains becomes unstable and give way to a homogeneous liquid structure. Small amounts of a homopolymer added to a block copolymer can be accommodated in the microdomains consisting of the same type of monomeric units, up to a solubility limit that depends on the relative lengths of the homopolymer and the copolymer block and on the temperature. The order-disorder transition temperature of the block copolymer is also affected by the added homopolymer. At the other extreme of concentration, spherical micelles of block copolymer is formed when a small amount of the copolymer is added in the bulk homopolymer, and its critical micelle concentration again depends on the relative lengths of the molecules and blocks involved and on the temperature. Measurements were made with light scattering and small-angle X-ray scattering techniques to determine the phase behavior of mixtures containing a styrene-butadiene block copolymer and either a polystyrene or a polybutadiene. The resulting phase diagram exhibits a fascinating complexity. Comparison with recent theories treating these phenomena shows that a good agreement is generally obtained on a qualitative or semi-quantitative level, but a quantitative agreement is often not attained.

I. INTRODUCTION

Block copolymers exhibit many interesting and unusual properties. These properties arise from the fact that the different types of blocks constituting the copolymer segregate into microdomains which then form regular lattice-like arrangements. The beautiful morphological features consisting of spheres, cylinders or lamellae, obtained by electron-microscopy, are now well documented.

Further variations in the properties and morphology can be attained when one blends an A-B block copolymer with an A or B homopolymer. With a block copolymer alone, the important parameter determining the type of morphology (spherical, cylindrical or lamellar) is the relative lengths of the two types of blocks. When the homopolymer is blended in, one has the additional variables of the relative concentration of the homopolymer to the copolymer and the relative length of the homopolymer to the copolymer. With these additional variables at our disposal, the types of behavior that can be expected are now much more complex. In order to interpret their behavior one has to develop a more systematic understanding of the factors governing their miscibility and microphase separation.

Let us briefly examine the possible effect that can arise when we change the relative concentration of the homopolymer. When the concentration is very small, the relatively small number of molecules of A homopolymer will be dissolved into A microdomains of the copolymer, and not much change in the morphology occurs. When the concentration of the homopolymer is increased, however, the ratio of the volume of A microdomains to that of B microdomains is altered, and may lead to a change in the morphology, say from spheres to cylinders. With still further increase in the concentration, the solubility limit of the homopolymer in the microdomains may be reached and macro-phase separation then occurs. The solubility limit, of course, depends on the relative chain lengths of the homopolymer and of the A block in the copolymer. If we start from the other concentration extreme, where a small amount of the copolymer is dissolved in the bulk phase of A homopolymer, B blocks of the copolymer will aggregate to produce spherical micelles. When the concentration of the copolymer is very small, these micelles are only sparcely populated and remain independent of each other. With increasing population of the micelles, their mutual interaction (mostly repulsive) will provide a liquid-like short-range order, or even a solid-like lattice structure.

The possible phase behavior of the homopolymer-copolymer blends sketched above will be modified as we change the temperature, since the degree of incompatibility between the A and B repeating units usually depends sensitively on the temperature. Thus, the phase diagrams of these blends depicting the stability limits of various types of macro- and micro-phases as a function of the concentration and temperature are expected to portray interesting complexities. By combination of small-angle X-ray scattering and light scattering (cloud points) techniques, we have determined the phase diagrams[1,2] of three blend systems containing a styrene-butadiene diblock copolymer and either a (low mol. wt.) styrene homopolymer or a butadiene homopolymer. We have also determined the detailed characteristics of the micelles formed in similar systems[3,4] by means of small-angle X-ray scattering. Before the study of the blends, we have also investigated[5] the behavior of the block copolymer alone, especially with regard to its order-disorder transition induced by temperature change. The results obtained in the study of the transition in the pure block copolymer form the basis for understanding the phase behavior of the blends. The details of these results are published elsewhere, and in this article we summarize the main facet of the phase diagram obtained.

II. ORDER-DISORDER TRANSITION OF BLOCK COPOLYMER

Binary mixtures containing polystyrene, polybutadiene, and/or styrene-butadiene random copolymer exhibit[6] the upper critical solution behavior, indicating that the degree of incompatibility between the styrene and butadiene monomeric units can be reduced by raising the temperature. Similarly, with block copolymers, the segregated microdomains become unstable at high temperatures and give way to a completely disordered state where the two types of blocks are molecularly dissolved in each other. The possibility of such order-disorder transition was discussed in the theory of block copolymers by Leibler.[7] He predicts the transition temperature as a function of the interaction parameter χ between the two types of repeating units, the total number N of repeating units in the copolymer molecule, and the relative lengths of the two blocks. Experimentally, the occurrence of such transition was first suggested in the rheological data obtained with a styrene-butadiene-styrene triblock copolymer by Chung and coworkers[8,9] and Porter and Gouinlock.[10] Chung and Lin,[9] for example, report that the dynamic modulus of the triblock copolymer, as the temperature is raised, drops abruptly and its rheological behavior changes from non-Newtonian to Newtonian over a narrow transition region 140-150°C.

We have utilized the SAXS technique to obtain evidence for such a transition.[5] Two polymer samples were studied: a styrene-butadiene-styrene triblock copolymer (block mol. wt. 7000-43000-7000), which is the same polymer as used[8-10] for the rheological studies mentioned above, and a styrene-butadiene diblock copolymer (block mol. wt. 7000-20000). Figure 1 shows the scattered X-ray intensities plotted against the scattering angle s ($= 2\sin\theta/\lambda$), which were obtained with the triblock copolymer at 20, 100, 140, 176, 200, and 250°C. The small-angle peak, at $s \sim 0.042 \mathrm{nm}^{-1}$, arises from the regular lattice-like arrangement of spherical butadiene microdomains. These scattering curves were reproducible and thermally reversible. Although detailed analyses can be performed on these scattering curves, the most interesting feature in the present context is the fact that the peak intensity decreases steadily with increasing temperature and disappears almost completely above 200°C. (The very small peak persisting at the highest temperature 250°C probably arises, not from any residual microdomains, but from the "correlation hole" effect discussed by deGennes.[11])

In Figure 2 the peak intensities obtained with both the triblock and diblock copolymers are plotted against temperature. The plot for the triblock copolymer shows that the microdomain structure evidently persists to temperatures much higher than the rheologically observed transition region of 140-150°C. This difference may arise partly from the fact that the small oscillatory strain imposed for the rheological measurement itself could be conductive to the destruction of the microdomain structure somewhat. It is more likely, however, that the phenomena of transition measured by the two techniques are not identical. The X-ray scattering intensity gives the measure of the total volume of the segregated styrene domains remaining, whereas the rheological behavior will manifest a transition as soon as all the butadiene blocks linking different styrene domains have disappeared even when some isolated styrene domains may still persist.

The results in Figure 2 suggest that the microdomain structure is destroyed over a rather broad temperature range. This raises a question as to what the structure in the intermediate stages would be like. Suggestions were sometimes made that in such intermediate structures the boundary layers of the styrene microdomains become more and more diffuse, while the number and the size of the microdomains remain unchanged. More detailed analysis, however, shows that our scattering curves are more consistent with the model that the boundary layer is not affected much, but with increasing temperature the size of the styrene microdomains become smaller as more and more of the styrene blocks become solubilized in the continuous butadiene matrix.

Leibler's theory[7] predicts that the order-disorder transition will occur when the product χN is equal to about 17 in the case of diblock copolymers where the ratio of the two block lengths is approximately 1/3. One can write:

$$\chi N = (\Lambda/kT)Mv_{sp} \tag{1}$$

where the right-hand member contains quantities that can be determined experimentally unambiguously: the molecular weight M of the copolymer, its specific volume v_{sp} and the polymer-polymer interaction energy density Λ. The interaction energy density between styrene and butadiene was previously determined[6] from the measurements of cloud points of binary mixtures containing homopolymers and random copolymers. With appropriate numerical values substituted in equation 1, it can be shown that the value of χN equal to 17 corresponds to a transition temperature of about 580K. Figure 2 suggests that the transition temperature of our diblock sample lies at about 400K. Although not perfect, the agreement is considered good, especially in view of the fact that no adjustable or ambiguous parameters are involved in this comparison.

III. PHASE DIAGRAM OF HOMOPOLYMER-COPOLYMER BLENDS

Many interesting phase separation behaviors are expected to develop when a block copolymer is mixed with a homopolymer. But the most immediate questions that can be raised are concerned with the solubility limit of the homopolymer in the block copolymer microdomains and whether the order-disorder transition temperature of the block copolymer is modified by the presence of the homopolymer. We investigated three mixture systems,[1,2] all of which contain the same styrene-butadiene diblock copolymer discussed in the previous section and as the second component a homopolymer, either a polystyrene of M_w 2400, a polystyrene of M_w 3500, or a polybutadiene of M_w 26000. Light scattering was utilized to determine the macrophase separation (cloud points) and the small-angle X-ray scattering technique was utilized to determine the order-disorder transition of the microdomain structure. The most detailed studies were made with the mixtures containing the lowest mol. wt. polystyrene (M_w 2400). The results presented below pertain to this mixture system unless otherwise mentioned.

Figure 3 shows the cloud points obtained with the light scattering technique. In region I the mixture is visually transparent, although X-ray scattering results, to be discussed later, clearly indicate the presence of microdomains. In region II the mixture is also transparent, and behaves as a homogeneous liquid of moderate viscosity (which contains no microdomains as revealed by the X-ray study). The boundary between regions I and II cannot be detected by light scattering technique because of the fact that the microdomains are much smaller than the wavelength of light. When a mixutre containing more than about 20% of polystyrene is heated, the transparent mixture in region I quickly turns to an opaque one characteristic of phase-separated systems. On further increasing the temperature, it reaches region II and becomes transparent again. At low temperatures, with increasing amounts of polystyrene added, the mixtures remain transparent until, with more than about 45% polystyrene, the mixture turns translucent, signaling that in region III the polystyrene cannot be accommodated completely in the styrene-microdomains, and the excess polystyrene beyond the solubility limit is now rejected into a separate macroscopic phase. Although both region III and IV denote macrophase-separated systems, their characters are different from each other and, as the temperature is raised, the turbidity increases rapidly on crossing from III to IV at the temperatures indicated by open circles in Figure 3.

Figure 4 shows the slit-smeared X-ray intensity I(s) obtained at 50°C with the mixtures containing various amounts of the polystyrene. The numbers on the curves denote the weight fraction of polystyrene in the mixture. Although the detailed shape of these curves can be quantitatively analyzed to obtain other information, the most prominent features that are displayed by these curves are that, with increasing fraction of polystyrene, the peak intensity increases and the peak angle decreases. The increase in the peak intensity is related to the fact that the scattering power of a sample is essentially proportional to $\phi(1-\phi)$ where ϕ is the volume fraction of one of the constituents. Since the block copolymer already contains about 27% styrene, the value of $\phi = 0.5$, at which $\phi(1-\phi)$ attains the maximum, is reached when the fraction of added polystyrene is equal to about 30%. The peak intensity and the total scattering power[1] (often called the invariant Q) are not necessarily strictly proportional, but usually show similar trends, which the data given in Figure 4 evidently exhibit.

The shift in the peak angle in Figure 4 with increasing amounts of polystyrene reflects the fact that as more polystyrene is added the styrene microdomains increase in size and consequently their mutual distances increase. In Figure 5, the peak angle is plotted against the weight fraction of polystyrene in the mixture. It shows that the peak angle decreases until about 50% polystyrene, beyond which the peak angle ceases to change since any additional polystyrene will no longer enlarge the microdomains but separates out as distinct macrophases. The solubility limit thus deduced from Figure 5 agrees fairly well with the value obtainable from the cloud point measurement as given in Figure 3.

Direct visual comparison of scattering curves obtained at different temperatures with mixtures containing different amounts of polystyrene does not immediately reveal in what way the order-disorder transition temperatures are affected by the added polystyrene. A more quantitative way of analyzing such curves is to plot the reciprocal of the peak intensity against 1/T. Such a plot was suggested by Leibler's block copolymer theory,[7] and a similar procedure is also used in the analysis of light scattering data.[12-14] In such plots[1] the points obtained above the transition temperature lie on a straight line and its extrapolation to $1/I_{max} = 0$ gives the spinodal temperature and the first derivation of the observed points from the straight line gives the binodal temperature. Figure 6 plots the binodal and spinodal temperatures obtained in this manner against the weight fraction of polystyrene, and shows that the order-disorder transition temperature is raised as a result of addition of polystyrene.

Combining the data obtained from the light and X-ray scattering, we now construct the phase diagram showing the phase transition and phase separation behavior as a function of temperature and composition. In the construction, we are guided by the thermodynamic principles embodied, for example, in the Gibbs phase rule, and also made use of the several convenient rules[15] formulated to guide the construction of phase diagrams.

The resulting phase diagram is shown in Figure 7. In the two liquid phases, designated L_1 and L_2, the block copolymer is molecularly dispersed and no ordered structure remains. The cloud point curve delineating the boundary of the two phase region $L_1 + L_2$ is essentially governed by the Flory-Huggins free energy of mixing. In the mesophase M_1 microdomains, swollen with dissolved polystyrene, are organized into an ordered structure. Point A is the order-disorder temperature (binodal) of pure block copolymer. At small polystyrene concentrations, the regions L_1 and M_1 are bounded to each other not by a single line but by two lines enclosing a small region of two coexisting phases. The thermodynamic principles dictate that in phase diagrams two single phase regions cannot be separated by a single line denoting transition temperatures if the underlying transition is of a first order. If, on the other hand, the underlying transition is of a second order, the two single phase regions should be separated by a single line. The theory by Leibler[7] suggests that the block copolymer order-disorder transition should be of a first order, although our X-ray results[1,5] show that it is very diffuse. In our light scattering study, no increase in turbidity was noted in the transition region between M_1 and L_1 on raising the temperature. This suggests that the two phase region BAC, if it exists at all, would be very narrow and could not be detected by our technique.

The line BCD is horizontal, signifying that three phases L_1, M_1 and L_2 coexist at a fixed temperature (under a given pressure), which is often called the peritectic point.[15] The lines CE and EH denote the solubility of polystyrene in the ordered block copolymer phase as a function of temperature. The presence of discontinuity in the solubility curve suggests that point E constitutes a part of an eutectic or peritectic region. In other words, there must exist in the phase diagram another new, single-phase region which terminates at the temperature corresponding to E, so that three phases coexist at this temperature. Although the nature of this new phase is not known clearly at this time, we speculate it to be a mesophase M_2 consisting of an ordered suspension of block copolymer micelles in the medium of polystyrene. Thus, whereas mesophase M_1 consists of ordered microdomains of styrene in the medium of butadiene, mesophase M_2 would represent the inverted structure consisting of ordered microdomains of butadiene in the medium of styrene. The features in Figure 7 drawn with broken lines are based on such speculative considerations and have to be confirmed by future studies.

The phase diagrams obtained with the mixture systems containing polystyrene of M_w 3500 or polybutadiene of M_w 26000 are qualitatively the same as the one discussed above. Among the quantitative differences we note that the solubility of homopolymer (at 90°C) in the styrene-butadiene diblock copolymer studies is equal to 0.48 weight fraction of polystyrene M_w 2400, 0.18 weight fraction of polystyrene M_w 3500, and 0.27 weight fraction of polybutadiene M_w 26000. The theory by Meier[16] predicts that the solubility of a homopolymer in a block copolymer is governed by the ratio of the homopolymer chain length to the length of the block having the same constituent units. In this qualitative sense our results confirm the prediction of the theory. The numerical values for the solubility of the homopolymers calculated from the theory are, however, smaller by about an order of magnitude than the observed values for all the three cases.

The recent theory by Hong and Noolandi[17] treats the phase equilibria in mixtures containing a homopolymer and a block copolymer. Many of the features deduced from the theory are qualitatively in agreement with our observation, including the predictions that there exists an eutectic point and that the order-disorder transition temperature is modified by the addition of the homopolymer. Quantitative comparison is difficult at this time because the calculated numerical results presented in their paper[17] do not closely correspond to the mixture systems we studied.

IV. CRITICAL MICELLE CONCENTRATION OF BLOCK COPOLYMER MICELLES

When an extremely small amount of an A-B block copolymer is added to an A homopolymer, the copolymer molecules remain in solution and molecularly disperse. As the concentration is increased beyond a certain concentration (called critical micelle concentration), the B blocks of the copolymer aggregate into spherical micelles. We have utilized[3,4] the small-angle X-ray scattering technique to determine the characteristics of such micelles: for example, the radius, the critical micelle concentration (CMC), the degree of swelling of the micelle core by the homopolymer, and the number density of the micelles, as a function of concentration and temperature. We have studied three block copolymers of differing styrene/butadiene ratios, all dispersed in a medium of low molecular weight (M_n = 2350) polybutadiene. The first copolymer, denoted 25/75, has M_w = 28000 with 27% styrene, and is the same polymer studied for the phase behavior as described in the previous two sections. The second copolymer, denoted 50/50, has M_w = 26000 and contains 52% styrene, while the third, denoted 75/25, has M_w = 22000 with 77% styrene.

In the present context of discussing the phase behavior of homopolymer/copolymer mixtures, the dependence of the CMC on the temperature and on the block length ratios is the most relevant. Detailed discussion on other characteristics determined, such as the radii of micelles, can be found elsewhere.[3,4] The determination of CMC relies on the fact that the scattering of X-ray by the B block of the copolymer dissolved molecularly is very weak, whereas the scattering due to the micelle core consisting predominantly of the aggregated B block is strong and displays a characteristic scattering curve. Thus, by plotting the intensity of micellar scattering against the concentration of copolymer, one obtains a linear relationship, and from its extrapolation to zero intensity one determines the CMC, or the minimum concentration of the copolymer required for micelle formation.

Figure 8 shows the CMC against temperature for the mixtures containing one of the three block copolymers. Copolymer 75/25, having the longest styrene blocks, is least compatible with polybutadiene and hence exhibits the lowest CMC, whereas copolymer 25/75, having short styrene blocks and long butadiene blocks, can be dissolved to a much higher concentration before micellar aggregates are formed. With increasing temperature the compatibility between styrene and butadiene increases[6] and therefore the CMC increase in all the three cases. Figure 8, in which the temperature is deliberately chosen as the ordinate, resembles conventional cloud point curves obtainable with polystyrene/polybutadiene mixtures or with mixtures containing a polystyrene and a styrene-butadiene copolymer. This is because essentially the same factor, that is, the incompatibility between styrene and butadiene and its variation with temperature, determines the shape of the cloud point curves and the CMC. It should be remarked, however, that the onset of micelle formation at the CMC does not constitute a phase transition and the curves shown in Figure 8 do not represent a true phase diagram.

Recently, theories of block copolymer micelles have been developed by Leibler et al.[18] and by Noolandi and Hong.[19] In particular, the theory by Leibler et al.[18] discusses CMC of block copolymer micelles in a homopolymer medium. Comparison of our results given in Figure 8 with the curves calculated according to the theory,[18] with the parameter values appropriate to our systems, shows that the agreement is semi-quantitative in general and that the trend of increasing CMC with increasing temperature and with increasing butadiene block lengths is correctly predicted. The details of this comparison will be published separately elsewhere.[20]

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LEGENDS TO FIGURES

Figure 1. Slit-smeared X-ray intensity $\tilde{I}(s)$, obtained with the S-B-S triblock copolymer sample, plotted against s (= 2sinΘ/λ). The curves show the data obtained at 20, 100, 140, 176, 200, and 250°C in the order of decreasing peak intensity.

Figure 2. The scattered X-ray intensity $\tilde{I}_{max}$ at the peak (from which the background has been subtracted) is plotted against temperature. Filled circles: triblock copolymer; filled squares: diblock copolymer.

Figure 3. Cloud points obtained with mixtures containing diblock copolymer (styrene 27%) and polystyrene (M_w = 2400). In regions I and II the mixture is transparent, while in regions III and IV it is turbid. The turbidity increases sharply on crossing from region III to region IV at the temperatures indicated by open circles.

Figure 4. Slit-smeared X-ray intensity plotted against s. The data were obtained at 50°C with diblock copolymer samples containing various amounts (weight fractions) of polystyrene (M_w = 2400) as indicated on the curves. For the sake of legibility the curves are drawn thin and thick alternately.

Figure 5. Angle s_{max} of the small-angle X-ray peak (at 50°C) plotted against the weight fraction of polystyrene (M_w = 2400) which was added to S-B diblock copolymer (styrene 27%). With increasing amount of polystyrene

the peak angle decreases, indicating an increase in the distance between microdomains. The solubility limit is reached at around 50% polystyrene and the peak angle thereafter ceases to change on further addition of polystyrene.

Figure 6. Spinodal (circles) and binodal (squares) temperatures associated with the order-disorder transition of diblock copolymer mixtures containing various weight fractions of polystyrene.

Figure 7. Phase diagram of the mixture system containing styrene-butadiene diblock copolymer (styrene 27%) and polystyrene (M_w = 2400). The cloud points (circles) and the block copolymer order-disorder transition temperature (squares) are also given. The liquid phases L_1 and L_2 consist of homogeneous solutions of disordered block copolymer and polystyrene. Mesophase M_1 consists of ordered microdomains of the block copolymer swollen with polystyrene. Mesophase M_2 probably consists of ordered microdomains (or micelles) of aggregated butadiene blocks in the medium of styrene (polystyrene and styrene blocks of the copolymer). The lines BCD and EFG represent peritectic temperatures where three phases coexist. The features on the lower right, drawn in broken lines, are more speculative than the rest.

Figure 8. Critical micelle concentration of three S-B diblock copolymers in polybutadiene, plotted against

temperature. The copolymers designated 75/25, 50/50, and 25/75 contain 77%, 52%, and 27% of styrene, respectively.

FIGURE 1

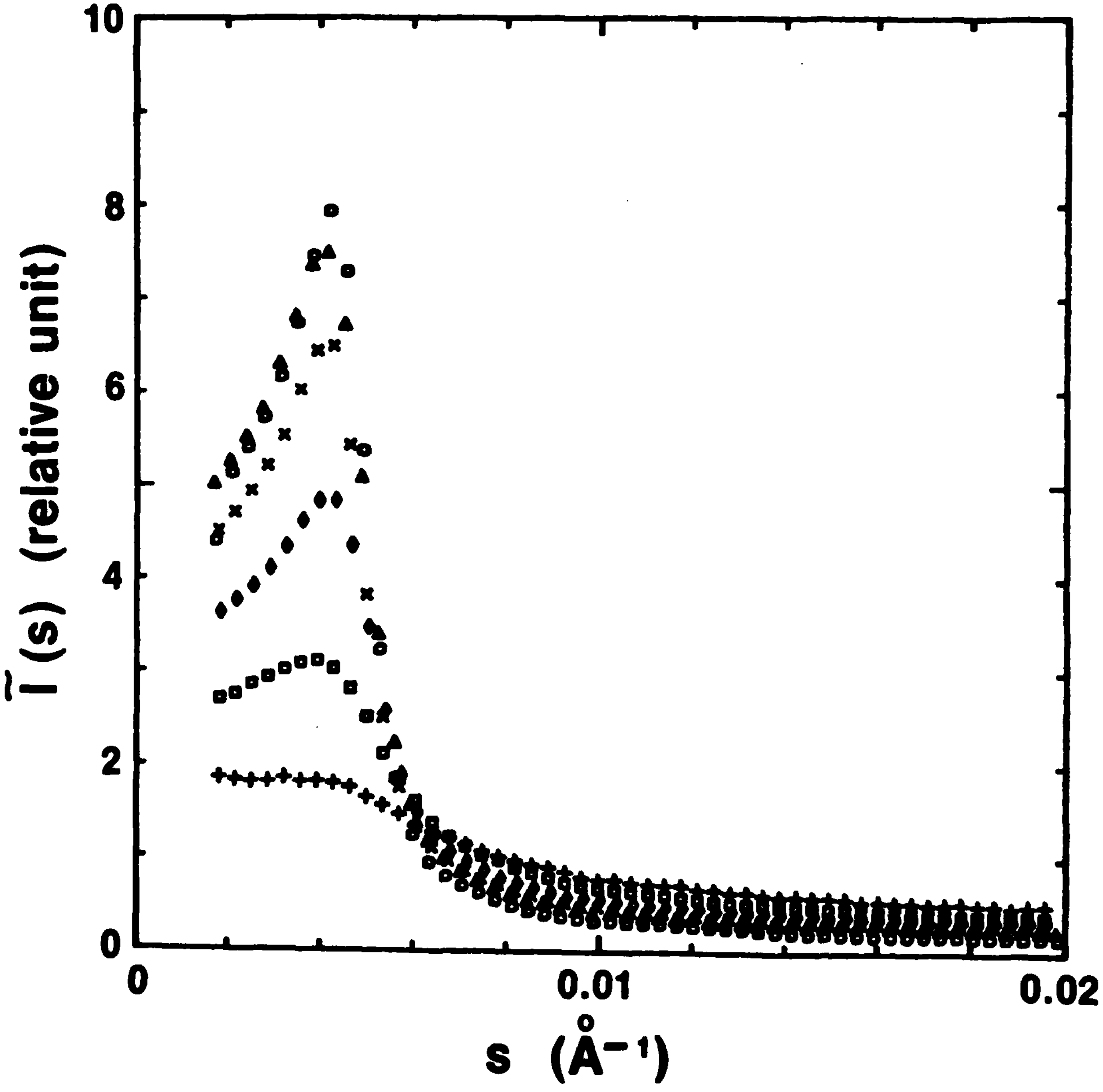


FIGURE 2

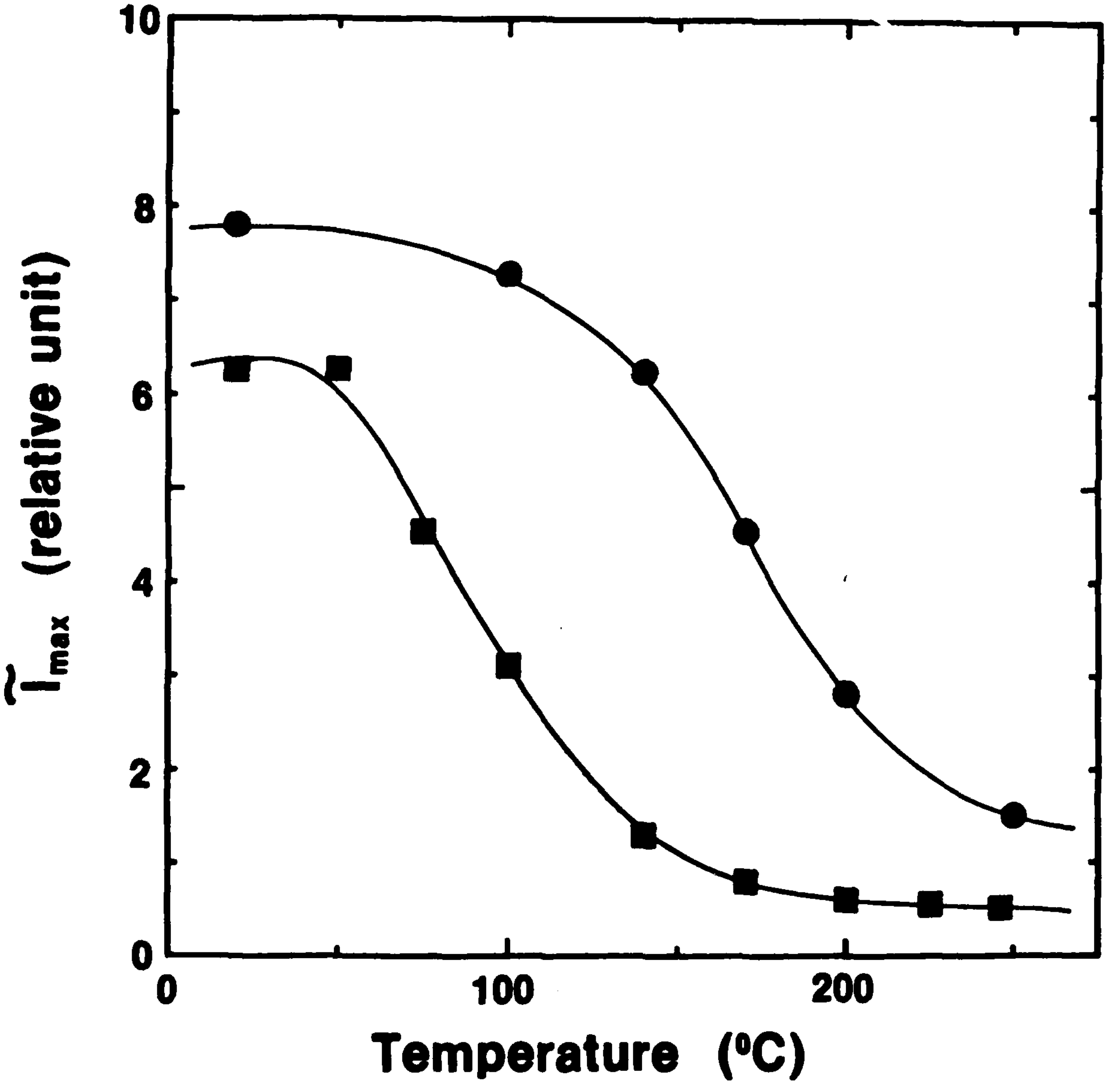
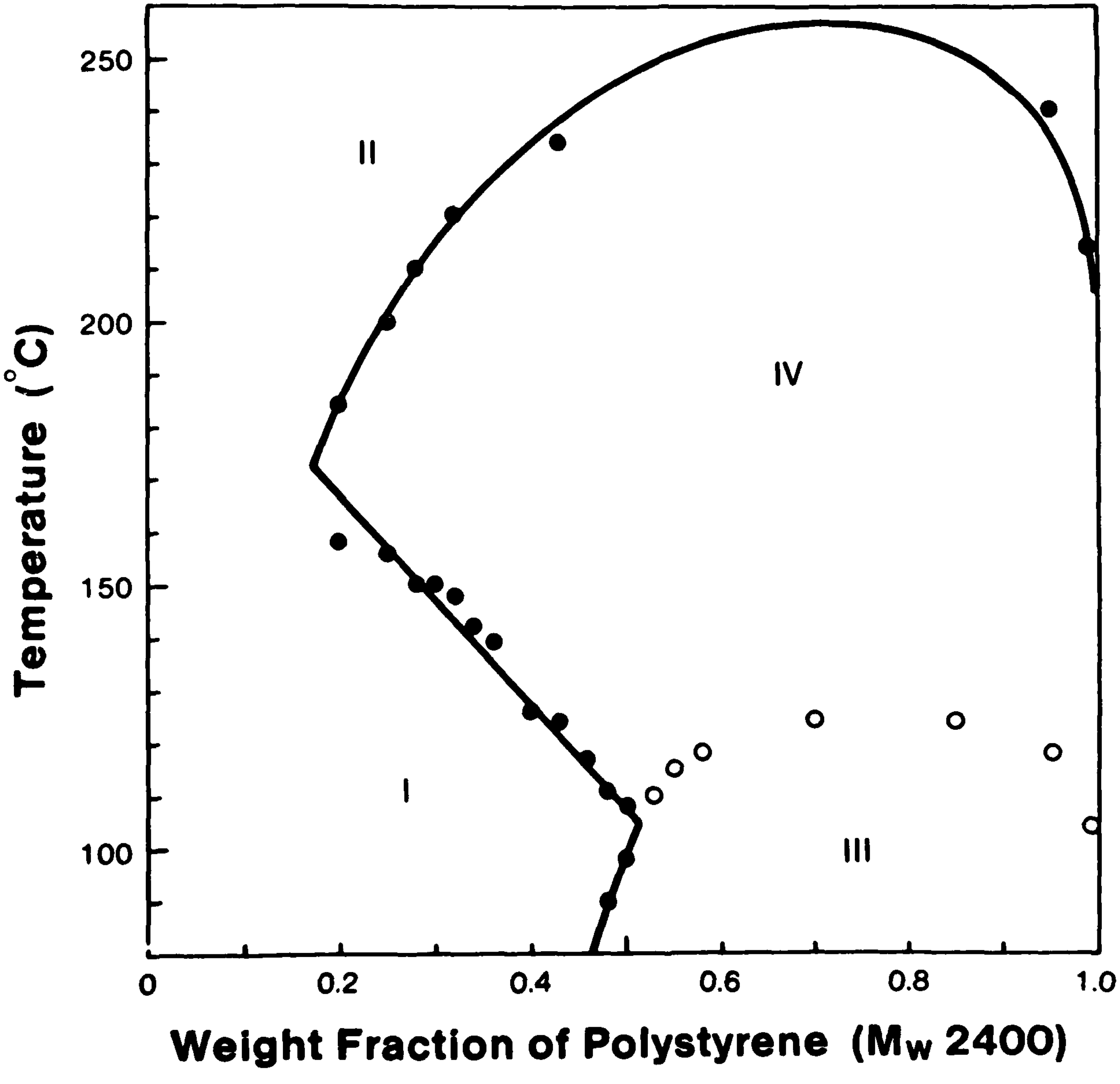
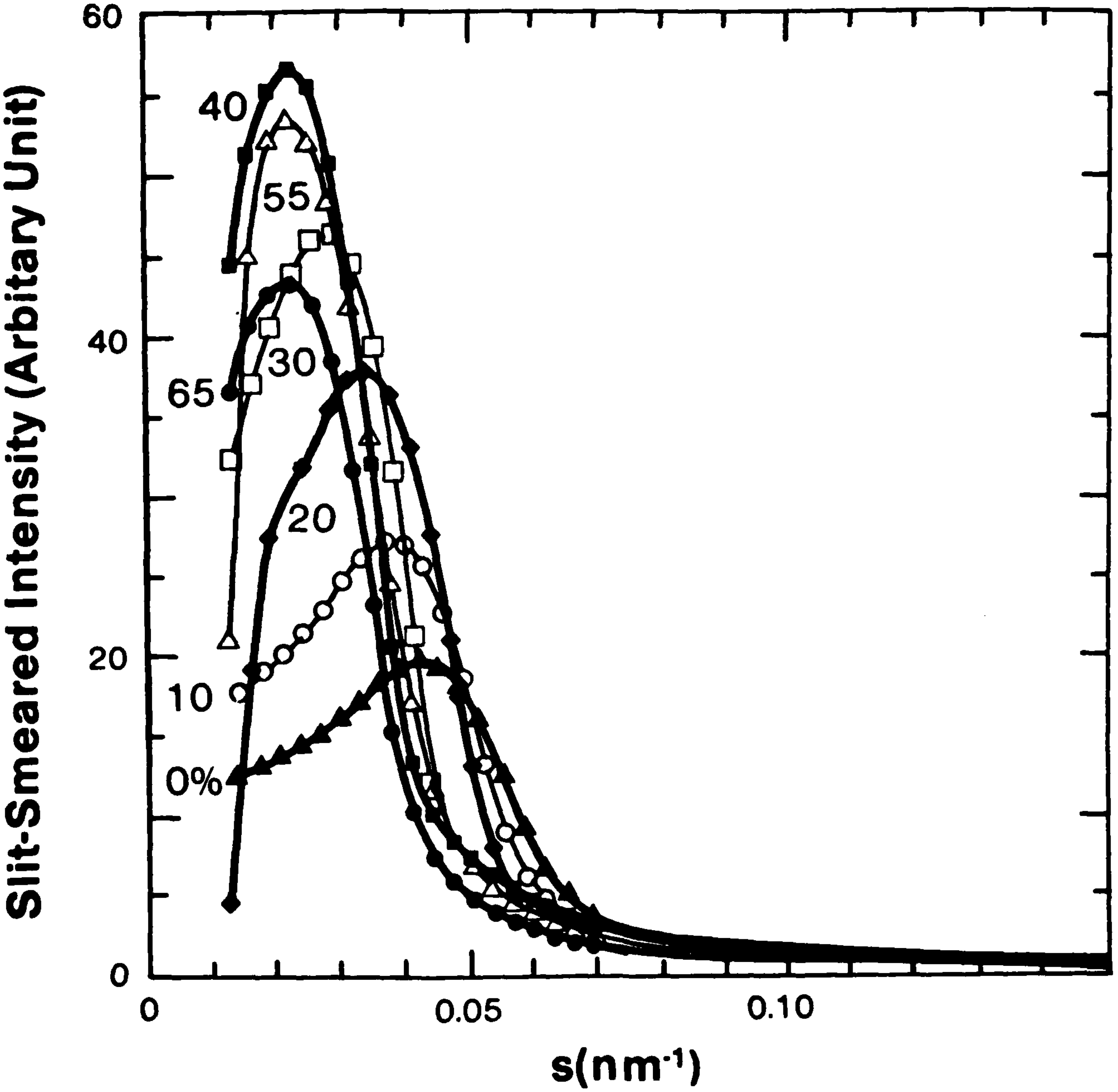


FIGURE 3



250
200
150
100
Temperature (°C)
0
0.2
0.4
0.6
0.8
1.0
Weight Fraction of Polystyrene (M_w 2400)
I
II
III
IV

FIGURE 4



60
40
20
0
0
0.05
0.10
Slit-Smeared Intensity (Arbitary Unit)
s(nm-1)
40
55
65
30
20
10
0%

FIGURE 5

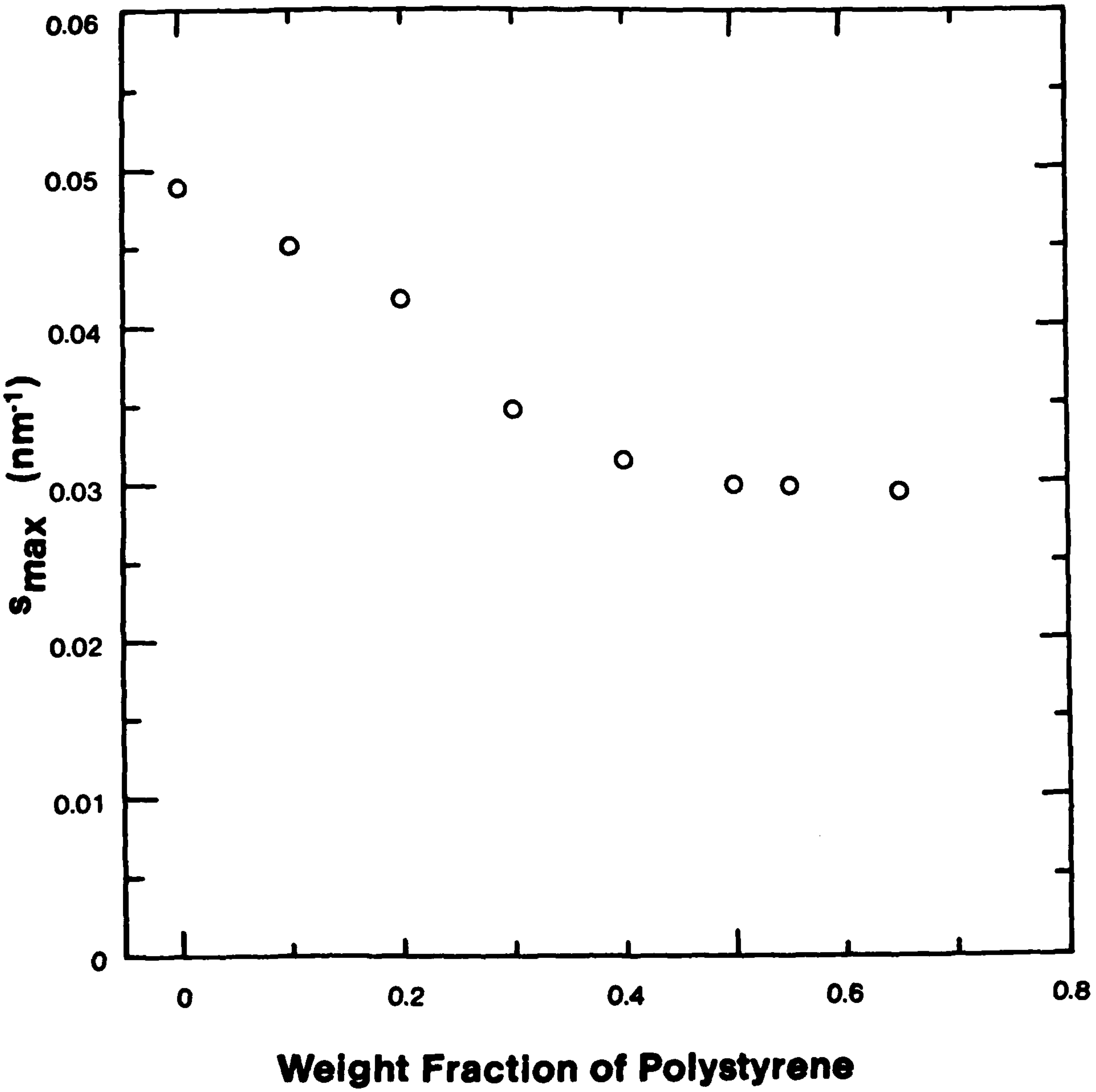
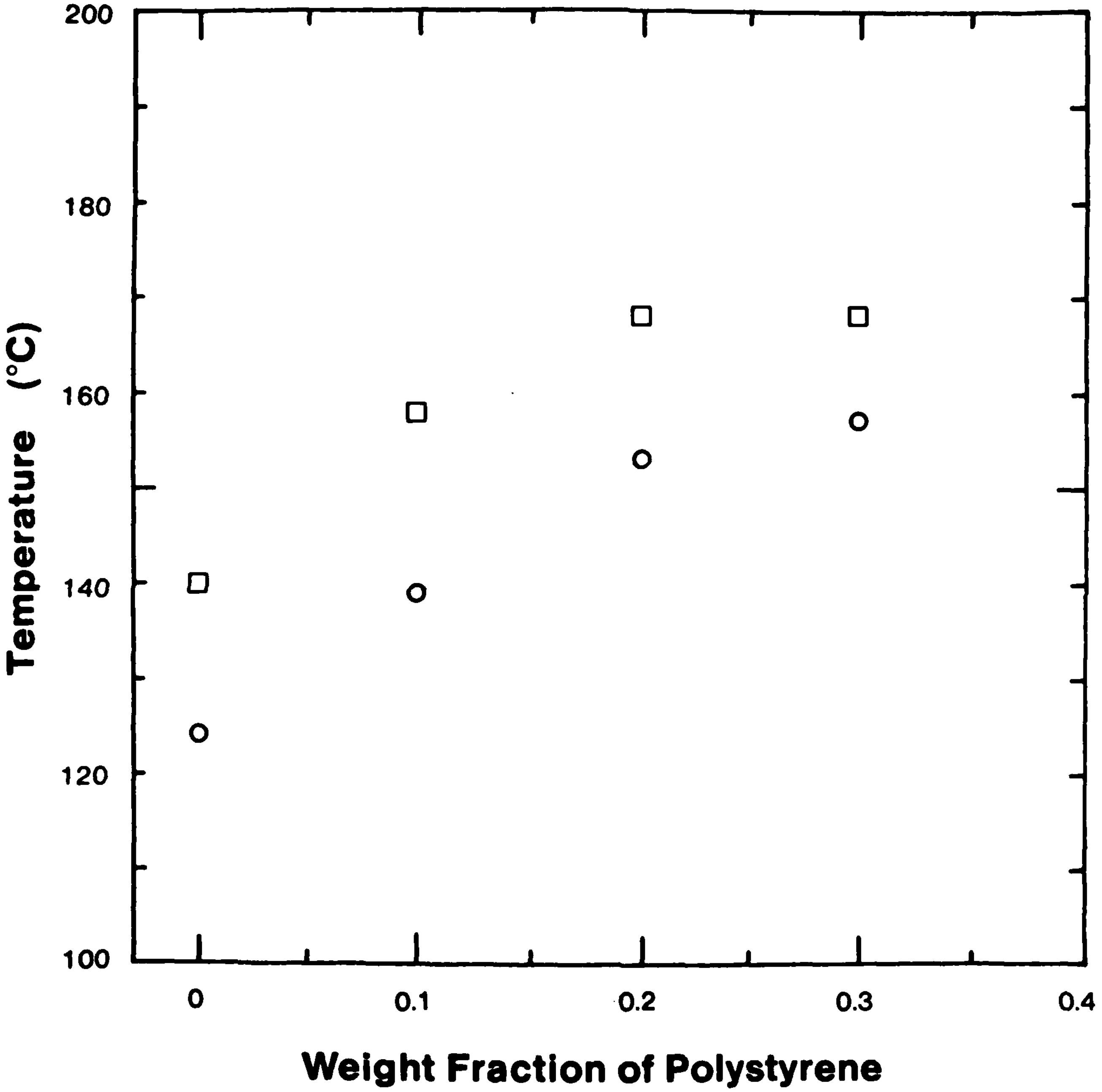
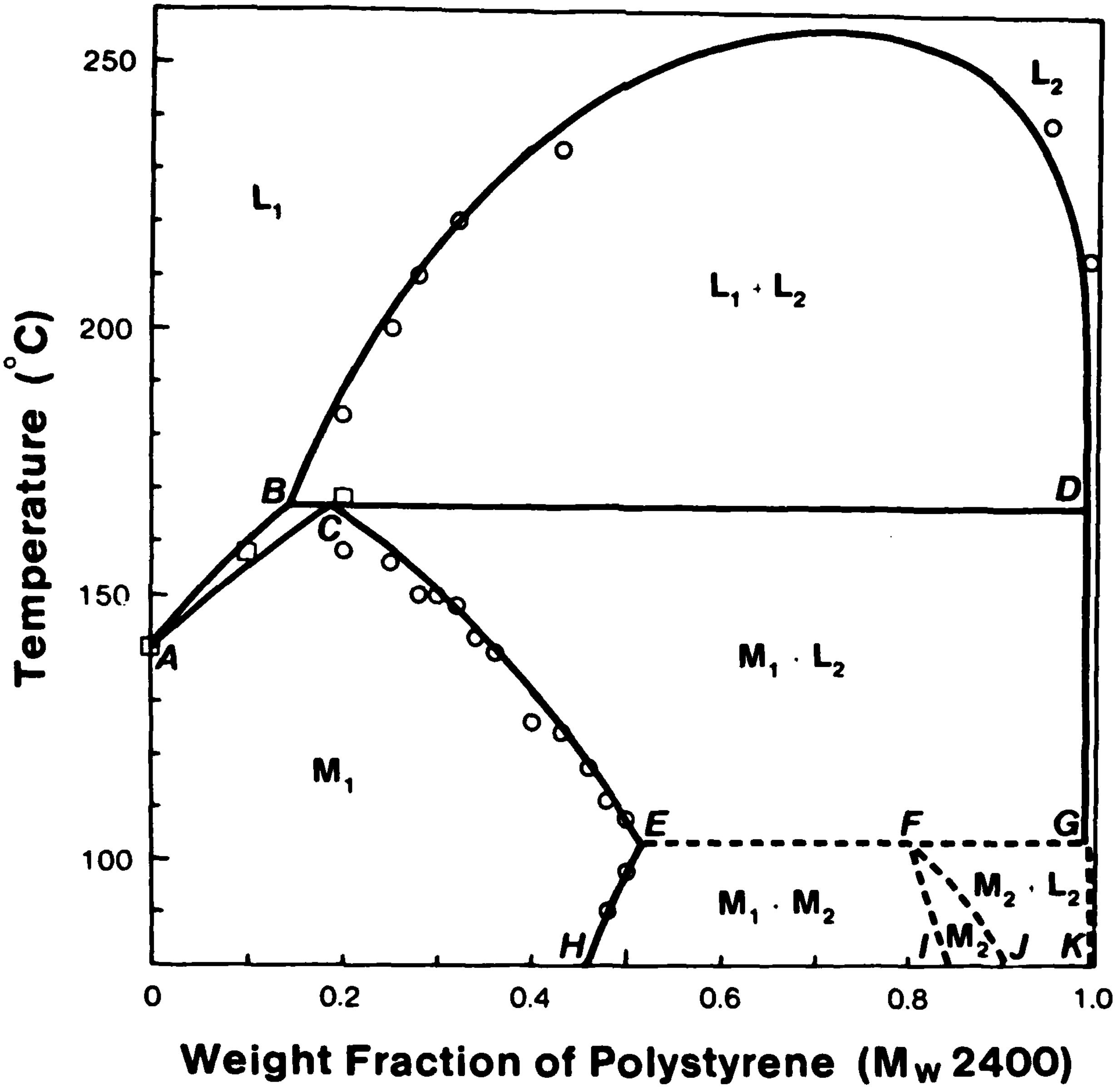

0.06
0.05
0.04
0.03
0.02
0.01
0
s_{max} (nm^{-1})
0
0.2
0.4
0.6
0.8
Weight Fraction of Polystyrene

FIGURE 6



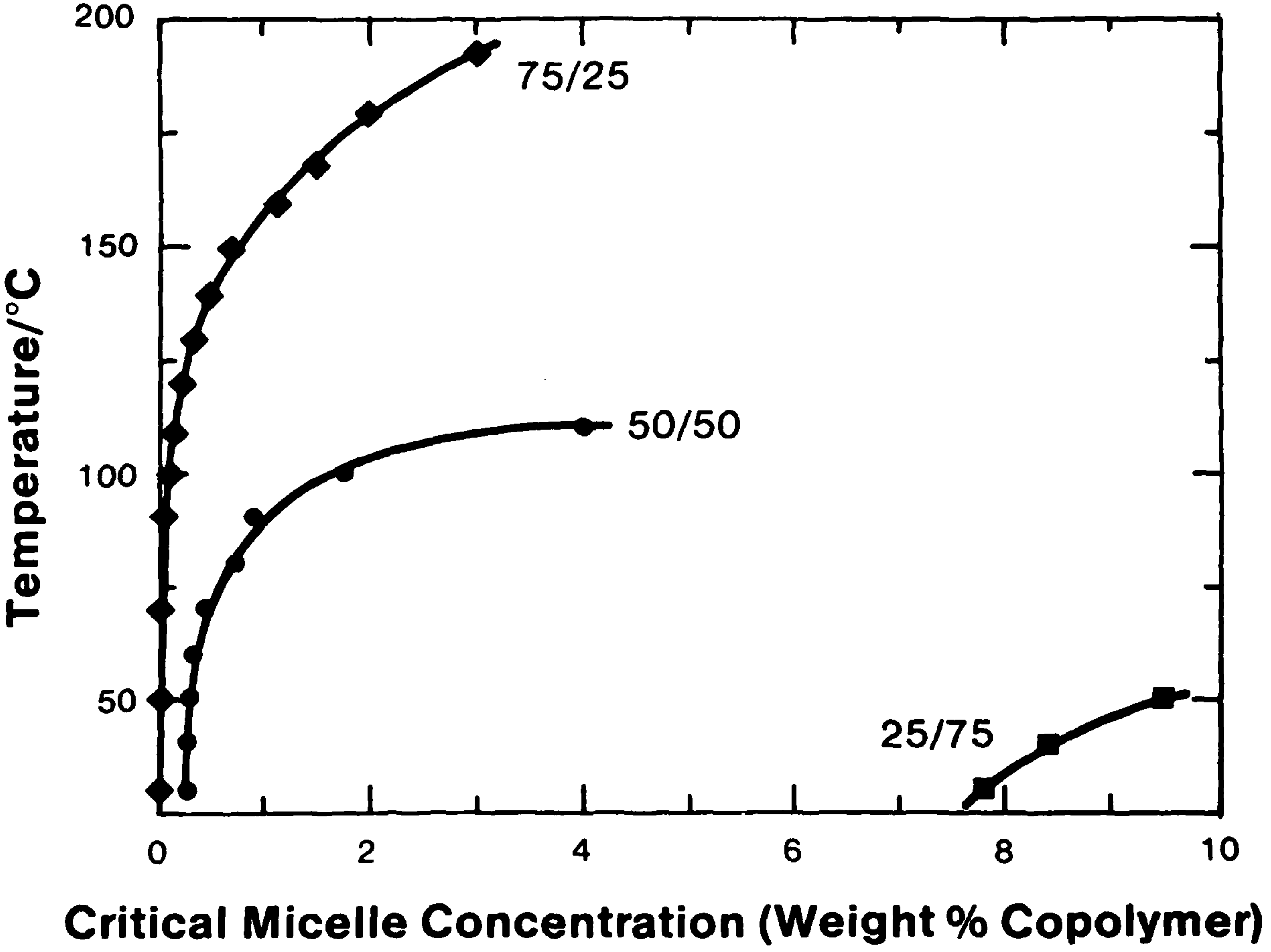
200
180
160
140
120
100
Temperature (°C)
0
0.1
0.2
0.3
0.4
Weight Fraction of Polystyrene

FIGURE 7



250
200
150
100
Temperature (°C)
0
0.2
0.4
0.6
0.8
1.0
Weight Fraction of Polystyrene (Mw 2400)
L1
L2
L1 + L2
M1 · L2
M1
M1 · M2
M2 · L2
M2
A
B
C
D
E
F
G
H
I
J
K

FIGURE 8


200
150
100
50
Temperature/°C
0
2
4
6
8
10
Critical Micelle Concentration (Weight % Copolymer)
75/25
50/50
25/75

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