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SMALL ANGLE X-RAY SCATTERING STUDY OF MICRO- AND
MACRO-PHASE SEPARATIONS I. (U) CINCINNATI UNIV OH DEPT
OF MATERIALS SCIENCE AND ENGINEERING. R J ROE ET AL.
15 DEC 86 TR-5 N00014-85-K-0245

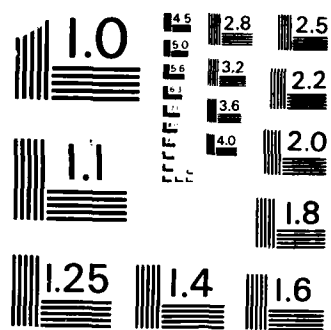
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DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS None	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release, Distribution Unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		DTIC ELECTED DEC 16 1988	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 5			
6a. NAME OF PERFORMING ORGANIZATION University of Cincinnati	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION ONR	
6c. ADDRESS (City, State, and ZIP Code) Clifton Avenue Cincinnati, OH 45221		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N-00014-85-K-0245	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Small Angle X-Ray Scattering Study of Micro- and Macro-Phase Separations in Blends of Block Copolymer with Homopolymer			
12. PERSONAL AUTHOR(S) R. J. Roe and S. Nojima			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) December 15, 1986	15. PAGE COUNT 8
16. SUPPLEMENTARY NOTATION Prepared for Proceedings of the Materials Research Society Meeting			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	Small-Angle X-ray Scattering, Phase Separation, Blends, Block Copolymer
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <i>Approach</i> <p>The order-disorder phase transition behavior exhibited by blends of a styrene-butadiene diblock copolymer (76% styrene) with a polystyrene of various molecular weight (from 2,200 to 50,000) is studied by means of small-angle X-ray scattering. With a polystyrene of a relatively short chain length the blend, on lowering the temperature, undergoes a microphase separation, and the scattering curve shows a peak at a finite scattering angle. With a polystyrene of relatively long chain length, the scattered intensity curve shows additional low angle component with intensity increasing rapidly as $q \rightarrow 0$, and this is interpreted in terms of the macrophase separation accompanying the transition from the disordered to ordered phase.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Wynne		22b. TELEPHONE (Include Area Code) 202-696-4409	22c. OFFICE SYMBOL

DTIC FILE COPY

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Contract N00014-85-K-0245

Task No. NR 356-655

TECHNICAL REPORT NO. 5

Small-Angle X-Ray Scattering Study of Micro-
and Macro-Phase Separations in Blends
of Block Copolymer with Homopolymer

by

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Prepared for Proceedings of the
Materials Research Society Meeting

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December 15, 1986

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SMALL-ANGLE X-RAY SCATTERING STUDY OF MICRO-
AND MACRO-PHASE SEPARATIONS IN BLENDS
OF BLOCK COPOLYMER WITH HOMOPOLYMER

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ABSTRACT

The order-disorder phase transition behavior exhibited by blends of a styrene-butadiene diblock copolymer (76% styrene) with a polystyrene of various molecular weight (from 2,200 to 50,000) is studied by means of small-angle X-ray scattering. With a polystyrene of a relatively short chain length the blend, on lowering the temperature, undergoes a microphase separation, and the scattering curve shows a peak at a finite scattering angle. With a polystyrene of relatively long chain length, the scattered intensity curve shows additional low angle component with intensity increasing rapidly as $q \rightarrow 0$, and this is interpreted in terms of the macrophase separation accompanying the transition from the disordered to ordered phase.

INTRODUCTION

A block copolymer ordinarily exhibits an ordered structure in which microdomains of either spherical, cylindrical, or lamellar shape are arranged on a macrolattice. Such a block copolymer, when heated, may undergo a transition into a disordered phase if the block lengths are not too long and the incompatibility between the blocks is only moderate. Such an order-disorder transition temperature is modified when a homopolymer (which shares the monomeric unit with one of the blocks) is added to the copolymer. The transition temperature can be either raised or lowered depending on the chain length of the homopolymer and the overall composition of the two types of monomeric units in the mixture. More specifically, the transition temperature is raised when the chain length of the homopolymer is large in relation to the chain length of the copolymer and when the addition of the homopolymer shifts the overall composition of the repeat units toward 50% each.

A block copolymer in the disordered state behaves, in many respects, very similar to a random copolymer of the same monomeric composition. When homopolymer A is added to a random copolymer consisting of A and B monomeric units, the mixture may or may not undergo phase separation depending on the temperature, chain lengths and compositions. Such a phase separation behavior can be described fairly satisfactorily in terms of the Flory-Huggins free energy of mixing. The same is true also with the mixture of a homopolymer and a disordered block copolymer, as we have shown earlier [1]. This means that a mixture of a homopolymer added to a disordered block copolymer has the potential of undergoing either a microphase separation into an ordered structure or a macrophase separation into two coexisting phases. Among these two possibilities, one which occurs at a higher temperature is the one actually realized as the disordered, homogeneous mixture is cooled from a high temperature.

This competition between the microphase and macrophase separation can be described by means of the random phase approximation theory, which was introduced into polymer problems by de Gennes [2] and elaborated by Leibler [3] with reference to block copolymer systems. The theory is

applicable to any bulk, amorphous polymer blends containing homopolymers, block copolymers, random copolymers or graft copolymers, provided that the blend as a whole contains only two types of monomeric units. The theory predicts the structure factor $S(q)$, or the Fourier transform of the segment density correlation function, in the form

$$1/S(q) = Q(q) - 2\Lambda/kT \quad (1)$$

where q is the wave vector $2\pi\sin\theta/\lambda$, Λ is the interaction energy density, and $Q(q)$ is a function which is independent of temperature but depends on the composition of the blend and the structure of each component polymer, such as the chain length and the end-to-end distance. The detailed expression for $Q(q)$ depends on the types of blends being considered. The usefulness of eq. (1) derives from the fact that the structure factor $S(q)$ can be obtained experimentally by dividing the scattered intensity of X-rays or neutron by the square of the contrast (in electron density or scattering length) between the two monomeric units.

The q dependence of $S(q)$ is governed by $Q(q)$ on the right of eq. (1), while the temperature dependence of $S(q)$ is governed by the term $-2\Lambda/kT$. Thus, eq. (1) predicts that the angular position of intensity maximum is invariant with temperature. Depending on the type of blend studied, the intensity maximum could be at $q = 0$ or at $q = q^*$, i.e., at some finite value. The former case arises with blends of homopolymers and random copolymers, and the latter case with pure block copolymers. The maximum at $q = 0$ occurs from the concentration fluctuations present at all distance scales, while the maximum at $q = q^*$ signifies that a short range order remains in the disordered block copolymer as a result of the blocks belonging to the same copolymer molecule being confined to their mutual proximity.

With blends of a homopolymer and a block copolymer one may find either a single intensity maximum at $q = 0$ or $q = q^*$, or two maxima at $q = 0$ and $q = q^*$. In the latter case, the larger of the two maxima is of importance. As the temperature is lowered, these maxima will grow in intensity, and the spinodal temperature is defined as the temperature at which the intensity diverges. In practice, before the spinodal is reached, the microphase or macrophase separation intervenes, depending on whether the intensity maximum is at $q = q^*$ or $q = 0$. Thus, whether the blend will eventually undergo a microphase or macrophase separation is indicated already at high temperatures from the position of the true maximum in the intensity curve. For the blends of homopolymer A and block copolymer AB under consideration, the explicit expression for $Q(q)$ can be written as follows.

$$Q(q) = \frac{S_{11}(q) + S_{22}(q) + 2S_{12}(q)}{S_{11}(q)S_{22}(q) - S_{12}^2(q)} \quad (2)$$

$$S_{11}(q) = (1-\phi_h)V_1f_1g(x_1) + \phi_hV_hg(x_h) \quad (3)$$

$$S_{22}(q) = (1-\phi_h)V_2f_2g(x_2) \quad (4)$$

$$S_{12}(q) = (1-\phi_h)(V_1+V_2)(f_1/x_1)(f_2/x_2)[1-\exp(-x_1)][1-\exp(-x_2)] \quad (5)$$

$$g(x) = 2(x+e^{-x}-1)/x^2 \quad (6)$$

$$x_1 = q^2R_1^2/6; \quad x_2 = q^2R_2^2/6; \quad x_h = q^2R_h^2/6 \quad (7)$$

where ϕ_h is the volume fraction of the homopolymer in the blend, V_1 , V_2 and V_h are the molecular volumes of the block A and block B in the copolymer and of the homopolymer respectively, and R_1 , R_2 and R_h are the corresponding rms

end-to-end distances. The composition of the block copolymer is represented by the volume fractions $f_1 = V_1/(V_1+V_2)$ and $f_2 = V_2/(V_1+V_2)$. To illustrate the point discussed above, numerical calculations are made by means of eqs. (1)-(7) and presented in Figures 1 and 2. The case of the blends containing various volume fractions ϕ_h of polystyrene of M_w 35,000 added to a styrene-butadiene diblock copolymer of block molecular weights 16,850 and 5,150, respectively, is shown in Figure 1, and the case of the blends containing polystyrene of M_w 70,000 added to the same block copolymer is shown in Figure 2. In both figures the curves give the structure factor $S(q)$ calculated in the limit of high temperature ($T \rightarrow \infty$), at which the effect of the second term on the right of eq. (1) vanishes and $S(q)$ is given by $1/Q(q)$. The position q^* of the intensity maximum is indicated by a dot on each curve. It

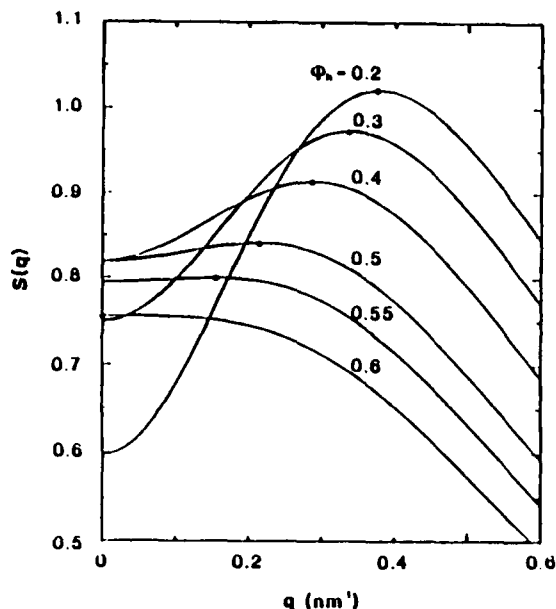


Figure 1. The structure factor $S(q)$ expected at high temperature ($T \rightarrow \infty$) is plotted against q . The calculation is for the mixture of polystyrene of M_w 35,000 added to a styrene-butadiene diblock copolymer of block molecular weights 16,850 and 5,150, respectively. The location q^* of the intensity maximum is indicated by a dot.

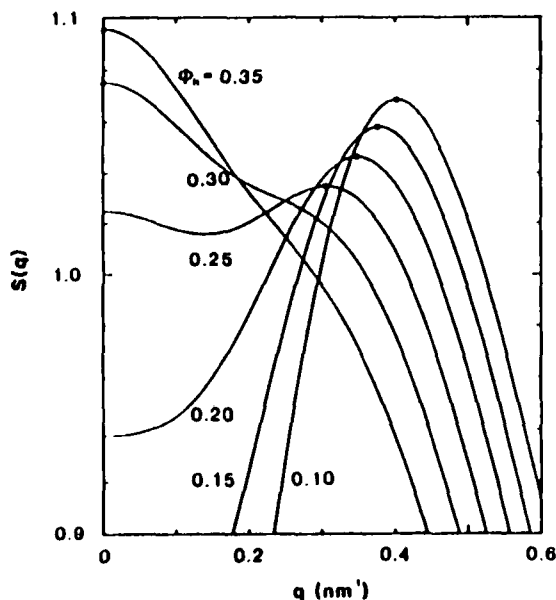


Figure 2. Similar to Figure 1, but calculated for addition of polystyrene of M_w 70,000 to the same diblock copolymer. Note that between $\phi_h = 0.25$ and 0.30 , q^* jumps discontinuously from a finite value to zero, indicating an abrupt changeover from a microphase to a macrophase separation behavior.

is seen that in the case of Figure 1 q^* decreases continuously toward zero as the volume fraction of homopolymer is increased, while in the case of Figure 2 q^* makes a discontinuous jump from a finite value to zero as the volume fraction changes from 0.25 to 0.30. They thus illustrate that the increasing addition of homopolymer to the copolymer induces a transition from a microphase separation to a macrophase separation, but also that such a transition can be a gradual or abrupt process, depending on the molecular weight of the homopolymer. Figure 3 shows the change in q^* induced on addition of polystyrene of various molecular weights to the same styrene-butadiene block copolymer. The discontinuous decrease in q^* to zero is indicated clearly in the case of polystyrenes of M_w 70,000 and 100,000.

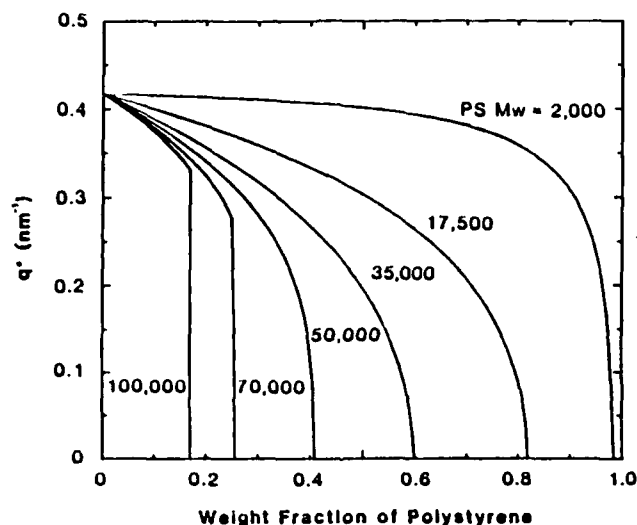


Figure 3. The calculated change in q^* on addition of polystyrene is plotted against the weight fraction of the latter in the mixture.

EXPERIMENTAL SECTION

The styrene-butadiene diblock copolymer, kindly synthesized by Dr. H. L. Hsieh of Philips Petroleum Company, is the one designated as copolymer 75/25 in our earlier study [4], and is characterized as follows: 76.6 weight percent styrene (by NMR), $M_n = 21,000$ (by GPC), $M_w/M_n = 1.05$ (by GPC), and 48% trans 1,4 and 24% cis 1,4. The polystyrene samples of M_w equal to 2,200, 4,000, 10,300, 17,500, 35,000, 50,000 and 100,000 were purchased from Pressure Chemical Company.

Small-angle X-ray scattering data were obtained with a Kratky camera fitted with a one-dimensional position-sensitive detector made by M. Braun Company. The procedure of measurements was essentially similar to that described earlier [4,5]. Background scattering correction was made by subtracting the scatterings from pure polystyrene and pure polybutadiene, each weighted according to the amounts of styrene and butadiene present in the sample. The correction for the slit-length smearing was applied by means of Strobl's algorithm [6].

RESULTS AND DISCUSSION

Blends containing the diblock copolymer and one of the polystyrenes (weight fraction 40-60%) were prepared. Of these, the one containing polystyrene of M_w 100,000 was cloudy, but the rest were all visually clear. The small-angle X-ray scattering data were obtained with these transparent samples at various temperatures. Some of these results are shown in Figure 4, in which all data are plotted on the same ordinate scale to make the comparison of the magnitude of intensities easier. The solid curves drawn in Figures 4a and 4b are the ones calculated from eqs. (1) to (7) with the molecular parameters such as V_1 , R_1 , etc., appropriate for the polymers in the sample, except that Λ was treated as an adjustable parameter and was assigned the value giving the best match of the peak intensity. The angular position q^* of the intensity maximum evidently gives very good agreement between the observed and calculated curves. The shape of the intensity curves at angles larger than q^* also show good agreement, but the observed intensity curve tends to rise above the calculated curve at angles much smaller than q^* . This tendency for the intensity at very small angles to rise becomes progressively more pronounced as the molecular weight of the polystyrene is increased. The curves in Figure 4e obtained with the blend containing polystyrene of M_w 50,000 show most clearly the contribution by this low angle component of scattering.

Acknowledging the possible existence of two independent components of scattering, we adopt the following empirical equation to fit to the observed data.

$$S(q) = \frac{S_1(0)}{1 + \xi_1^2 q^2} + \frac{S_2(q^*)}{1 + \xi_2^2 (q - q^*)^2} \quad (8)$$

where the first term is the Ornstein-Zernike form of the scattering arising from concentration fluctuation in binary solutions, and the second term is the approximation for eq. (1) obtained by its Taylor expansion up to the second order term around q^* [7]. Equation (8) thus assumes that the observed intensity is a superposition of two independent components, one related to macrophase separation and the other to microphase separation. Figure 5 shows the degree of fit obtained with eq. (8), where among the five adjustable parameters $S_1(0)$, ξ_1 , $S_2(q^*)$, ξ_2 and q^* , the set of the first two and the set of the last three were relatively uncorrelated with each other and could be adjusted independently to a large degree.

The spinodal temperature T_s of microphase separation can be obtained, as suggested by eq. (1), by plotting $1/S(q^*)$ against $1/T$ and extrapolating to the temperature at which $1/S(q^*)$ vanishes. Because of the presence of two components of scattering, we evaluated T_s by plotting $1/S_2(q^*)$, evaluated by means of eq. (8), against $1/T$. For the mixtures shown in Figures 4a-4d, T_s thus obtained is 53°, 133°, 176°, and 210°C, respectively. The intensity curves shown in Figures 4c-4e correspond mostly to the ordered state below the transition temperature. Therefore, their interpretation cannot be based entirely on eqs. (1)-(7), which apply to disordered states only. Nevertheless, useful inferences can be made on the basis of the results calculated from these equations. In particular, Figure 3, giving the calculated value of q^* against the weight fraction of polystyrenes of various molecular weight, is informative on the question of microphase vs. macrophase separation. Our observation that the mixtures containing more than 30 wt.% polystyrene of M_w 100,000 are all cloudy and evidently have undergone macrophase separation is in line with the prediction that the value of q^* falls discontinuously to zero on addition of polystyrene of this molecular weight. In the case of mixtures containing polystyrenes of M_w 17,500 or

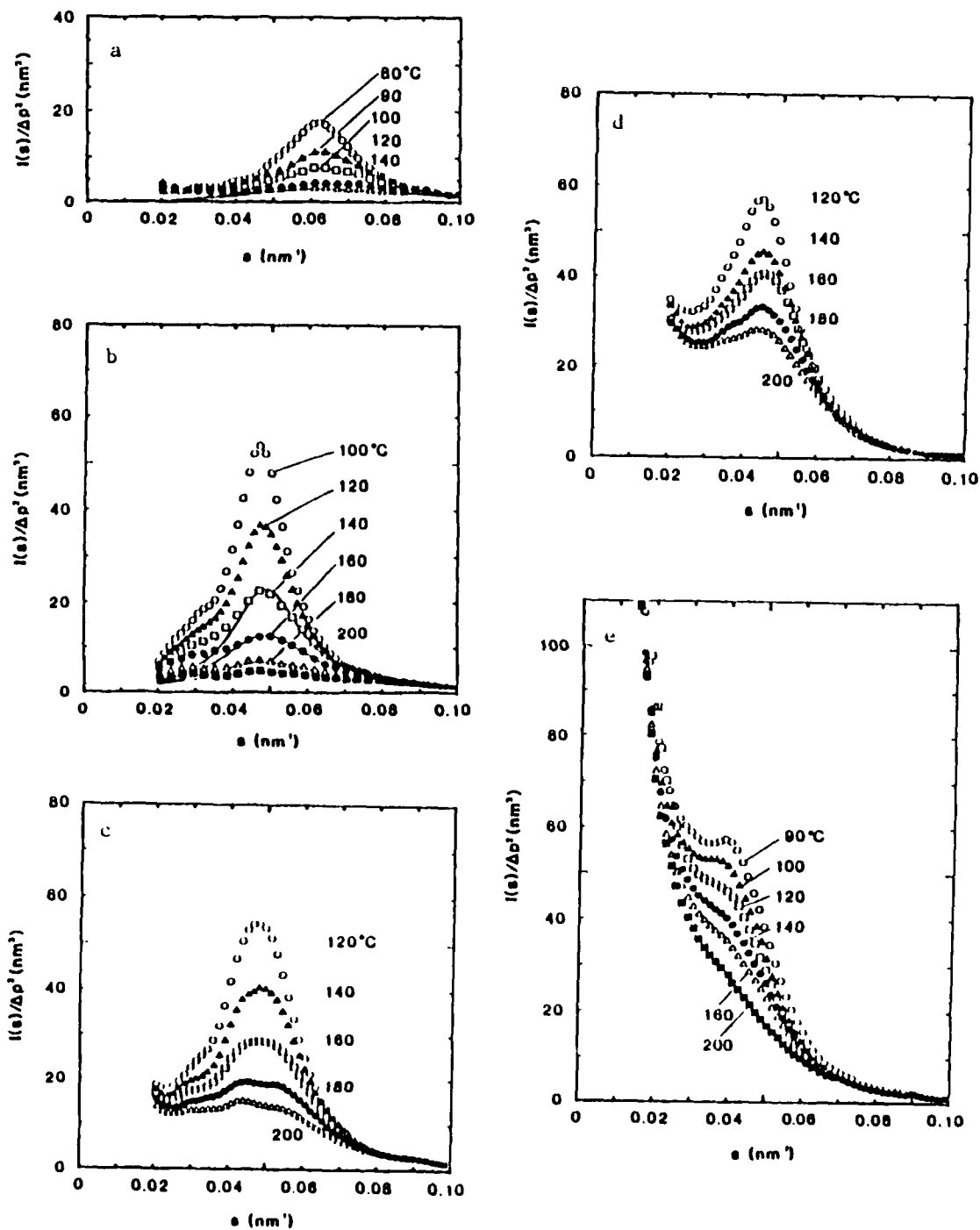


Figure 4. The scattered intensity observed at various temperatures is plotted against the scattering angle s ($= q/2\pi$). (a) Mixture containing 50 weight percent polystyrene of M_w 2,200; (b) 60 percent of M_w 10,300; (c) 60 percent of M_w 17,500; (d) 60 percent of M_w 35,000; (e) 50 percent of M_w 50,000.

smaller, q^* does not fall to zero until the weight fraction of polystyrene exceeds 80%, which is beyond our experimental composition range. These mixtures are therefore expected to undergo microphase separation and no macrophase separation while still in the disordered state. The presence of the appreciable extent of long-range concentration fluctuation (i.e., the component of scattering with peak at $q = 0$) in the mixture containing polystyrene of M_w 17,500, shown in Figure 4c, then has to be explained on the basis of some other effects.

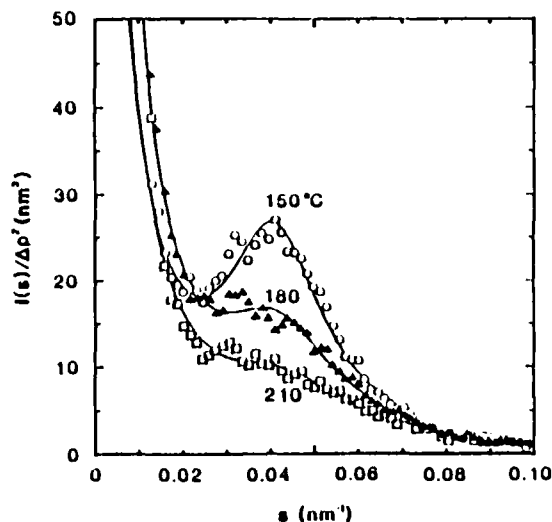


Figure 5. The plots illustrate the degree of fit achieved by the empirical equation (8). The observed intensities were obtained with a mixture containing 70 weight percent polystyrene of M_w 17,500.

When a disordered pure block copolymer is cooled toward the spinodal temperature, it undergoes a transition to an ordered phase at temperatures somewhat above the spinodal temperature. Such a transition, according to Leibler [3], is expected to be of first order. On the other hand, when a disordered mixture of block copolymer and homopolymer is cooled, the formation of an ordered structure proceeds not by a phase transition at a fixed temperature but by a process of successive phase separation over a finite temperature range. The composition of the ordered phase that emerges is, moreover, different from the composition of the disordered phase from which it is formed. This can be understood in terms of the phase diagram of such systems, an example of which was previously obtained [8] in our laboratory and is reproduced in Figure 6. Region L_1 in the diagram consists of the disordered mixture and region M_1 consists of the ordered mixture. The boundary between these two single phase regions is not a single line but is a narrow region representing the coexistence of two phases. Although in the blend systems studied in this work the transition region falls in temperature with increasing polystyrene content, and many of the features shown in

Figure 6 at high concentration of polystyrene are not relevant, the qualitative feature relating to the boundary between the ordered and disordered phases should be similar. Most of the data shown in Figures 4c-4e refer to temperatures below T_g and thus we interpret the low-angle component, increasing in intensity strongly as $q \rightarrow 0$, to arise from the phase separation undergone while the temperature was lowered from the disordered to the ordered region.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

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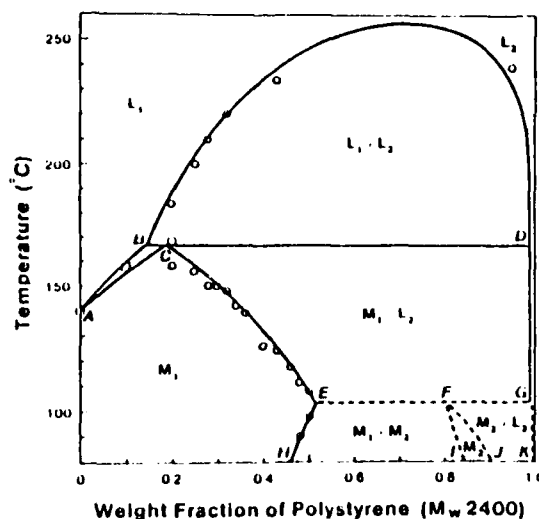


Figure 6. The phase diagram previously obtained for the mixture containing a styrene-butadiene diblock copolymer (27% styrene, M_w 28,000) and a polystyrene (M_w 2,400). (From reference [8].)

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