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Phase Relations and Miscibility in
Polymer Blends Containing Copolymers

by

R. J. Roe and D. Rigby

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This article reviews the reported work on thermodynamics of polymer blends in which at least one of the components is a copolymer. Theoretical and experimental studies of miscibility and phase transition and separation behaviors in such systems are summarized. Chapter 2 deals with blends involving random copolymers, including the cases in which a random copolymer AB is mixed with either a homopolymer A, or a homopolymer C, or two

homopolymers A and B. Chapter 3 deals with blends involving a block copolymer, and after giving a brief overview of systems containing a pure block copolymer alone, it reviews the blend systems containing a block copolymer AB mixed with a homopolymer A or two homopolymers A and B.

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PHASE RELATIONS AND MISCIBILITY IN POLYMER BLENDS CONTAINING COPOLYMERS

1. INTRODUCTION

The possibility of using block or random copolymers as compatibilizers in immiscible polymer blend systems has long been a subject of interest, with the first papers appearing in the patent literature during the 1940's in connection with the emerging synthetic rubber industry. Since then, and particularly during the past several years, a large number of publications has appeared. Of these, however, only relatively few studies deal with the basic thermodynamics of compatibility, though this is a subject of fundamental importance. In the present article we attempt to review recent progress made in understanding the thermodynamic factors which govern miscibility. We are not concerned with studies involving mechanical behavior of copolymer-containing blends, except where the results have a bearing on the compatibility question, and instead refer the reader to the summary given in Tables I and II and to the references cited therein. These tables list all those blend systems, involving random or block copolymer, which have been examined in recent years either for their compatibility behavior or for their mechanical, rheological, and morphological properties. We note also that a number of earlier reviews contain material of relevance to the subject of copolymer-containing blends. For example, Krause[1] has given an extensive description of the blends known to be compatible up to 1977. Paul[2] has discussed the role of block copolymers as emulsifiers, while other more general reviews have been given by Schmitt[3] and Bywater,[4] among others.

In the following two chapters we address recent developments in understanding the thermodynamic behavior of mixtures containing random and

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block copolymers, respectively. In each case we will review the current state of theoretical understanding before describing the results of experimental studies, attempting to assess the extent to which present theory is able to explain (and predict) observed behavior. In our consideration we include only mixtures containing non-crystallizable components, since the crystallization of any of the components introduces a whole new aspect of complexity which requires a separate, thorough study.

2. SYSTEMS CONTAINING RANDOM COPOLYMER

2.1 Binary Mixtures Containing One or Two Random Copolymers

2.1.1 Theory

2.1.1.1 Free Energy of Mixing

For discussion of polymer mixture thermodynamics one can take the Flory-Huggins free energy of mixing as the starting point. The basic approximation embodied in the Flory-Huggins treatment is of the mean-field nature, ignoring the local concentration fluctuations around individual segments. It is well-known that for polymer solution in low molecular weight solvent the mean-field approach becomes grossly inadequate near the critical point and at dilute concentrations. deGennes[5] has noted, however, that the mean-field approximation is fairly satisfactory when the mixture consists of all long chain molecules. In such mixtures the chains assume ideal gaussian conformation unperturbed by the excluded volume effect, thus resulting in further simplification. In fact, the method of random phase approximation, which is also of mean-field nature, was applied to the problem of polymer mixtures by deGennes,[5,6] and was found to lead to results that are identical to those obtainable from the Flory-Huggins approach.

The Flory-Huggins free energy of mixing, ΔG_M, per unit volume of the mixture can be written as[7,8]

$$\Delta G_M = RT[(1/V_1)\phi_1 \ln\phi_1 + (1/V_2)\phi_2 \ln\phi_2] + \Lambda_{12}\phi_1\phi_2 \qquad (1)$$

where V_1 and V_2 are the molar volumes of the polymers 1 and 2, and ϕ_1 and ϕ_2 are the volume fractions of the two polymers in the mixture. The first term in eq. (1) is the combinatorial entropy of mixing originally derived by Flory and Huggins, and the second term containing Λ_{12} includes all other

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contributions to the free energy of mixing that are not accounted for by the combinatorial term. Λ_{12} has the dimension of energy per unit volume, and can be called the polymer-polymer interaction energy density.

More traditionally the Flory-Huggins free energy of mixing is written in the form

$$\Delta G_M'/RT = (1/N_1)\phi_1 \ln\phi_1 + (1/N_2)\phi_2 \ln\phi_2] + \chi_{12}\phi_1\phi_2 \qquad (2)$$

where $\Delta G_M'$ is the free energy of mixing per lattice volume (or segment), and N_1 and N_2 are the numbers of segment in polymers 1 and 2. If V_{ref} is the volume of a lattice (or a segment), then ΔG_M is equal to $\Delta G_M'/V_{ref}$, and it is seen that

$$\chi_{12} = \Lambda_{12}V_{ref}/RT . \qquad (3)$$

The interaction parameter χ_{12} is dimensionless, and its numerical value depends on the choice of the lattice volume V_{ref}. In the case of polymer solutions, V_{ref} is usually equated to the volume of a solvent molecule and no ambiguity arises, but in the case of polymer blends, the practice of implicitly equating V_{ref} to the volume of a monomer unit is not satisfactory since the monomer volumes of polymers 1 and 2 are usually significantly different from each other. For experimental evaluation the interaction energy density Λ_{12}, given in terms of a specific unit such as joules/cm^3, avoids such ambiguity.

In the model of "regular" solution (or its extension to polymer mixtures) the Λ_{12} term is purely enthalpic and Λ_{12} is thus a true constant. In a real mixture, Λ_{12} is a function of T, p, and the composition of the mixture, but the utility of eq. (1) relies on the fact that the dependence of Λ_{12} on these variables is only moderate in most cases. Only in the case

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of the systems exhibiting LCST behavior is the temperature dependence of Λ_{12} appreciable. The strong concentration dependence of χ_{12}, often found with dilute polymer solutions, is not encountered with polymer mixtures. This is mainly due to the fact that the mean-field approximation, as stated earlier, is fairly satisfactory and the entropy of mixing two polymeric components is reasonably well represented by the combinatory entropy term.

2.1.1.2 <u>Effective Interaction Parameter for Systems Containing Copolymers</u>

The binary mixtures considered here can be classed into two categories. In the first, only two different monomers are involved in the mixture. This includes a mixture $(AB)_1/(AB)_2$ of two AB copolymers which differ in composition, and a mixture A/AB containing a homopolymer A and a copolymer AB. In the second category, three or more different monomers are involved. Its most general case would be a mixture AB/CD containing a copolymer AB and a different copolymer CD which has none of its segments in common with the other copolymer.

The free energy of mixing in such systems can still be written in the form of eq. (1). What we desire is to be able to express the effective interaction parameter Λ_{12} in terms of the interaction between the constituent segments (i.e., in terms of Λ_{AB}, Λ_{AC}, etc.). If Λ_{AB} denotes the interaction parameter between homopolymers A and B, and f_{A1} denotes the volume fraction of A in copolymer 1, etc., then the following relationships hold.

$(AB)_1/(AB)_2$ mixture:

$$\Lambda_{12} = \Lambda_{AB} (f_{A1} - f_{A2})^2 \tag{4}$$

A/CD mixture:

$$\Lambda_{12} = \Lambda_{AC} f_{C2} + \Lambda_{AD} f_{D2} - \Lambda_{CD} f_{C2} f_{D2} \tag{5}$$

AB/CD mixture:

$$\Lambda_{12} = \Lambda_{AC}f_{A1}f_{C2} + \Lambda_{AD}f_{A1}f_{D2} + \Lambda_{BC}f_{B1}f_{C2} + \Lambda_{BD}f_{B1}f_{D2} - \Lambda_{AB}f_{A1}f_{B1} - \Lambda_{CD}f_{C2}f_{D2} \qquad (6)$$

These relationships can be derived easily when Λ arises from a purely enthalpic effect contributed by nearest neighbor interactions. Then eqs. (4) - (6) can be obtained by counting the number of contacts between various types of segment pairs A-B, A-C, etc., present in the mixture, and then by subtracting from it the number of similar pairs that were already present in copolymers 1 and 2 before mixing. Even when the Λ term contains the effect of non-combinatorial entropy of mixing, these relationships can be justified from a more general ground, and any interested reader is referred to the original literature[8] for the argument leading to this justification.

The necessary (but not sufficient) condition for mixing is that the free energy of mixing be negative. The first term in eq. (1), arising from the combinatorial entropy of mixing is always negative, with its absolute magnitude diminishing with increasing molar volumes V_1 and V_2. Obviously, to attain a miscibility, Λ_{12} ought to be negative, or if it is positive, its magnitude should be as small as possible. In the case of $(AB)_1/(AB)_2$ and A/AB mixtures, eq. (4) shows that Λ_{12} can be negative only if Λ_{AB} is itself negative. The magnitude of Λ_{12}, when Λ_{AB} is positive can, however, be made as small as desired, to achieve miscibility, by making the compositions of copolymers 1 and 2 as close as possible. In eqs. (5) and (6) for A/CD and AB/CD mixtures, some of the terms have a negative sign in front, suggesting that a negative Λ_{12} value can be obtained even when individual Λ_{AB}, Λ_{AC}, etc., are all positive. Such a possibility has been pointed out by a number of workers.[9-11] For example, Paul and Barlow[9] have discussed the various possibilities for Λ_{12} in the A/CD system. These are

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illustrated in Figure 1. Panel (a) there shows the basic features, where Λ_{12} plotted against the composition of the copolymer is either concave or convex upward depending on whether Λ_{CD} is positive or negative, respectively. Panel (b) shows the interesting situation in which both Λ_{AC} and Λ_{AD} are positive yet Λ_{CD} is sufficiently positive and large to make Λ_{12} negative over part of the composition range where miscibility might occur. Physically interpreted, this behavior would occur when there is a highly unfavorable interaction between segments C and D in the copolymer. Mixing with homopolymer A thus results in dilution of the unfavorable interactions between C and D and leads to a negative interaction parameter Λ_{12}. Figures lc and ld illustrate the remaining possibilities; panel (c) shows that an overall positive interaction parameter Λ_{12} may result even when Λ_{AD} is negative, while panel (d) shows the opposite effect to panel (b), namely that Λ_{12} can be positive over part of the composition range even when the homopolymer forms attractive interactions with both components of the copolymer. The situation described above is also clearly applicable to mixtures of two different copolymers AB and CD, although the possible combinations are more numerous. Thus there remains the possibility that, even if all intersegmental interactions are positive, mixing will occur when Λ_{AB} and/or Λ_{CD} are sufficiently large relative to Λ_{AC}, Λ_{AD}, Λ_{BC}, and Λ_{BD}.

While eqs. (5) and (6) suggest the possibility of a negative effective interaction parameter even with all individual interactions positive, Paul and Barlow[9] have shown that such result is impossible if the interaction parameter depends exactly on the solubility parameter difference according to

$$\Lambda_{ij} = (\delta_i - \delta_j)^2 \ . \tag{7}$$

If this is the case, then, eq. (6) for the AB/CD mixture can be rewritten as

$$\Lambda_{12} = (<\delta_1> - <\delta_2>)^2 \tag{8}$$

where

$$<\delta_1> = \delta_A f_{A1} + \delta_B f_{B1}$$
$$<\delta_2> = \delta_C f_{C2} + \delta_D f_{D2} \tag{9}$$

showing that Λ_{12} is always positive. Eq. (7) results when the cohesive energy density C_{ij} between unlike segments is given by the geometric mean of the c.e.d.'s of the pure components,

$$C_{ij} = (C_{ii}C_{jj})^{\frac{1}{2}} \tag{10}$$

Paul and Barlow concluded, however, that if this restriction is relaxed by writing instead

$$C_{ij} = (1 - k_{ij})(C_{ii}C_{jj})^{\frac{1}{2}} \tag{11}$$

then only a small value of k_{ij} is sufficient to produce a negative interaction parameter Λ_{12}. (The authors considered the system A/CD with $f_{C2} = 0.5$, $\delta_A = 9$, $\delta_B = 8$, $\delta_C = 11$ $(cal/cm^3)^{0.5}$, and with $k_{AC} = k_{AD} = 0$. They then showed that Λ_{12} would become negative for $k_{CD} < 1/176$).

2.1.2 Experiment

2.1.2.1 A/AB and $(AB)_1/(AB)_2$ Systems

A number of blend systems in which only two monomeric species, A and B, are involved have been studied over the years. These include styrene/acrylonitrile,[12,13] styrene/(n-butyl methacrylate),[14] styrene/butadiene,[8] (methyl methacrylate)/(n-butyl acrylate),[15,16] (methyl methacrylate)/(methyl acrylate),[15] (methyl methacrylate)/(ethyl acrylate),[15] and (methyl methacrylate)/(butyl methacrylate).[15] The

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techniques employed to determine the compatibility include visual observation of cloudiness/turbidity, cloud point determination by light scattering,[8,17] determination of light transmission by visible spectroscopy,[14] phase contrast optical microscopy,[12] electron microscopy,[15] differential scanning calorimetry[14] for determination of single or double T_g's, dynamic mechanical spectroscopy (torsion pendulum),[15,16] dielectric relaxation spectroscopy,[14] inverse gas chromatography,[14] and neutron scattering.[13] When several techniques were employed at the same time, the threshold of compatibility determined by different techniques were often different,[14,16] making quantitative interpretation of the results difficult. Qualitatively, however, the expectation is borne out in all cases that the two polymers are compatible when their comonomer compositions are sufficiently close to each other.

Schmitt, Kirste, and Jelenic[13] utilized neutron scattering to determine the coil sizes and the second virial coefficients with mixtures containing two styrene/acrylonitrile copolymers, one of which was deuterated. The interaction parameter calculated from the second virial coefficient was indeed positive and increasing with the composition difference. The coils were found to be unperturbed in all mixtures except one in which it was slightly contracted.

Roe and Zin[8] investigated mixtures of polystyrene with styrene/butadiene random copolymer. Mixtures of polystyrene with styrene/butadiene block copolymer in the disordered state were also studied by them and by Rameau, Lingelser, and Gallot.[17] In these studies, cloud points were determined by light scattering as a function of temperature and concentration. Roe and Zin[8] fitted the resulting cloud point curve (see Figure 2) with a calculated curve based on eq. (1), thereby determining the

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best fitting value of the interaction energy density Λ_{12}. The values of Λ_{12} thus obtained were found to agree well with those calculated by eq. (4) from the knowledge of the composition f_{A1} of the copolymer and the value of the interaction parameter Λ_{AB} between polystyrene and polybutadiene that were previously determined in a similar manner. The result thus demonstrates the essential validity of the thermodynamic considerations described in sections 2.1.1.1 and 2.1.1.2.

On a more quantitative level, some of the detailed features in the experimental results were found to deviate from the predictions based on the Flory-Huggins theory. Fujioka et al.[14] studied mixtures of styrene/(n-butyl methacrylate) copolymer with either polystyrene or poly(n-butyl methacrylate). Although it is expected that A/AB mixture with the A fraction in AB equal to f should show exactly the same behavior as B/AB mixture with the A fraction in AB equal to 1 - f, such symmetry was not strictly observed. (The deviation from such symmetry might occur, aside from the possible inadequacy of eq. (1), from the differences in the molecular weight or its distribution in the A and B homopolymers and in the compositional heterogeneity in the copolymer samples.) Probably a more serious deviation from the prediction of eq. (1) is encountered in the observations of Kollinsky and Markert.[15,16] As pointed out by Scott[18] long ago, it follows from eq. (1) that the maximum difference $\Delta = f_{A1} - f_{A2}$ between the compositions allowed for a compatible mixture of two copolymers $(AB)_1$ and $(AB)_2$ will be independent of the mean $(f_{A1} + f_{A2})/2$ when the mixture concentration and the molecular weights of the copolymers are fixed. As is illustrated in Figures 3 and 4, Kollinsky and Markert[15,16] found that the maximum difference Δ for compatibility of two copolymers consisting of methyl methacrylate and one of acrylate or methacrylate

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monomers drifted as the overall proportion of the methyl methacrylate in the mixture increased. Koningsveld and coworkers[19] noted two possible explanations for the observed behavior. It can arise[19a] if the polydispersity, either in molecular weights or in the comonomer composition, in the copolymer samples used changes with increasing methyl methacrylate content. It can also arise[19b] if the sizes of the A and B segments are different, so that the interaction parameter itself no longer depends on $f_{A1} - f_{A2}$ alone, as in eq. (4), but depends also on the average composition.

2.1.2.2. A/CD Systems

A number of studies have uncovered instances of miscibility in mixtures of homopolymer A with copolymer CD when the corresponding homopolymer pairs A/C, A/D, and C/D are immiscible. The copolymer of styrene and acrylonitrile has been found to be miscible with a fairly large number of polymers, including poly(vinyl chloride),[20] poly(ϵ-caprolactone),[4] sulfone based polymers,[21] poly(methyl methacrylate),[22-27] and poly(ethyl methacrylate).[24] Copolymers of α-methylstyrene with acrylonitrile are also found[28] to be miscible with poly(ethyl methacrylate) and atactic and isotactic poly(methyl methacrylate). Other examples of A/CD compatible systems are copolymers of ethylene and vinyl acetate with poly(vinyl chloride)[29,30] and copolymers of acrylonitrile and butadiene with poly(vinyl chloride).[31,32] In the list of compatible polymer pairs compiled by Krause,[1] there are many cases which involve copolymers and some of them might belong to the A/CD systems discussed here.

In recent years, a systematic investigation was made by Karasz, MacKnight, and coworkers[10,33-41] on the miscibility of halogen-substituted

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styrene copolymers with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (and also with polystyrene). The interesting aspect here is (i) that PPO and polystyrene are compatible with each other in all proportions, (ii) that neither PPO nor polystyrene is compatible with any of the halogen-substituted styrene homopolymers such as poly(ortho-chlorostyrene), poly(para-chlorostyrene), poly(ortho-fluorostyrene), poly(para-fluorostyrene), etc., and yet (iii) that many of the copolymers of these halogen-substituted styrenes (having a certain limited range of comonomer composition) exhibit compatibility with PPO. To cite a specific example, neither poly(ortho-chlorostyrene) nor poly(para-chlorostyrene) is compatible with PPO, but a random copolymer of these two types of chlorostyrenes is compatible with PPO, provided that the copolymer contains between 23 and 64 mole % of para-chlorostyrene.[33] The compatibility between polymer pairs was ascertained by the presence of a single T_g obtained by DSC, and was additionally confirmed by visual observation of the clarity of the films. The phenomenon of the miscibility "window" is well illustrated in Figure 5, which[10] summarizes the miscibility limit of PPO when mixed with the three types of random copolymers of halogen-substituted styrenes. Only the copolymers having the composition of comonomers corresponding to the inside region of the curves are miscible with PPO. As the temperature is raised, the width of the miscibility "window" narrows, and this suggests a LCST behavior. In fact, all miscible pairs belonging to A/CD systems observed show a LCST behavior. Thus when a miscible pair at certain temperatures is annealed at a higher temperature, it was observed[33] that the mixture became cloudy and the DSC curve showed two T_g's. Figure 6 shows the cloud point curves obtained[28] with mixtures containing copolymer of α-methylstyrene/acrylonitrile and either atactic or

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isotactic poly(methyl methacrylate) or poly(ethyl methacrylate), and demonstrates the LCST behavior clearly.

The occurrence of the miscibility window can be explained readily[9,10] by means of eq. (5) and can be attributed to the strong "repulsion" between C and D being mitigated by A. The LCST behavior can then be ascribed to the same effect that gives rise to the LCST behavior of compatible blends of high molecular weight homopolymers. Paul and Barlow[9] extended the reasoning based on eq. (5) to explain the miscibility behavior of a homologous series of aliphatic polyesters with polycarbonate,[42] poly(vinyl chloride),[43] polyhydroxyether of bisphenol-A,[44] etc., by treating as if the homologous polyesters were copolymers.

2.2 Ternary Mixtures Containing a Random Copolymer and Two Homopolymers

2.2.1 Theory

Interest in A/B/AB systems arises from the potential utility of random copolymers as compatibilizers, i.e., their ability to produce a single phase mixture from two otherwise immiscible homopolymers.

Phase diagrams for the $(AB)_1/(AB)_2/(AB)_3$ system containing three AB copolymers of different compositions were considered by Leibler.[45] Manageable results could be obtained for the symmetric case where the molecular sizes of all three polymers are equal and the fraction of monomer A in the three copolymers are given by $f_{A1} = f + \Delta$, $f_{A2} = f - \Delta$, and $f_{A3} = f$. The A/B/AB blend considered here then becomes a special case corresponding to $f = 0.5$, $\Delta = 0.5$. He identified four distinct types of phase behavior, which for A/B/AB systems read as follows:

(1) For $\Lambda_{AB}V/RT < 2$ (where V is the molar volume of the polymer molecules), the mixture is miscible at all compositions.

(2) For $2 < \Lambda_{AB}V/RT \leq 6$ --Figure 7a-- there is one critical point of demixing, located at $\phi_1 = \phi_2$, $\phi_3 = 1 - RT/\Lambda_{AB}V$.

(3) For $6 < \Lambda_{AB}V/RT \leq 8$ --Figure 7b-- there are three critical points, two of which are physically meaningful. The third critical point is located in an unstable region, associated with the occurrence of a three phase triangle in the phase diagram.

(4) For $8 < \Lambda_{AB}V/RT$ --Figure 7c-- there are no critical points; all three of the binary pairs show a miscibility gap, and the three phase triangle remains.

Recently Koningsveld and Kleintjens[46] made some numerical analyses of possible phase diagrams of three random copolymers, in particular with the aim of identifying conditions necessary for a given copolymer to act as a compatibilizer. They deduced that addition of copolymer 3 with the composition intermediate between the other two copolymers 1 and 2 would not in general induce compatibilization unless components 1 and 2 were already of fairly low molecular weight.

The conditions necessary for the lowering of the critical, spinodal, or binodal temperature of binary mixtures of homopolymers A and B by addition of copolymer AB was also examined analytically by Rigby, Lin, and Roe.[47] They showed that under some special conditions, spinodal temperature T can be lowered linearly with the amount of added copolymer AB, so that

$$T/T^{o} = (\Lambda_{AB}/\Lambda_{AB}^{o})(1 - \phi_3) \qquad (12)$$

where ϕ_3 is the copolymer volume fraction, T^o is the spinodal temperature in the binary A/B blend and Λ_{AB}^{o} is the value of Λ_{AB} at T^o. The condition under which eq. (12) is obeyed is

$$\phi_1 V_1 / f_{A3} = \phi_2 V_2 f_{B3} \tag{13}$$

where f_{A3} and f_{B3} are volume fractions of A and B in the copolymer and V_1 and V_2 are the molar volumes of the homopolymers A and B. Eq. (12) represents the maximum possible lowering of spinodal temperature attainable with a given amount ϕ_3 of a copolymer AB. When the condition (13) is not satisfied, the lowering of spinodal temperature is always less than that given by eq. (12). When the above condition is not satisfied, it is even possible for the spinodal temperature to increase initially on addition of copolymer AB, as is illustrated in Figure 8. Rigby et al.[47] showed also that both binodal and critical temperatures can be lowered by addition of copolymer, but the condition under which eq. (12) is obeyed for binodal or critical temperature is different from eq. (13). Thus, for a linear reduction of critical temperature the two separate conditions

$$\phi_1 V_1^{1/2} = \phi_2 V_2^{1/2}; \quad V_1^{1/2} / f_{A3} = V_2^{1/2} / f_{B3} \tag{14}$$

have to be satisfied. For the linear reduction of binodal temperature the conditions to be satisfied are

$$V_1 = V_2; \quad f_{A3} = f_{B3} \quad . \tag{15}$$

It remains, however, to be established whether the lowering of cloud point according to eq. (12) under conditions of eq. (15) is the maximum possible.

Related to the compatibilization of homopolymers A and B by addition of copolymer AB is the question of so-called mutual miscibility enhancement[16] in heterogeneous copolymer samples; that is, whether the presence of molecules of a continuous spectrum of compositions in practical copolymer samples enhance the miscibility of components of extreme compositions in them. This problem was addressed by Koningsveld et al.,[19b]

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who, on analysis based on Flory-Huggins equation, concluded that such mutual miscibility enhancement can indeed occur.

2.2.2 Experiment

Early experimental work of Riess et al.[48] substantially supports the above conclusion that the compatibilizing effect of added copolymer is only moderate in many cases. These authors studied mixtures of polystyrene/ poly(methyl methacrylate) with added copolymer, and evaluated in terms of optical clarity. Compatibility was found only when substantial amount of S/MMA copolymer was added.

Quantitative examination of eq. (12) applied to cloud points of mixtures was reported by Rigby et al.[47] using low molecular weight polystyrene and polybutadiene (M_n = 2000 and 2350, respectively) with added S/B copolymer (M_n = 16,000, 25,000, and 250,000). The linear relationship predicted by this equation was found to be obeyed on addition of either of the two lower molecular weight copolymers (see Figure 9). The temperature dependence of the interaction energy density Λ_{AB} was determined from the slope in Figure 9, and was found to give excellent agreement with the value previously obtained from a study of binary mixtures of the two homopolymers.[8] Lowering of the cloud point by added copolymer of molecular weight 250,000 was much smaller than the values found for the other two copolymers. This was attributed to the occurrence of separation into three phases, calculated to occur at only 2% copolymer content according to the criteria by Leibler.[45]

3. SYSTEMS CONTAINING BLOCK COPOLYMER

Among blends containing block copolymer, systems of primary interest to be reviewed in this section are binary mixtures of block copolymer AB with homopolymer A, and ternary mixtures containing immiscible homopolymers A and B combined with corresponding diblock copolymer AB. A study of the former is indicated by the need to understand to what extent and in what manner block copolymer structure and properties can be modified by the addition of homopolymer; while studies of the ternary system can lead to understanding of the emulsifying role of block copolymer which is exploited technologically.

3.1 Mixtures Containing a Diblock Copolymer and a Homopolymer

3.1.1 Overview

Before describing the behavior of these blend systems in detail, we here give a brief summary of the features exhibited by a block copolymer by itself, and of the types of phase behavior which are expected on addition of a homopolymer.

In pure block copolymer having two types of blocks, A and B, which are mutually incompatible, the blocks segregate out into their own microdomains. The number of like blocks that can aggregate to a microdomain is limited by the geometric constraint to form a space-filling structure, and consequently the dimension of the microdomains is usually of the same order of magnitude as the radii of gyration of the blocks themselves. When synthesized by an anionic polymerization mechanism, polydispersity of the block lengths is kept to a minimum and, as a result, the shape and size of the microdomains in a block copolymer sample can be very uniform. Depending on the relative lengths of the A and B blocks, and depending to some extent on the conditions of sample preparation, such as

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the solvent used, the collection of microdomains forms regular structure

consisting of spheres, cylinders, or lamellae. Beautiful electron

micrographs showing such ordered arrays of microdomains abound in the

literature.

The segregated microdomain structure is not attained when the two

types of blocks are mutually compatible. Such compatibility arises either

when the blocks are very similar (e.g., 1,2-butadiene vs.

cis-1,4-isoprene[49]), when the block lengths are relatively short, or when

the temperature is altered (i.e., raised if the corresponding homopolymer‧

pair exhibits UCST behavior). The structure of such disordered block

copolymer is essentially liquid-like, forming a single homogeneous phase

lacking any long range order. It differs, however, from the mixture of

compatible homopolymers in that the two types of blocks, by virtue of the

covalent linkage between them, maintains a fairly well defined distance

between them. As a result, small-angle X-ray or neutron scattering from

disordered block copolymer shows a peak[50] at a finite scattering angle, and

this phenomenon has been termed the "correlation hole effect" by deGennes.

The transition between the ordered, microdomain structure and the

disordered, homogeneous structure, induced by temperature change, can be

observed by rheological measurement[51-53] or by small-angle scattering.[54]

The transition, often called the order-disorder transition or microphase

separation transition, resembles the solid-liquid transition, and should be

of a first order according to the theory of Leibler,[55] but experimentally

its character has not yet been established clearly.

Next we consider what will happen when we take the pure block

copolymer in its ordered state and add to it increasing amounts of

homopolymer A. Initially, the homopolymer will dissolve in the

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microdomains of block A of the copolymer until a solubility limit is reached, beyond which the excess homopolymer will separate out in a separate macroscopic phase. Even before the solubility limit is reached, as the relative volume of the A and B microdomains change, there might arise a change in the ordered structure, for example, transitions from spherical to cylindrical and to lamellar morphology. The solubility limit and these morphological transition points would depend on the relative lengths of the two types of blocks and the homopolymer molecules. The thermodynamic stability of the microdomains, and hence the microphase separation temperature (MST), will also be affected by the addition of the homopolymer. Unlike the melting point of a solid in the presence of a diluent, which is always depressed, the MST might go up or down, again depending on the relative lengths of the various species involved. If we look at the other end of the concentration scale, a small amount of block copolymer, added to a pure homopolymer, will initially dissolve into a homogeneous solution, but with increasing concentration of block copolymer, a critical micelle concentration (CMC) is eventually reached, beyond which any excess copolymer aggregates into micelles. Further addition of the block copolymer will increase the population of micelles, and may finally lead to agglomeration of micelles into ordered macroscopic structure. These are some of the features expected and the questions likely to be raised when we examine the behavior of the mixtures containing block copolymer AB and homopolymer A.

3.1.2 Theory

3.1.2.1 Block Copolymer Theory

Before discussing the theories describing the mixture of block copolymer and homopolymer, it is necessary to review the theories dealing

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with pure block copolymer very briefly. The latter can be divided into three categories, the first dealing with ordered microdomain structure, the second dealing with the disordered phase and the third dealing with the transition between them.

The theories dealing with the ordered phase were first developed as soon as the fascinating properties of block copolymers became known. Main concerns of these theories were the delineation of the conditions necessary for the formation of spherical, cylindrical or lamellar morphology, the prediction of the size of the microdomains of these morphologies in relation to the block lengths, and the question of the thickness and density profile across the boundary between microphases. These theories were extensively reviewed over the years in monographs and symposium proceedings and will not be discussed further here.

Thermodynamic and scattering properties of block copolymer in the disordered state were evaluated by Leibler[55] by means of the random phase approximation method, which was introduced into the study of polymers by deGennes.[6] In the method, one starts with the segment density correlation function of ideal, independent polymer chains, and then calculates the modification to it arising from the requirement of uniform segment density in space; this is done by subjecting each segment to an extra potential determined in a self-consistent manner. The result gives the expression for the Fourier transform of the segment density correlation function, $\tilde{s}(q)$, (which is proportional to the scattered intensity of X-ray or neutron) as follows[55]

$$\frac{1}{\tilde{s}(q)} = \frac{s_{11}(q) + s_{22}(q) + 2s_{12}(q)}{s_{11}(q)s_{22}(q) - [s_{12}(q)]^2} - \frac{2\Lambda}{RT} \qquad (16)$$

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where $s_{ij}(q)$ is the Fourier transform of the correlation function between segments of type i and type j of ideal, independent chains in the sample, and q is the scattering vector equal to $4\pi\sin\theta/\lambda$. Eq. (16) is applicable not only to disordered block copolymer but also to any amorphous polymer blend in which only two types of segments are present. For example, for a mixture of two homopolymers of molar volumes V_1 and V_2 and mean end-to-end distances R_1 and R_2,

$$s_{11}(q) = \phi_1 V_1 g_D(x_1); \quad s_{22}(q) = \phi_2 V_2 g_D(x_2); \quad s_{12}(q) = 0 \tag{17}$$

where x_i is equal to $q^2 R_i^2/6$, and $g_D(x)$ is the Debye function (the Fourier transform of the correlation function of a gaussian chain) given by

$$g_D(x) = 2(x + e^{-x} - 1)/x^2 \tag{18}$$

Substitution of (17) into (16) gives

$$\frac{1}{\tilde{s}(q)} = \frac{1}{\phi_1 V_1 g_D(x_1)} + \frac{1}{\phi_2 V_2 g_D(x_2)} - \frac{2\Lambda}{RT} \tag{19}$$

By letting $q \rightarrow 0$ in eq. (19) we obtain

$$\frac{1}{\tilde{s}(0)} = \frac{1}{\phi_1 V_1} + \frac{1}{\phi_2 V_2} - \frac{2\Lambda}{RT} \tag{20}$$

which is equal to the second derivative (with respect to ϕ_1) of the Flory-Huggins free energy of mixing given in eq. (1). The temperature at which $\tilde{s}(0)$ diverges gives the spinodal temperature signifying the limit of metastability of homogeneous single phase. Eq. (20) implies the equivalence of the random phase approximation and the Flory-Huggins treatment, both being mean field theories. More recently Benoit and

Benmouna[56-58] have shown that eq. (16) can be derived by direct, methodical enumeration of correlations between segments belonging to the same molecule or to neighboring molecules, thus reaffirming the mean-field nature and equivalence of these three different approaches.

Although the possibility of the order-disorder transition was recognized in most of the block copolymer theories, it is Leibler[55] who has expressedly addressed this problem. He derived the free energy of a block copolymer system in a series expanded in powers of the order parameter ψ denoting the deviation of the local density from the mean. The coefficients of this expansion up to the fourth order term were evaluated by a method which is a generalization of the random phase approximation method described above. [Eq. (16) was, in fact, derived as the second order term in the free energy expansion]. The MST, determined from the condition that the excess free energy due to the ordered structure should vanish, are shown in Figure 10. Here the abscissa gives the fraction f of one of the blocks in a diblock copolymer and the ordinate gives the value of χN at the MST, where N is the total number of segments in the copolymer molecule. Since χ (= $\Lambda V/RT$) is inversely proportional to T when Λ is independent of temperature (as is approximately true for polymer pairs exhibiting UCST behavior), the MST among molecules of the same total length is the highest when the lengths of the two blocks are equal to each other. The spinodal temperature, obtainable as the temperature at which $\tilde{s}(q)$ given by eq. (16) diverges for some value of q, shows a closely similar dependence on f. When f = 0.5, the spinodal and the MST coincide, and at other values of f the spinodal temperature is somewhat lower than the MST, but the difference is so small and cannot be shown clearly in Figure 10.

3.1.2.2 Block-Copolymer Homopolymer Mixture Theory

Equation (16) derived from the random phase approximation is directly applicable to the mixture of block copolymers with homopolymers, provided that the correlation functions $s_{ij}(q)$ in it are duly evaluated for the collection of ideal, independent chains in the mixture concerned. The equation gives the X-ray or neutron intensity $\tilde{s}(q)$ scattered from such mixtures in the disordered state, and also leads to the prediction of the spinodal temperature. The MST itself is of more general interest, but because of the close relationship between MST and spinodal, the knowledge of the latter and its dependence on variables such as the size of the molecules and blocks involved is useful.

The prediction from eq. (16) of the change in the spinodal temperature on addition of homopolymer A to diblock copolymer AB is qualitatively as follows.[59] Whether the spinodal temperature is raised or lowered by the addition of homopolymer depends on two factors: the symmetry of the block copolymer itself and the relative size of the homopolymer in comparison to the copolymer. The spinodal temperature tends to rise if the addition of the homopolymer shifts the overall monomer concentration in the mixture toward the 50/50 composition and also if it increases the overall average molecular weight of the chains in the mixture. Thus, with an unsymmetric copolymer having block A very much smaller than B, addition of homopolymer A will raise the spinodal except when homopolymer A is very small. With a symmetric copolymer ($f = 0.5$), the spinodal will rise if the added homopolymer is larger than about one-fourth of the length of the copolymer. With an unsymmetric copolymer having block A very much larger than block B, addition of homopolymer A will in general depress the spinodal, except when the homopolymer is very much larger than the copolymer.

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Krause,[60] some years ago, applied a macroscopic thermodynamic consideration to the problem of change in MST by addition of homopolymer, and came to the conclusion which, in very qualitative terms, agrees with the above predictions based on eq. (16).

More recently Noolandi and Hong[61-63] undertook theoretical studies of this type of system by a method more rigorous mathematically. They expressed the free energy of the mixture as a series expansion in powers of the concentration fluctuation, in a manner analogous to Leibler's block copolymer theory.[55] The space filling requirement for the gaussian chains was likewise accommodated through the incompressibility condition and through the use of an effective, self-consistent potential. In the series, terms up to the fourth order were retained, and numerical results were obtained for some of the systems having lamellar morphology (for which the third order term vanishes). The phase diagrams calculated from the theory are illustrated in Figures 11 and 12, where M denotes the region of stability of ordered microphase structure (mesophase), H the region containing a single disordered phase, and HH and HM the region in which two phases coexist. In these two examples the MST is seen to increase with increasing amount of homopolymer. The complexity of the theoretical expressions does not allow ready evaluation of numerical results and it is therefore difficult to deduce from the theory the conditions necessary for the MST to rise or fall with addition of homopolymer.

The solubility limit of homopolymer in the microdomains of ordered block copolymer phase was treated earlier by Meier,[64] who, as in his earlier theories of block copolymer, enumerated the contributions to the free energy by separate factors, such as the interfacial energy, the entropy loss due to the confinement of joints in the interface and of

blocks within their own microdomains, and the entropy loss arising from the distortion of conformations to achieve uniform density requirement. His theory, although approximate, has the virtue of making the contributions by various physical factors more intuitively visible. The result shows that the length of the homopolymer has to be of the same order of magnitude or smaller in comparison to the corresponding block length for them to be soluble in the microdomains of the copolymer. The solubility limit would decrease with increasing homopolymer molecular weight. It predicts, for example, that in lamellar morphology the volume ratio of homopolymer A to block A of copolymer in the swollen microdomains would be equal at most to 1.0 and 0.08, when the molecular weight ratio of homopolymer to copolymer block is equal to 0.1 and 1, respectively.

On the question of the micelles formed by a small amount of block copolymer present in a large amount of homopolymer, two theories are available, one by Leibler, Orland and Wheeler[65] and the other by Whitmore and Noolandi.[66] They are very similar to each other in their approach, and take a model of micelles consisting of a spherical core, mainly of block B, surrounded by a spherical shell (or corona) in which block A of the copolymer intermixes extensively with homopolymer A (Figure 13). Contributions to the free energy from the core (in which conformations of block B chains are somewhat constrained), from the interface between the core and corona, from the corona (in which the effect of the entropy of mixing and the constraint to the conformation are taken into account) and from the bulk phase (in which some of the block copolymer remains dissolved) are all evaluated. Minimization of the free energy then gives the equilibrium values of a number of parameters characterizing the system, such as the critical micelle concentration, the radius of the core, the

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thickness and degree of swelling of the corona, and the number of copolymer chains per micelle. As the population of micelles in the system increases, copolymer chains in the coronae belonging to adjacent micelles may begin to interact with each other. Leibler and Pincus[67] considered such a situation and found that close approach of two micelles results in unfavorable entropic effect and thus develops a net repulsion tending to prevent extensive interpenetration. They calculate the effective potential $U(r)$ between micelles as a function of their separation distance r (Figure 14), and then predict the concentration at which the micelles will organize themselves into an ordered structure. This concentration will depend, of course, both on the length of block A and on the ratio of the chain lengths of homopolymer A and block A, but will depend only weakly on temperature.

3.1.3 Experiment

3.1.3.1 Microphase Separation Temperature

The influence of added homopolymer on the MST of block copolymer was studied first by Robeson et al.[68] with styrene/α-methylstyrene diblock copolymer (containing 50 mole % of each monomer) mixed with polystyrene. The presence of a single or double T_g's was determined by dynamic viscoelastic measurement to ascertain the occurrence of microphase separation. In the absence of added polystyrene, all three block copolymer samples of M_w equal to 80,000, 150,000, and 420,000 exhibited single phase behavior. On addition of 30% or 50% (by weight) of polystyrene (M_w = 270,000), the two block copolymers of lower molecular weights remained in a single phase state, but the third block copolymer of the highest molecular weight exhibited two separate T_g's. Krause et al.[69] also studied styrene/α-methylstyrene diblock copolymer (42% styrene, molecular weight 1.06×10^6). With DSC it was determined that the block copolymer

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possessed microphase-separated structure, and on addition of 25% by weight of polystyrene (M_w = 20,000) or poly(α-methylstyrene) (M_w = 37,000) the mixture could not be transformed into a single phase even though the homopolymer molecular weight was less than one-fourth of the corresponding copolymer block. In these studies relying on determination of T_g's, any change in MST could have been detected only when the effect was very large, and the results are therefore not necessarily in conflict with the prediction of Krause's own earlier theory.[60]

Cohen and Torradas[70] studied a diblock copolymer of 1,2-butadiene and 1,4-butadiene (with block molecular weights of 30,000 and 100,000, respectively) mixed with either 1,2-polybutadiene (M_w = 30,000) or 1,4-polybutadiene (M_w = 100,000). On the basis of measurement of loss tangent peaks obtained with a Rheovibron, they found that the pure diblock copolymer was homogeneous, as were its blends with the 1,4-polybutadiene in all proportions, while the 1,2-polybutadiene induced microphase separation at concentrations above about 10%. Since the block copolymer has a shorter 1,2-butadiene block, the addition of 1,2-polybutadiene shifts the overall composition of the two types of monomers in the mixture toward 0.5 and thus induces the microphase separation.

Quantitative measurement of the variation in the MST with added homopolymer was performed by Zin and Roe.[71] These authors studied blends of a styrene/butadiene diblock copolymer (styrene weight fraction = 0.27, M_w = 28,000) with polystyrene (M_w = 2400) using the small-angle X-ray scattering technique. The scattered X-ray intensity was determined at a number of temperatures and then $1/I_{max}$ was plotted against $1/T$, where I_{max} is the intensity of the characteristic low angle peak in the SAXS curves. Such a plot is suggested by eq. (16). Extrapolation of the linear portion

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of the high temperature data (above the MST) to $1/I_{max} = 0$ (illustrated in Figure 15) gives the spinodal temperature for microphase separation, while the point of deviation of the observed intensity from the straight line gives the MST. The latter was thus found to increase from ca. 140°C for the pure block copolymer to ca. 168°C for a mixture with 20% polystyrene.

3.1.3.2 Phase Diagram

The phase diagram of a mixture of block copolymer with homopolymer, extending over an extended range of temperature and composition, was first reported by Roe and Zin.[72] The phase diagram shown in Figure 16 refers to· the same mixture of styrene/butadiene diblock copolymer and polystyrene mentioned in the above. For its construction the data for the MST obtained by SAXS and the data for the macroscopic phase separation (cloud points) obtained by light scattering were combined and were interpreted in the light of the thermodynamic principles governing phase equilibria and phase diagrams.

In Figure 16, the left-hand ordinate gives the behavior of the pure block copolymer with its MST at around 140°C. When polystyrene is added to the copolymer in its ordered state, the homopolymer dissolves into the microdomains consisting of styrene blocks. The area denoted as M_1 represents the region in which a mesophase (ordered microdomain structure) is stable. When the amount of the homopolymer is not large (below about 18%), on heating, the ordered structure is transformed to a disordered, homogeneous mixture denoted as L_1. The MST increases, as described in Section 3.1.3.1, with increasing amount of the added homopolymer. The area $L_1 + L_2$ depicts the region in which the mixture undergoes a macroscopic phase separation into two coexisting, homogeneous mixtures L_1 and L_2. In this region, which is above the MST, the block copolymer behaves

essentially the same as a random copolymer, and the phase behavior of the mixtures can be described by the usual Flory-Huggins treatment. Below this lies the area denoted as $M_1 + L_2$, and the mixture having composition in this region undergoes a macroscopic phase separation into a mesophase M_1 and a disordered phase L_2. The boundary between the area $L_1 + L_2$ and the area $M_1 + L_2$ constitutes a eutectic point (or a peritectic point, the latter being the terminology more in conformity with the traditional usage[95] of these words), at which three phases, L_1, M_1, and L_2 coexist. The lower right areas in Figure 13, denoted as $M_1 + M_2$, M_2, and $M_2 + L_2$, are less well defined and more speculative. They probably involve the aggregation of block copolymer micelles into an ordered structure. The existence of the mesophase M_2 and the eutectic point associated with its upper extreme is contemplated mainly to satisfy the thermodynamic principles.

Roe and Zin[72] also gave the phase diagram of mixtures consisting of the same diblock copolymer and a polybutadiene (M_w = 28,000). The overall feature of this phase diagram is similar to that given in Figure 16, except that the MST is seen to decrease with increasing amount of added polybutadiene.

One can notice many similarities between the experimental phase diagram in Figure 16 and the phase diagrams in Figures 11 and 12, calculated from the theoretical treatment of Noolandi and Hong. More detailed, quantitative comparison is, however, difficult because the molecular parameters used for the calculation of these predicted phase diagrams are very different from the experimental ones.

3.1.3.3 Solubility of Homopolymer

Solubilization of homopolymer by copolymer was reported in an early work by Inoue et al.,[73] in which mixtures of styrene/isoprene diblock copolymer with polystyrene and/or polyisoprene were examined for optical clarity of toluene-cast films and for the microstructure by electron microscopy. The results, though not quantitative, suggest that the amount of solubilized homopolymer could be 2-3 times the volume of the like copolymer block when the corresponding molecular weight ratio was around unity, while films containing a much higher molecular weight homopolymer were invariably cloudy. Skoulios et al.[74] used SAXS and visual observation to determine the solubility of polystyrene of different molecular weights in the styrene domains of a styrene/(vinyl-2-pyridene) diblock copolymer in which the vinyl-2-pyridene block was swollen with octanol. On addition of a polystyrene with molecular weight equal to the copolymer styrene block, the solubility limit was reached when the volume ratio of polystyrene to the styrene block was roughly equal to unity, while cloudy macrophase-separated mixtures resulted when the polystyrene molecular weight was larger. Ptaszynski et al.[75] also used SAXS to study mixtures of polystyrene of varying molecular weight with a styrene/isoprene diblock copolymer with block molecular weights 40,000 and 50,000, respectively. Essentially corroborating the above results, they found that at fixed homopolymer concentration (15% w/w) the mixtures were transparent until a homopolymer molecular weight of 60,000 (i.e., 1½ times the styrene block length) was reached and thereafter the mixtures were visibly cloudy. With polystyrene of molecular weight 10,000, the solubility limit was reached when the polystyrene content was around 30%. Thus it was concluded that the statement that the homopolymer molecular weight must be less than or

equal to that of the corresponding copolymer block for solubilization to occur represents a good rule of thumb, but that a certain amount of solubilization occurs even at higher molecular weights.

Roe and Zin[72] investigated mixtures of styrene/butadiene diblock copolymer (block molecular weights 7600 and 20,400, respectively) with either polystyrene or polybutadiene. They found the solubility limit to increase with increasing temperature in the case of mixtures with polystyrene of M_w 2400, but to be fairly independent of temperature in the case of mixtures containing polystyrene of M_w 3500 and polybutadiene of M_w 26,000. The solubility limit at room temperature was about 48, 18, and 27% for polystyrene of M_w 2400, polystyrene of M_w 3500, and polybutadiene of M_w 26,000, respectively. These values are about an order of magnitude greater than those predicted by Meier's theory.[64] Roe and Zin[72] argue that the underestimation by Meier's theory arises because the theory assumes a model in which the homopolymer is uniformly distributed within the microdomain, whereas in practice it is more likely that the homopolymer will concentrate more toward the center of the microdomain in order to avoid overly stretching the block chains.

The morphology of blends of block copolymer with homopolymer was studied by means of electron microscopy and small-angle X-ray or neutron scattering by Hashimoto et al.[76] and by Bates et al.[77] The first group prepared blends of styrene/isoprene diblock copolymer and polystyrene cast from toluene solution. The second group studied blends of styrene/butadiene diblock copolymer and polystyrenes, cast from solution prepared with mixed solvents THF/MEK. Both groups noted that the long range order of microdomain packing, present with the pure block copolymer, was lacking in all the blends with added homopolymers. The SAXS results by

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the first group also showed that the radius of the spherical microdomains of isoprene block remained approximately constant but the distance between the spherical domains increased as the homopolymer content was increased (see Figure 17).

A question naturally arises as to whether the solubility limits and the morphology observed with these blends correspond to equilibrium states. Meier[64] suggests that the apparent disagreement between the observation and his theory may arise from non-equilibrium effects. When the molecular weights of the components are fairly large and the blends are prepared from solution, the morphology of the samples obtained frequently depends on the types of solvents used. Equilibrium values of the domain size and the solubility limit can be obtained only when the condition during the sample preparation allows migration of the block copolymer and the homopolymer molecules through the continuous matrix in the blends. Such a condition is more likely to be met when the molecular weights of the components are fairly small and the blends are heated to temperatures approaching or exceeding the MST.

3.1.3.4 Block Copolymer Micelles

The micelles formed when styrene-butadiene diblock copolymer is mixed with a large excess of low molecular weight polybutadiene were studied by Rigby and Roe[78,79] (by SAXS) and by Selb et al.[80] (by SANS). The first group employed three block copolymers in which the fractions of styrene are approximately equal to 25, 50, and 75%, respectively, and studied the effect of changing the temperature. The second group employed block copolymers in which the weight fraction of styrene ranged from 32 to 68% and blended them with polybutadiene of three different molecular weights and studied them at room temperature. Both groups report the radius of the

spherical micelle core, determined by SAXS or SANS technique, which agrees fairly well[66,81] with the value predicted on the basis of the theory by Leibler et al.[65] or by Whitmore and Noolandi.[66] The dependence of the critical micelle concentration on the relative lengths of the blocks and on temperature, reported by Rigby and Roe,[79] is shown in Figure 18. The CMC increases as the temperature is raised and as the butadiene block in the copolymer becomes longer, in accord with the accompanying increase in the compatibility between the block copolymer and polybutadiene. The theory by Leibler et al.[65] was shown to predict the overall trend and the order of magnitude of the CMC shown in Figure 18, but the agreement was not quantitative.[81] The results by Rigby and Roe[78,79] also show that as the temperature is raised, the micelle core consisting of styrene blocks becomes progressively swollen with polybutadiene even before the micelles eventually dissolves into the homopolymer matrix at higher temperature. This aspect was not predicted by either of the theories.

3.2 Mixtures Containing a Diblock Copolymer and Two Homopolymers

3.2.1 Theory

When a diblock copolymer AB is added to a phase-separated mixture of homopolymers A and B, one of the following three events is likely to occur.

(1) When the homopolymer pair is only moderately incompatible, addition of the copolymer may actually cause the two-phase system to become a single homogeneous phase. The copolymer may then be termed a compatibilizer in the thermodynamic sense of the word. In this case, the block copolymer is acting in essentially the same manner as does a random copolymer of the same composition as described in section 2.2.

(2) Homopolymers A and B become solubilized in the microdomains of the like components of the copolymer. This situation is more likely to be found at high copolymer content.

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(3) The mixture may remain macroscopically demixed, but the copolymer is located preferentially at the interface, with its A block in the A-rich phase and B block in the B-rich phase. The main effect in this case is to lower the interfacial tension between the two phases.

Two theoretical treatments, published so far, address themselves on the aspect (3) in the above. The first, by Noolandi and Hong,[82,83] considers the case in which the two homopolymers are highly incompatible (i.e., there is practically no homopolymer A dissolved in the B-rich phase and vice versa). The second, by Leibler,[84] deals with the opposite extreme in which the two homopolymers are relatively compatible (but are still demixed).

The treatment by Noolandi and Hong[82-83] is based on the functional representation of free energy density as developed in their earlier work, and the set of equations derived from it were solved numerically for the specific case of a symmetric system containing homopolymers A and B of infinite molecular weight, a diblock copolymer with A and B blocks of equal lengths, and a solvent which is equally good to polymers A and B. Some qualitative conclusions emerging from the analysis are as follows. With increasing copolymer concentration the interfacial tension is progressively reduced, and the reduction is approximately linear with the concentration of the copolymer and, at a fixed concentration, with the molecular weight of the copolymer. The calculated concentration profile across the phase boundary shows that the copolymer molecules accumulate in the boundary region, and this tendency is more pronounced with copolymers of higher molecular weight. Of the various physical factors contributing to the decrease in the interfacial tension, the main beneficial effect arises from the separation of homopolymers A and B at the boundary through the

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interposition of the copolymer between them, and the main counterbalancing

effect from the loss of entropy due to the localization of copolymers at

the boundary.

In the treatment by Leibler,[84] the free energy density is expanded in

a series in powers of concentration fluctuation, as in his earlier theory[55]

of pure block copolymer. He also treats the symmetric case in which equal

amounts of homopolymers A and B are mixed with a diblock copolymer AB

having blocks of equal lengths, and the molecular weights of all three

components are assumed equal. He finds also that the interfacial tension'

is reduced (very) approximately linearly with the amount of the copolymer

added. He treats the concentration regime, near the critical point, in

which the mixture is marginally incompatible, and finds that the copolymer

is distributed about equally between the two phases, rich in A and rich in

B. The reduction of interfacial tension arises mostly from the resulting

reduction in the difference between the concentration of the monomers A and

B between the two phases. The localization of copolymer at the interfacial

region is found to be minor and therefore contributes only little to the

reduction in the interfacial tension.

3.2.2 Experiment

There is a large body of experimental evidence supporting the

interfacial activity of block (or graft) copolymers in mixtures with one or

two homopolymers. For example, Gaines and Bender[85] have demonstrated a

lowering of polymer melt surface tension on addition of styrene/

dimethylsiloxane copolymer to polystyrene. Addition of only ~0.2% of the

copolymer was shown to give a surface tension close to that of

polydimethylsiloxane. More recently, the technique of X-ray photoelectron

spectroscopy (ESCA) was employed by Dwight et al.[86,87] to study the depth

profile in the surface layer of blends of polycarbonate with siloxane/carbonate diblock copolymer. At a copolymer content of ca. 1% it was found that there was a large increase in the surface excess concentration of siloxane blocks, giving rise to an almost pure siloxane surface layer.

Evidence of the interfacial activity of diblock copolymers at the interface between two immiscible homopolymers, rather than between a single homopolymer and air, has been presented by Gaillard et al.,[88] who used the spinning drop method to measure the interfacial tension in the system polystyrene/polybutadiene/styrene-monomer with addition of varying amounts of styrene/butadiene diblock copolymer. As expected, the interfacial tension decreases with increasing amount of copolymer, eventually levelling off beyond 5-10% of added copolymer. Noolandi and Hong[82] have compared these results with their theoretical prediction, the latter indicating that the interfacial tension should fall rapidly to zero for copolymer contents in excess of ca. 0.01%. Explanations offered for the discrepancy include non-equilibrium effects in the experimental system and possible shifts in the location of the block copolymer at the interface caused by rapid spinning of the drop during the experiment.

Other data illustrating the interfacial activity of diblock copolymers in homopolymer-homopolymer mixtures have involved measurements of the mechanical properties of blends and/or morphological investigations using the electron microscope. Early work of Riess et al.,[48] who studied the effects of added graft and random copolymers as well as block copolymers, showed that transparent blends (implying either single phase or formation of droplets too small to scatter light) could be obtained, provided that homopolymer molecular weights were kept lower than the corresponding copolymer blocks. Kawai et al.[73,89] have studied the morphology and

mechanical properties of blends of polystyrene and polyisoprene to which (relatively large) amounts of styrene-isoprene diblock copolymer were added (as well as the properties of binary blends containing just one of the homopolymers). Both solubilization of the homopolymers and apparent macrophase separation were observed, depending on copolymer content.

A series of studies of the emulsifying effect of hydrogenated-butadiene/styrene block copolymer on the morphology and mechanical properties of blends of high density or low density polyethylene with polystyrene has been presented by Fayt et al.[90-93] (see also ref. 94). Through hydrogenation of butadiene-styrene diblock copolymers in which the butadiene block had either mixed 1,4/1,2 addition or only 1,4 addition, these workers obtained LDPE/PS and HDPE/PS block copolymers. They have demonstrated the utility of small amounts (1-9%) of diblock copolymer in reducing the size of dispersed macrophases, and in some cases have shown that properties such as ultimate tensile strength can show synergistic improvement. The LDPE/PS copolymer was shown to act as a more efficient emulsifier when prepared in the form of a tapered diblock copolymer, possibly due to its lower tendency towards micelle formation.

Acknowledgment

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Table I

Blends Studied That Contain Random Copolymer

(a) Binary blends containing one random copolymer.

Copolymer	Homopolymer	Reference
styrene/butadiene	polystyrene	8,96
styrene/butadiene	polybutadiene	169,171
styrene/butadiene	polypropylene	97
styrene/acrylonitrile	polycaprolactone	98,99,101,161
styrene/acrylonitrile	poly(methyl methacrylate)	13,22,26,27,100,102
styrene/acrylonitrile	various acrylates & methacrylates	24
styrene/(methyl methacrylate)	polystyrene	103
styrene/(n-butyl methacrylate)	polystyrene or poly(n-butyl methacrylate)	14
styrene/(allyl alcohol)	polycaprolactone	104
styrene/α-methylstyrene	poly(2,6-dimethyl-1,4-phenylene oxide)	105
styrene/(halogenated styrene)	poly(2,6-dimethyl-1,4-phenylene oxide)	10,33-35,37,38,40,41,106-108
styrene/(halogenated styrene)	polystyrene	35,37,38
α-methylstyrene/acrylonitrile	poly(methyl methacrylate)	28
α-methylstyrene/methacrylonitrile	poly(vinyl chloride)	134
butadiene/acrylonitrile	poly(vinyl chloride)	127,169,170
butadiene/acrylonitrile	polychloroprene	169
(methyl methacrylate)/(alkyl methacrylates)	poly(methyl methacrylate)	109
(methyl methacrylate)/esters	polycarbonate	110
(glycidyl methacrylate)/(ethyl acrylate)	poly(2,3-dichloro-1-propylacrylate)	111
(ethylene terephthalate)/oxybenzoate	poly(butylene terephthalate)	112
(ethyl acrylate)/(4-vinyl pyridine)	poly(vinyl chloride)	113

TABLE I (CONT'D.)

Copolymer	Homopolymer	Reference
ethylene/(vinyl acetate)	polyethylene	164
ethylene/(vinyl acetate)	chlorinated polyethylene	29,114,116
ethylene/(vinyl acetate)	poly(vinyl chloride)	29,30,116,117,169
ethylene(vinyl acetate)	polychloroprene	169
ethylene/(vinyl acetate)	poly(vinyl nitrate)	118
ethylene/(N,N-dimethyl acrylamide)	poly(vinyl chloride)	122
ethylene/propylene	polypropylene	123-126
ethylene/propylene	polyethylene	123
propylene/(vinyl chloride)	polycarbonate	128
(vinylidene chloride)/(vinyl chloride)	polycaprolactone	129,130,132
various Sarans	polyesters	130
various Sarans	various polyacrylates and methacrylates	131
(butylene terephthalate)/tetrahydrofuran	poly(vinyl chloride)	163
(ethyl acrylate)/ethylene	poly(vinyl chloride)	119

(b) Binary blends containing two random copolymers.

Copolymer	Copolymer	Reference
styrene/acrylonitrile	styrene/acrylonitrile	13
styrene/acrylonitrile	butadiene/acrylonitrile	171
styrene/acrylonitrile	(methyl methacrylate)/(alkyl methacrylate)	109,133
α-methylstyrene/acrylontrile	(methyl methacrylate)/(alkyl methacrylate)	109
styrene/(methacrylic acid Na salt)	(ethyl acrylate)/(acrylic acid Na salt)	162
butadiene/acrylontrile	butadiene/acrylonitrile	169
styrene/butadiene	styrene/butadiene	169

TABLE I (CONT'D.)

(c) Binary blends containing one random terpolymer.

Terpolymer	Homopolymer	Reference
ethylene/(ethyl acrylate)/(carbon monoxide)	poly(vinyl chloride)	119
ethylene/(vinyl acetate)/sulfone	poly(vinyl chloride)	121
α-methylstyrene/methacrylonitrile/(ethyl acrylate)	poly(vinyl chloride)	167
EPDM	polypropylene	97,123
EPDM	polyethylene	123
ethylene/(vinyl acetate)/(carbon monoxide)	poly(vinyl chloride)	119,120
ethylene/(2-ethylhexyl acrylate/(carbon monoxide)	poly(vinyl chloride)	118
acrylonitrile/styrene/butadiene	polypropylene	165
acrylonitrile/styrene/butadiene	Nylon 6 or Nylon 12	166

(d) Ternary blends containing one or two random copolymers.

Copolymer	Homopolymer or Copolymer	Homopolymer	Reference
ethylene/propylene	polyethylene	polypropylene	135,136,138,139
styrene/(methyl methacrylate)	polystyrene	poly(methyl methacrylate)	48
styrene/butadiene	polystyrene	polybutadiene	47
butadiene/acrylonitrile	(vinylidene chloride)/(vinyl chloride)	poly(vinyl chloride)	137

Table II

Blends Studied That Contain Block Copolymer

(a) Binary blends containing one block copolymer.

Copolymer	Homopolymer	Reference
styrene/dimethylsiloxane	polystyrene	85,140,141
styrene/butadiene	polybutadiene	17,142
styrene/butadiene	polystyrene	8,17,71,72,77-78,143
styrene/isoprene	polystyrene	73,76
styrene/isoprene	polyisoprene	73,76
α-methylstyrene/isoprene	poly-α-methylstyrene or polyisoprene	144
1,4-butadiene/1,4-isoprene	poly(1,4-butadiene) or poly(1,4-isoprene)	49
dimethylsiloxane/styrene/dimethylsiloxane	polystyrene	145
styrene/butadiene/styrene	polystyrene	146,149
styrene/butadiene/styrene	polybutadiene	147-149
styrene/butadiene/styrene	polyethylene	150
styrene/isoprene/styrene	poly(2,6 dimethyl-1,4-phenylene oxide)	153
styrene/(ethylene-butene)/styrene	polypropylene	151
styrene/α-methylstyrene/styrene	polystyrene or poly-α-methylstyrene	154

(b) Binary blends containing two block copolymers.

Copolymer	Copolymer	Reference
styrene/butadiene	styrene/butadiene	157
styrene/butadiene	styrene/butadiene/styrene	146

TABLE II (CONT'D.)

(d) Ternary blends containing one block copolymer.

Copolymer	Homopolymer	Homopolymer	Reference
styrene/isoprene	polystyrene	polyisoprene	73
ethylene/propylene/ethylene	polyethylene	polypropylene	168
styrene/(hydrogenated butadiene)	polystyrene	polyethylene	90-92
styrene/(ethylene-butene)/styrene	polystyrene	polyethylene	155
styrene/ethylene	polystyrene	polyethylene or ethylene/propylene	83,94
butadiene/isoprene	poly(1,4-butadiene)	poly(1,4-isoprene)	156
styrene/(methyl methacrylate)	polystyrene	poly(methyl methacrylate)	48
styrene/butadiene	polystyrene	polybutadiene	47

Legends to Figures

Figure 1. Illustration of the various ways by which the effective interaction parameter Λ_{12} between homopolymer A and copolymer CD, given by equation (5), may vary with the volume fraction f_{C2} of comonomer C in the copolymer, according to whether Λ_{CD} is negative, equal to zero (broken line), or positive. (From Paul and Barlow.[9])

Figure 2. The observed cloud points are plotted against the volume fraction ϕ_1 of the polystyrene for the mixture of polystyrene (M_w 5480) and styrene/butadiene random copolymer (50% styrene, M_w 24000) (curve 6), for the mixture of polystyrene (M_w 2400) and styrene/butadiene random copolymer (25% styrene, M_w 29000) (curve 7), and for the mixture of polystyrene (M_w = 2400) and styrene/butadiene diblock copolymer (25% styrene M_w 28000, in the disordered state) (curve 9). The solid curves drawn are the results of the least-square fit using a temperature dependent Λ_{12} as an adjustable parameter. (From Roe and Zin.[8])

Figure 3. The maximum composition difference Δf_{MMA} permissible for compatibility between two (methyl methacrylate)/(butyl acrylate) copolymers (in 50/50 mixtures) plotted against the average content f_{MMA} of methyl methacrylate. The degrees of polymerization are indicated. (From Kollinsky and Markert.[15])

Figure 4. The maximum composition difference Δf_{MMA} permissible for compatibility between two copolymers, plotted against the average content f_{MMA} of methylmethacrylate. The types of copolymer are indicated. (From Kollinsky and Markert.[15])

Figure 5. Miscibility of PPO with random copolymer of o-fluorostyrene and p-chlorostyrene (curve 1), copolymer of o-fluorostyrene and copolymer of p-fluorostyrene (curve 2), and copolymer of o-chlorostyrene and p-chlorostyrene (curve 3). The insides of the curves represent the miscibility regions. (From ten Brinke, Karasz, and MacKnight.[10])

Figure 6. Comparison of cloud point curves for blends of α-methylstyrene/acrylonitrile copolymer with isotactic poly(methyl methacrylate), with poly(ethyl methacrylate), and with atactic poly(methyl methacrylate). (From Goh, Paul, and Barlow.[28])

Figure 7. Phase diagram of a ternary mixture of homopolymers A and B and a random copolymer AB (f = 0.5). (a) $\Lambda_{AB}V/RT = 3$, (b) $\Lambda_{AB}V/RT = 7$, (c) $\Lambda_{AB}V/RT = 9$. ————: coexistence curve; ------: spinodal curve; -·-·-·: tie line; C, C_1, C_2: critical point. In (b) and (c) Δ denotes the three coexisting phases. (From Leibler.[45])

Figure 8. Depression of spinodal temperature T with increasing volume fraction ϕ_3 of the added copolymer AB, calculated for the system homopolymer A, homopolymer B, and random copolymer AB with $V_1 = V_2$, $V_3 = 10V_1$, $f_1 = f_2 = 0.5$. The volume fraction ϕ_1^0 of homopolymer A in the initial binary mixture is indicated (From Rigby, Lin, and Roe.[47])

Figure 9. The cloud temperature T_b of the mixture of polystyrene (M_w 1900) and polybutadiene (M_w 2650), to which styrene/butadiene random copolymer was added, is plotted against the volume fraction ϕ_3 of the copolymer, to show the conformation of the observed data to equation (12). The open squares were obtained with a random

copolymer (52.5% styrene, M_w 25000) and the filled square with
a random copolymer (46.7% styrene, M_w 16300). The slope gives
the value of the temperature coefficient of the interaction
energy density Λ_{12} that agree well with the value determined
previously. (From Rigby, Lin, and Roe.[47])

Figure 10. The value of χN at the spinodal point (N is the number of
segments per copolymer molecule) plotted against the
composition f of the block copolymer molecule. The value of χN
at the microphase separation temperature is slightly smaller `
than at the spinodal, but the difference between them is small
and cannot be meaningfully displayed in this plot. (From
Leibler.[55])

Figure 11. Calculated phase diagrams of mixtures containing block
copolymer AB and homopolymer A, where the number of segments
per molecule of the copolymer and the homopolymer are equal to
N, and the fraction f_A of monomer A in the copolymer is as
indicated. (From Hong and Noolandi.[63])

Figure 12. Calculated phase diagram of a mixture similar to that in
Figure 9, but here the fraction f_A of monomer A in the
copolyemr is equal to 0.45. (From Hong and Noolandi.[63])

Figure 13. Model of a spherical micelle consisting of diblock copolymer AB
in the matrix of homopolymer A. (From Whitmore and
Noolandi.[66])

Figure 14. Interaction energy U between two micelles as a function of the
distance r between them, calculated for the system in which
diblock copolymer (N_A = 1800, N_B = 200) is mixed with
homopolymer N_h = 50 (solid line) or homopolymer N_h = 360

(dashed line). The interaction parameter χ is assumed to be 0.1. (From Leibler and Pincus.[67])

Figure 15. Reciprocal of the peak intensity I_{max} obtained from SAXS measurement of styrene/butadiene diblock copolymer plotted against the reciprocal of temperature T. Linear extrapolation of high temperature data to zero gives the spinodal temperature, while the first deviation of the observed intensity from the straight line gives the microphase separation temperature. (From Zin and Roe.[71])

Figure 16. Phase diagram of a mixture containing polystyrene ($M_w = 2400$) and styrene/butadiene diblock copolymer (27% styrene, $M_w = 28000$). Liquid phases L_1 and L_2 represent mixtures of disordered block copolymer and polystyrene. Mesophase M_1 consists of ordered microdomains of the block copolymer swollen with polystyrene. Mesophase M_2 probably contains aggregates of block copolymer micelles within the medium of polystyrene. The features on the lower right, drawn in broken lines, are more speculative. (From Roe and Zin.[72])

Figure 17. Desmeared small-angle X-ray scattering intensities for a styrene/isoprene diblock copolymer (78% styrene, M_n 320,000) and its mixtures with polystyrene (M_n 81,000) (the weight fraction of the latter in the mixture is indicated on the plot). The dotted curves are best fitting curves calculated for scattering from isolated spheres. (From Hashimoto, Fujimura, Hashimoto, and Kawai.[76])

Figure 18. The critical micelle concentrations of three styrene/butadiene diblock copolymer samples in the matrix of low molecular weight

polybutadiene are plotted against temperature. The approximate

compositions (styrene vs. butadiene) of the block copolymers

are indicated. (From Rigby and Roe.[79])

FIGURE 1
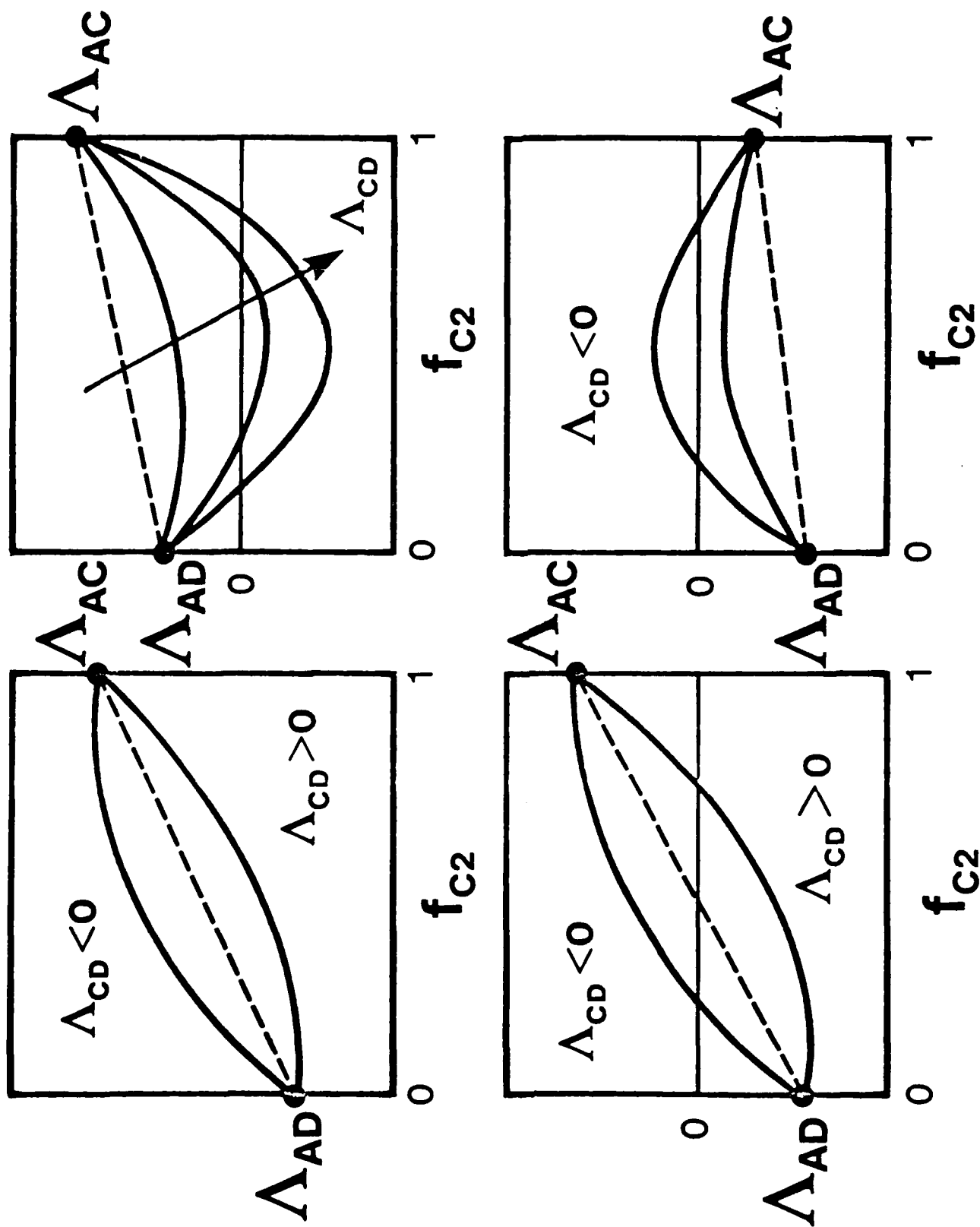
FIGURE 2
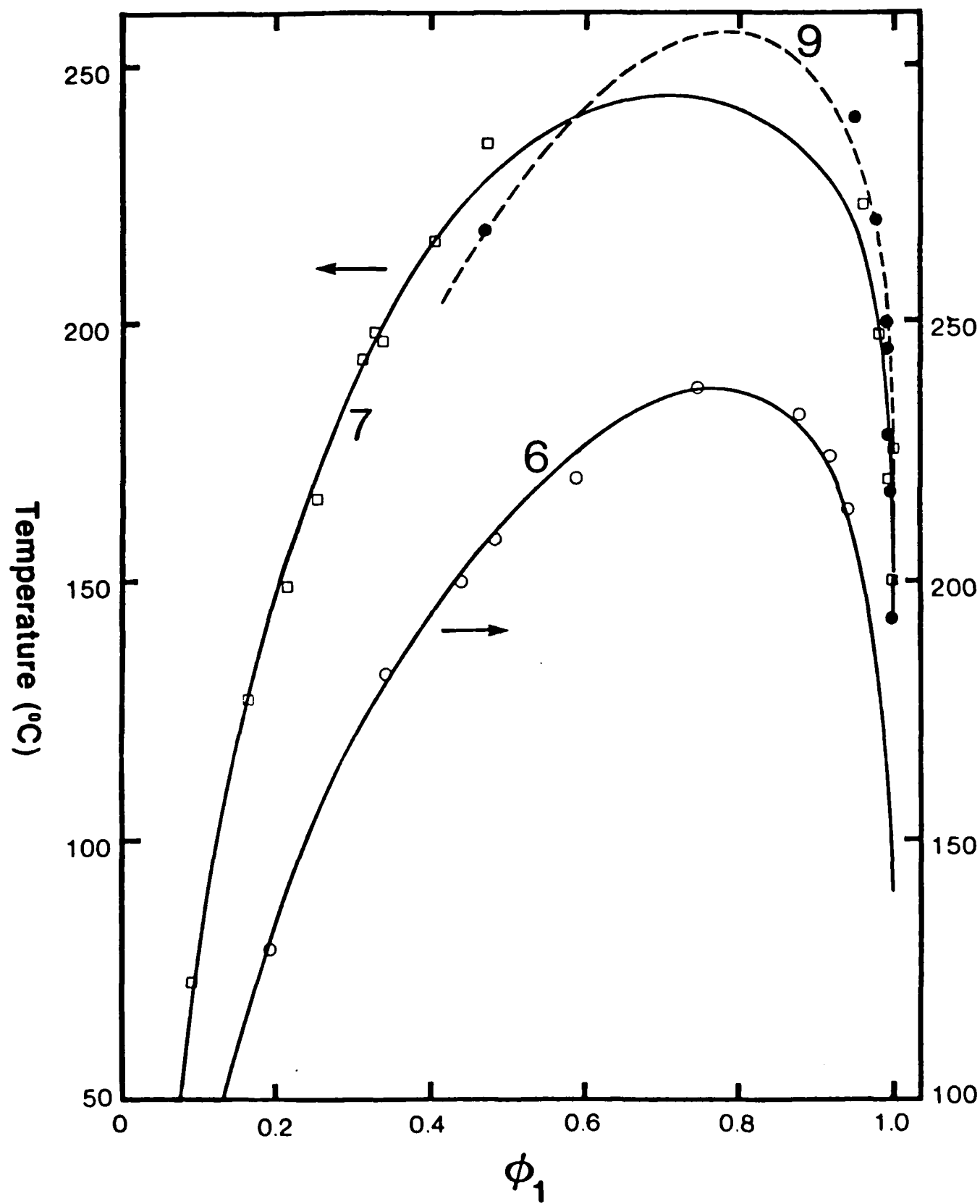
FIGURE 3

Figure 4

Figure 5

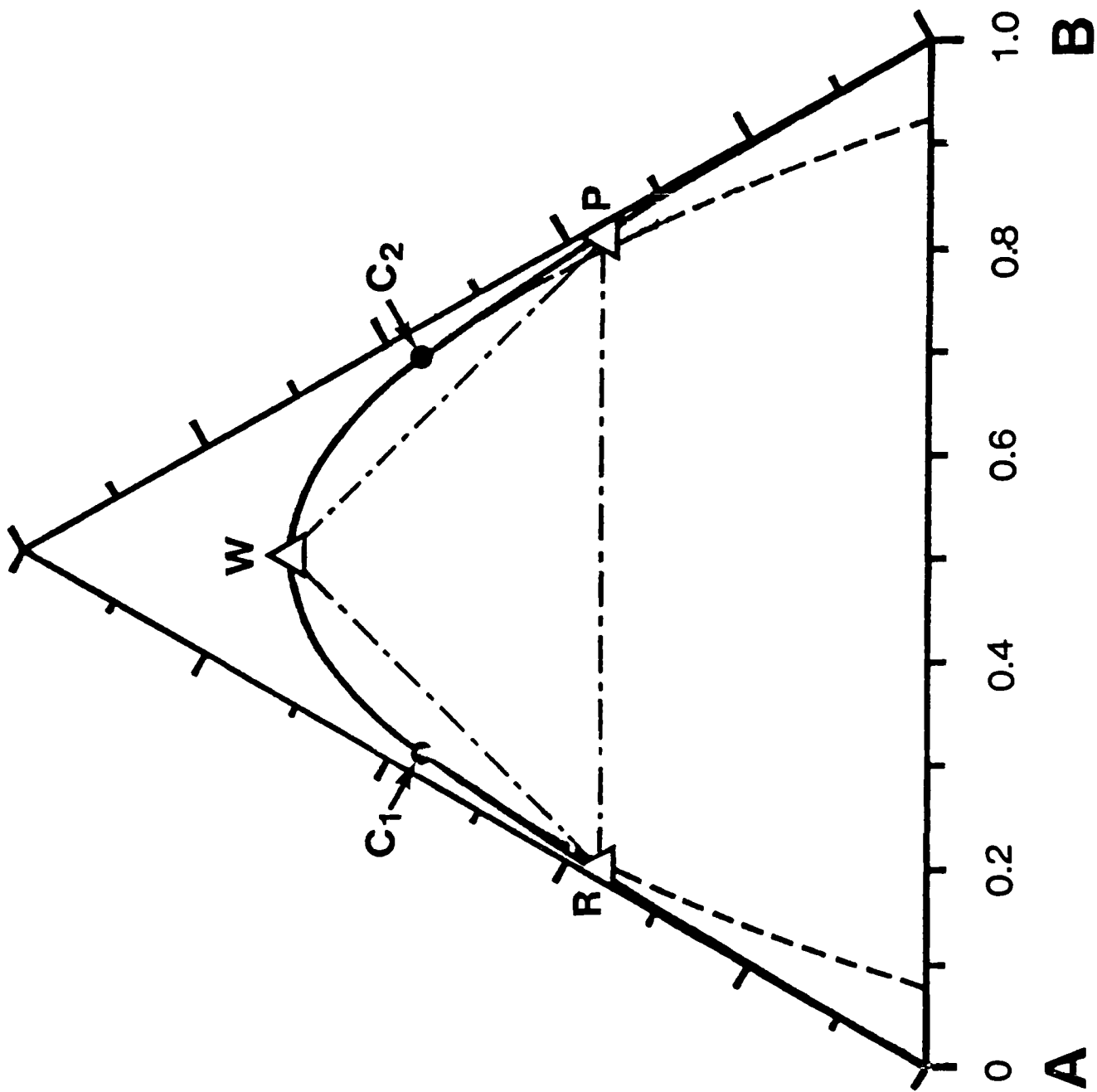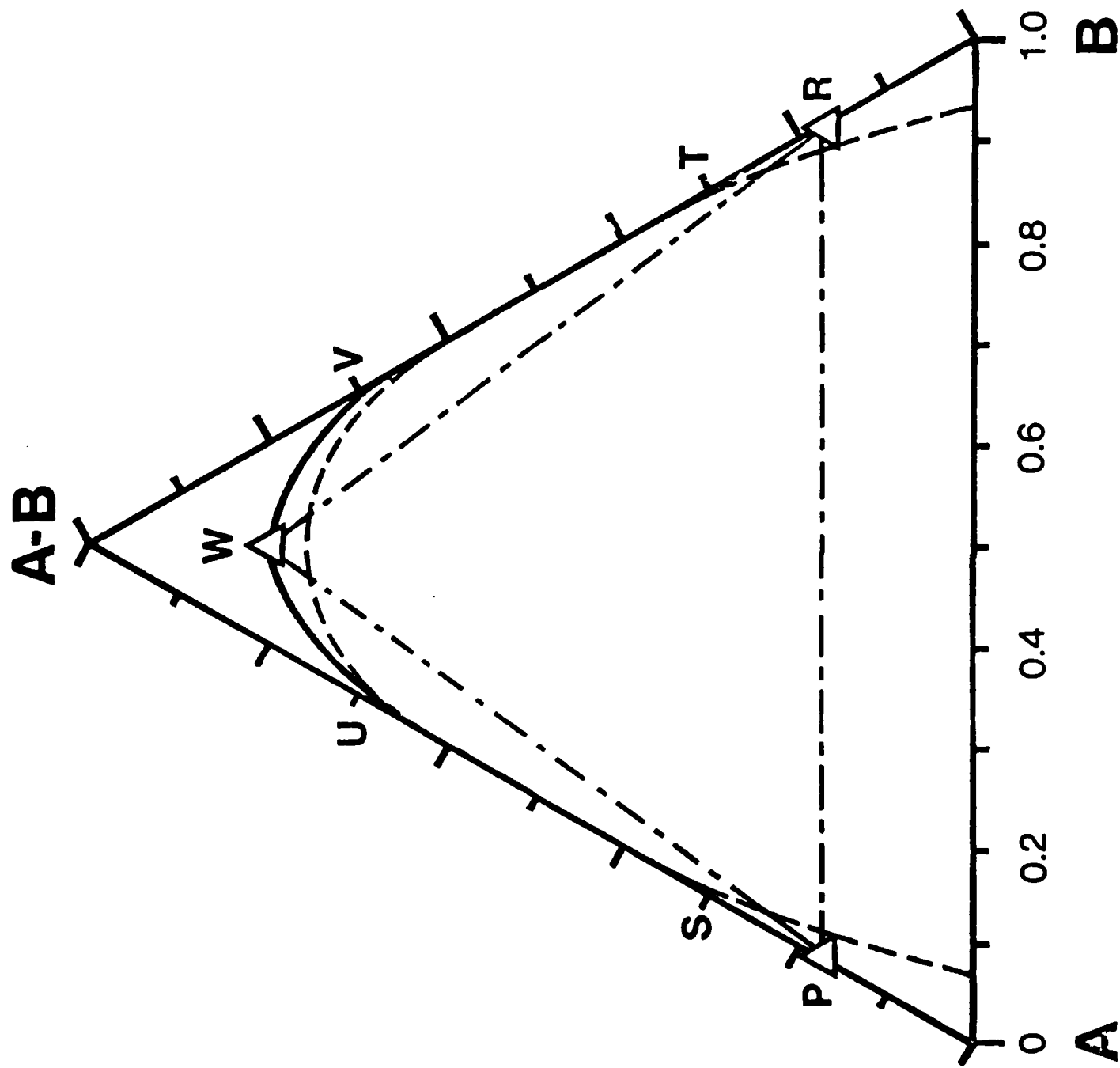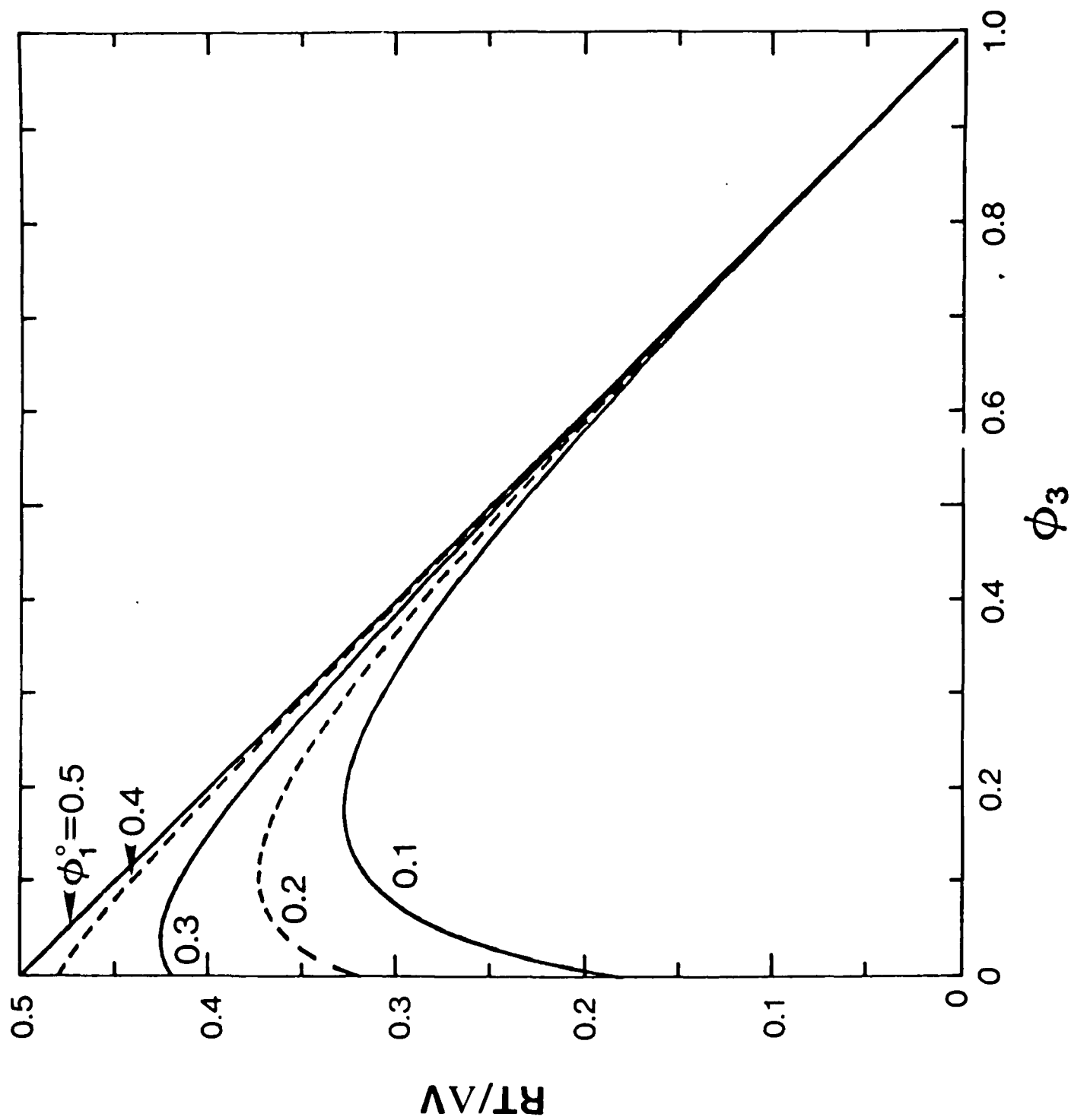Mole Fraction p-halostyrene

T °C
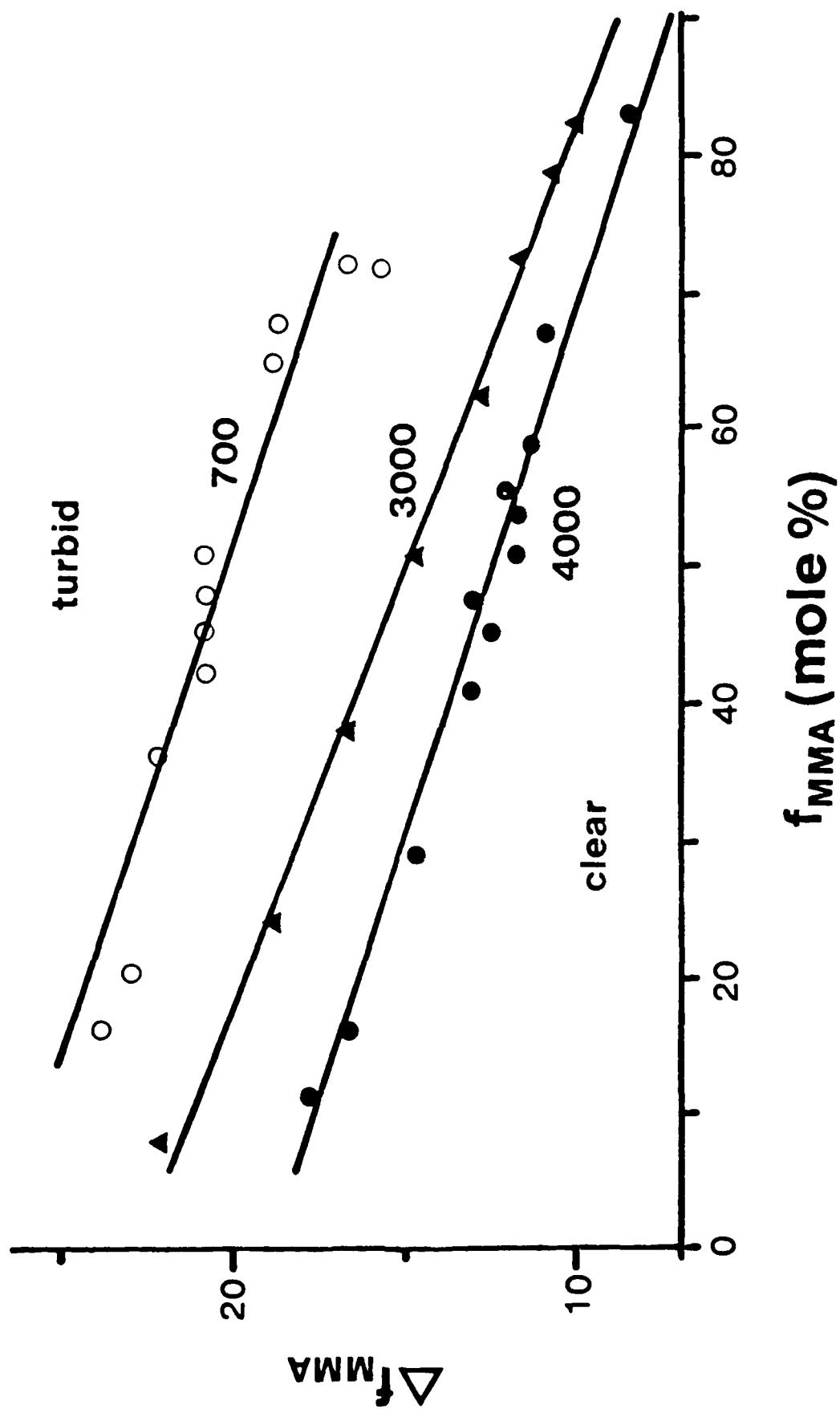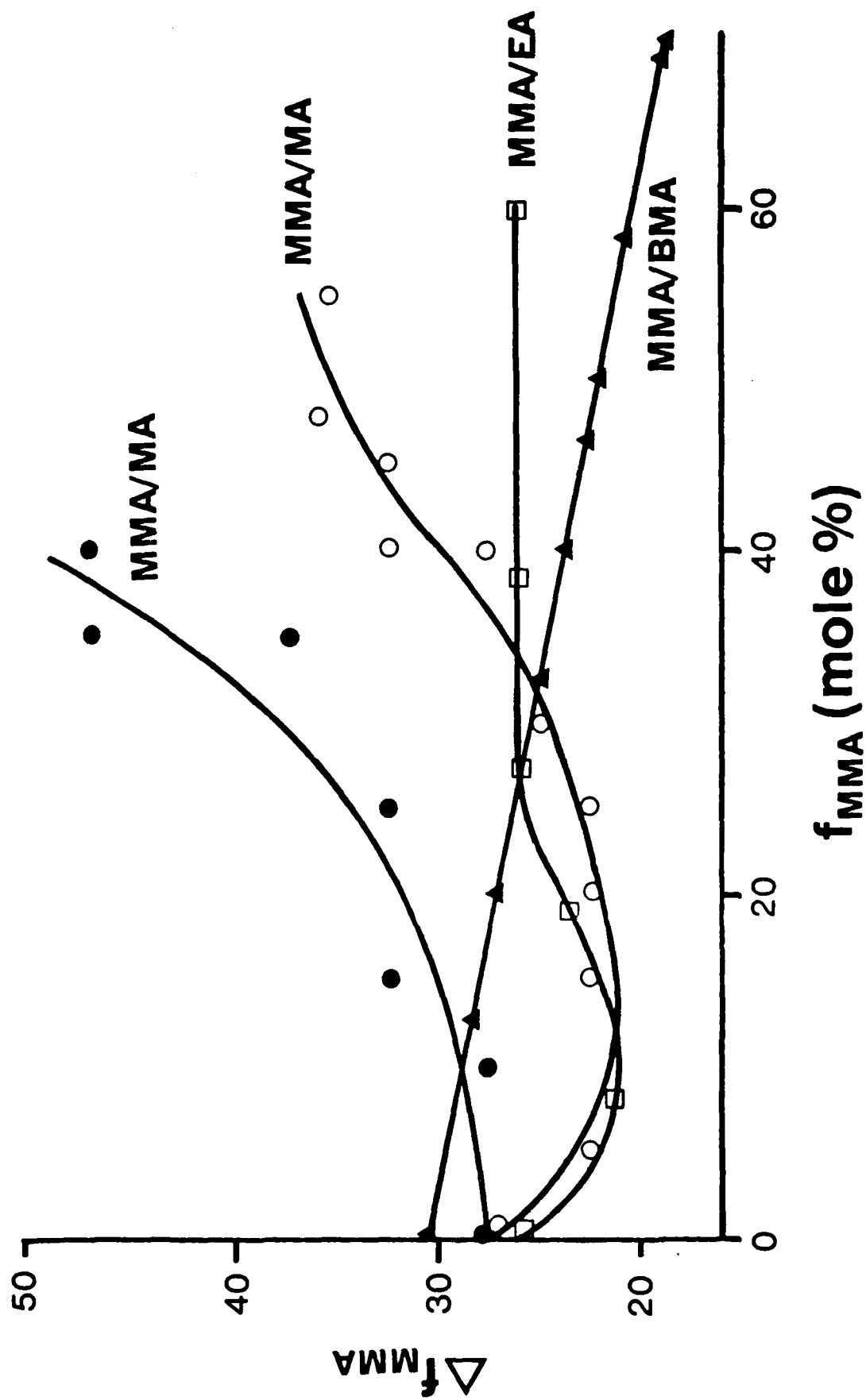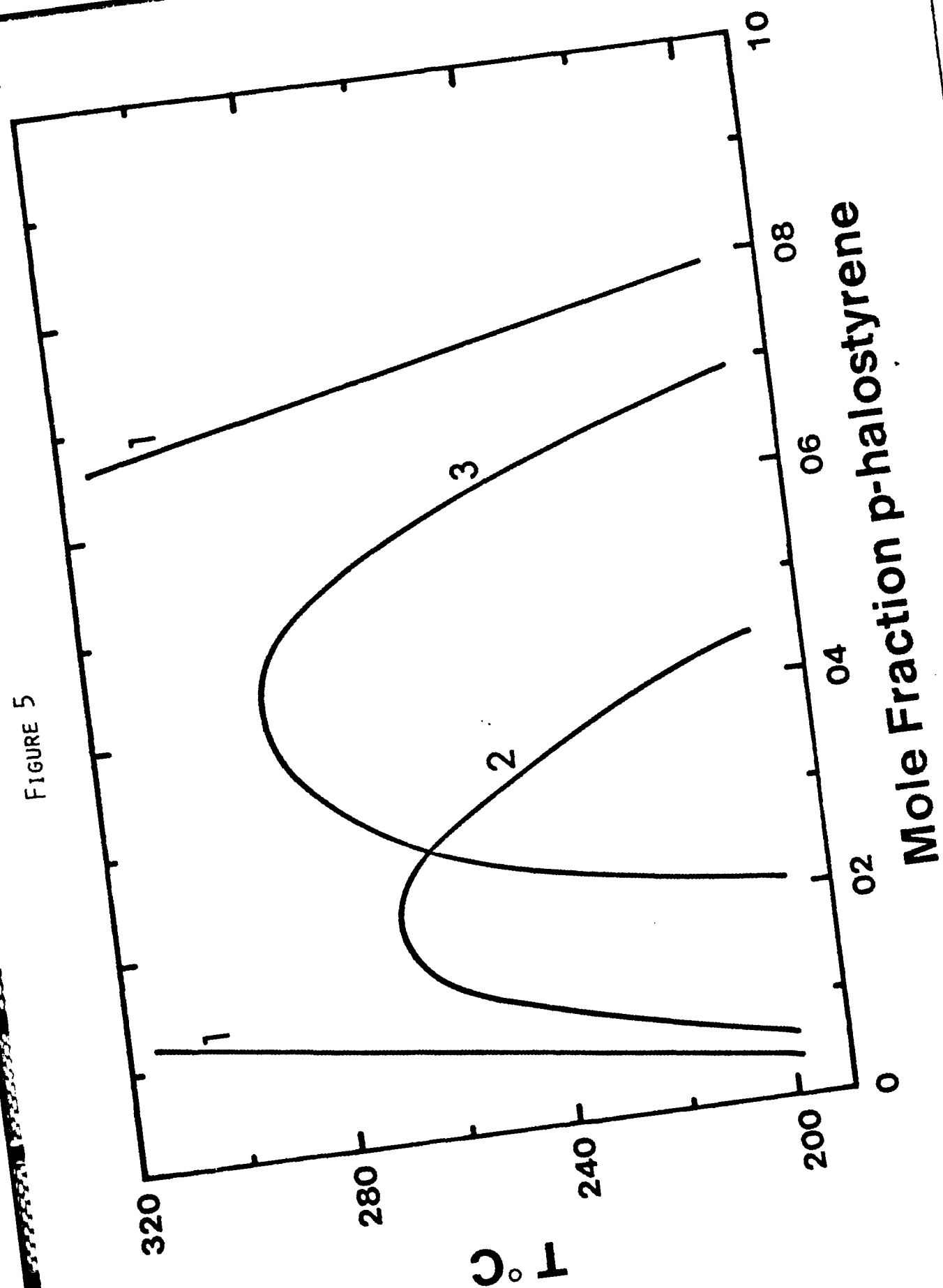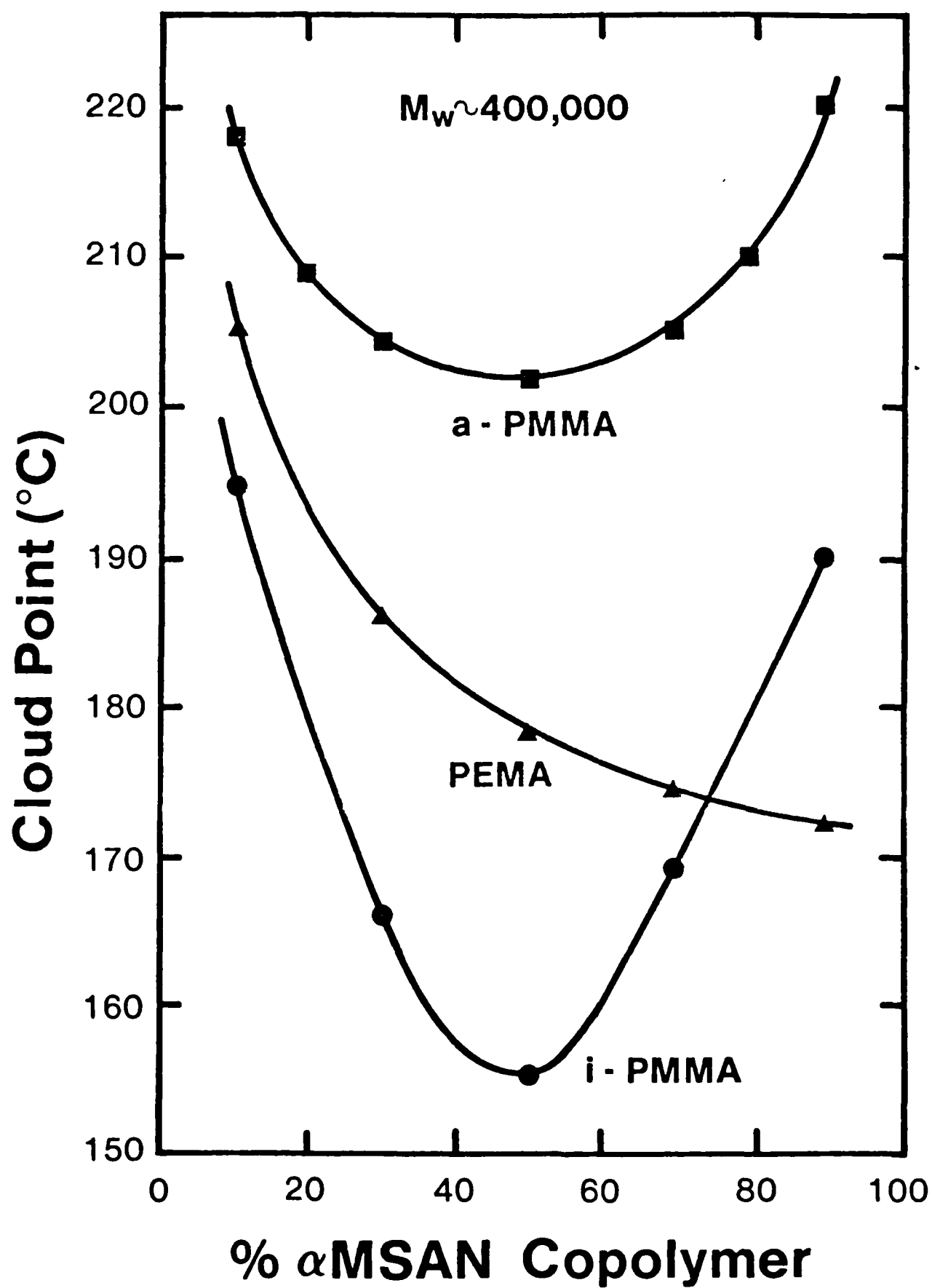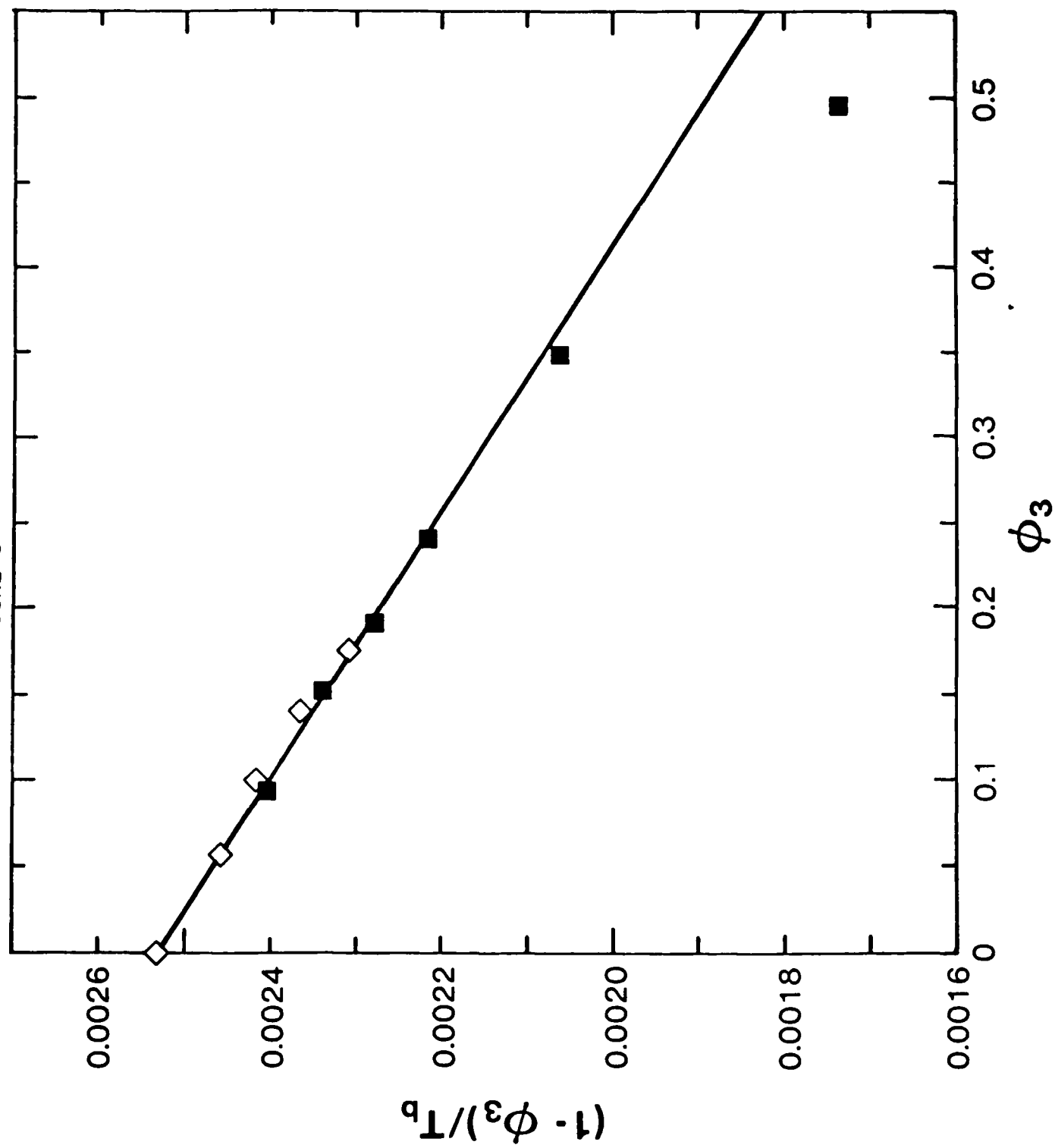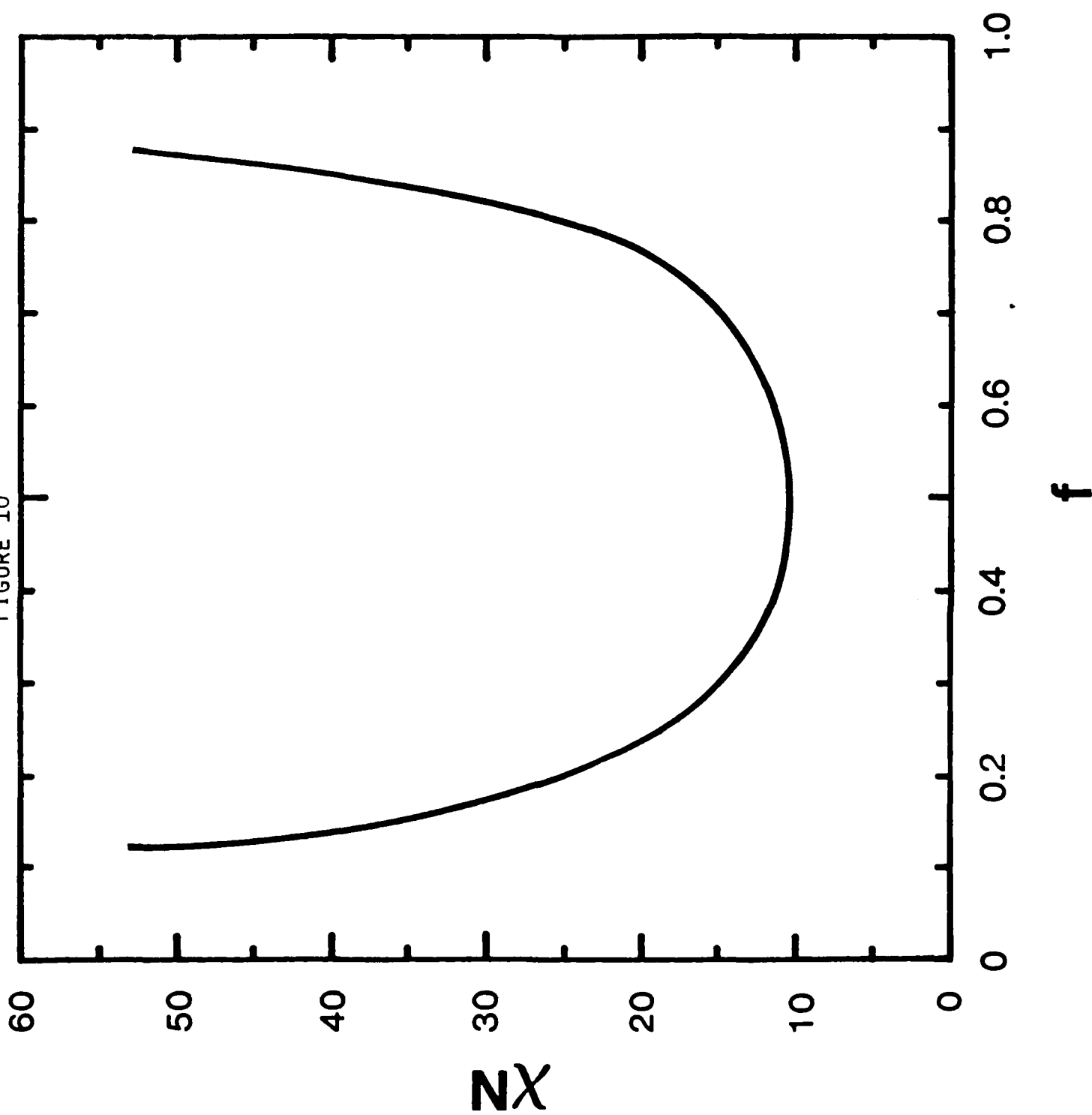
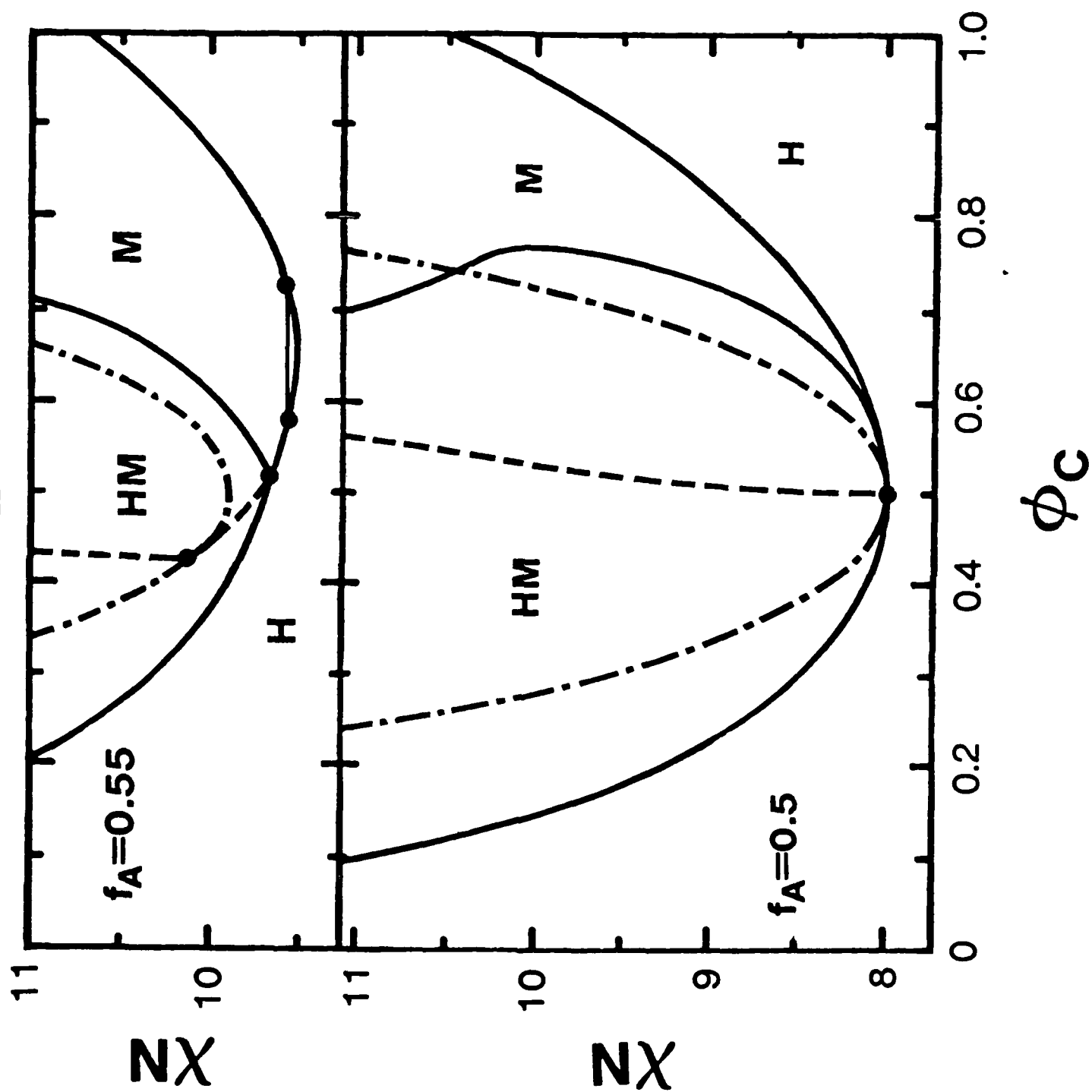FIGURE 6

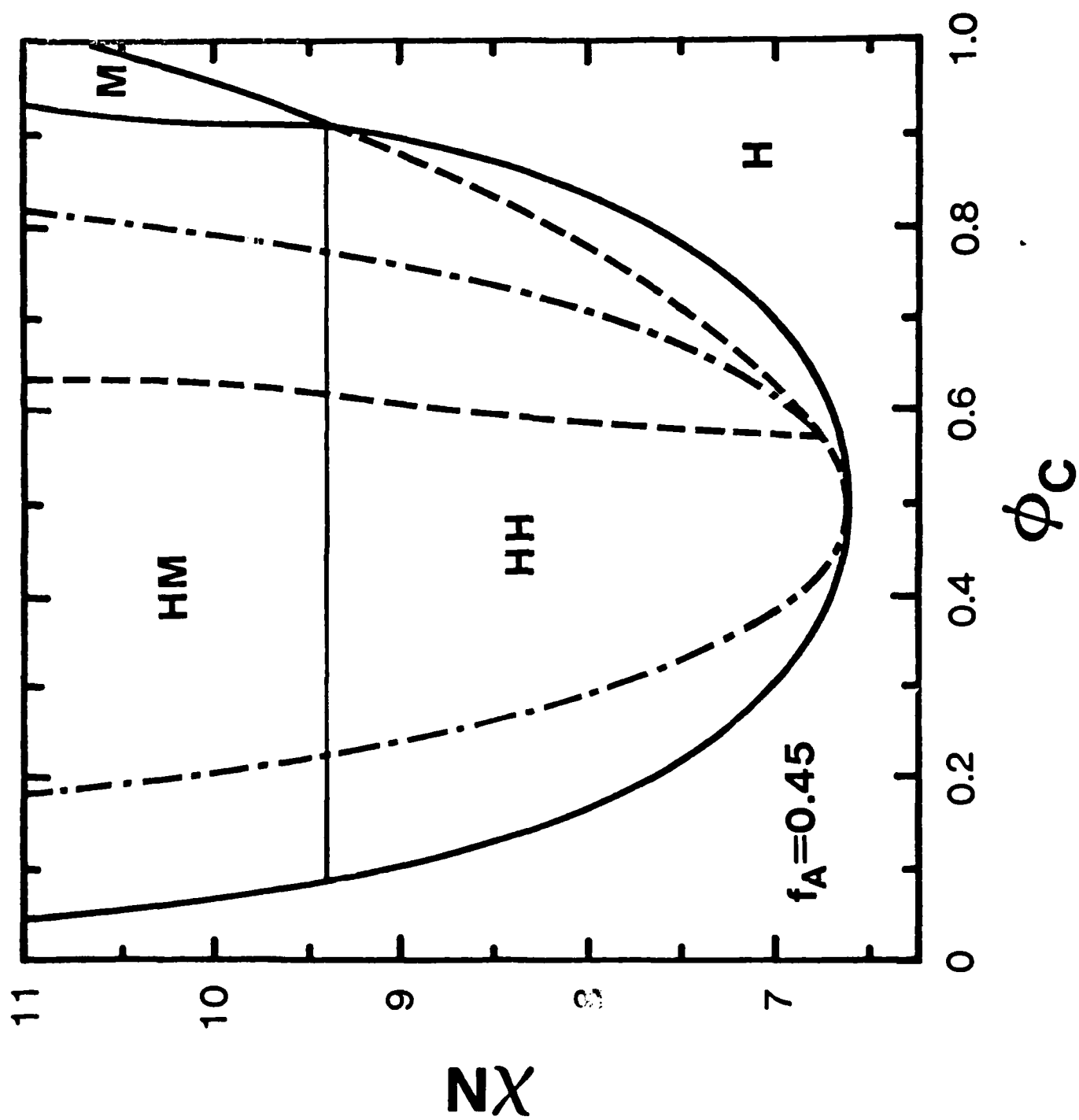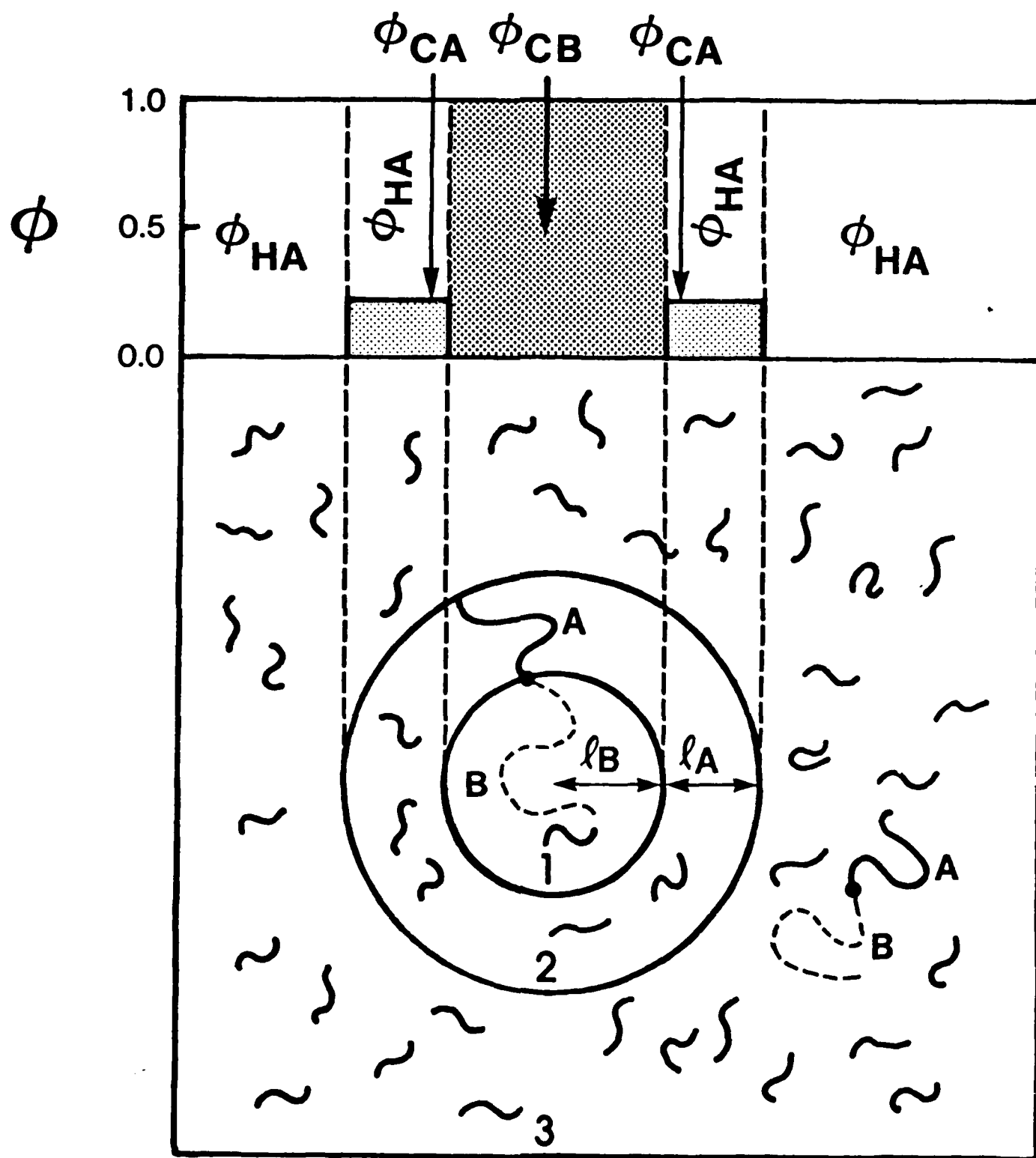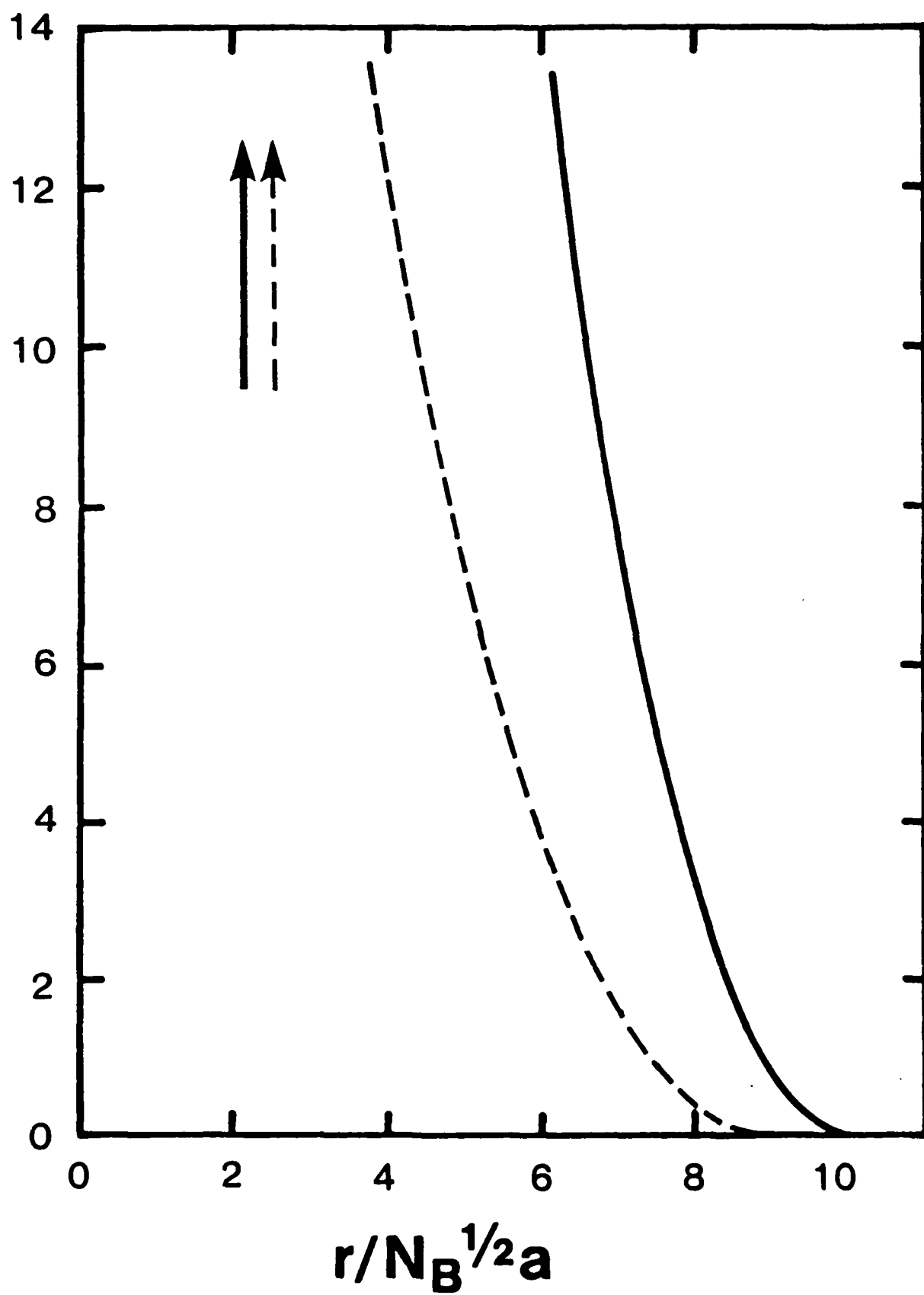Figure 7A

A-B
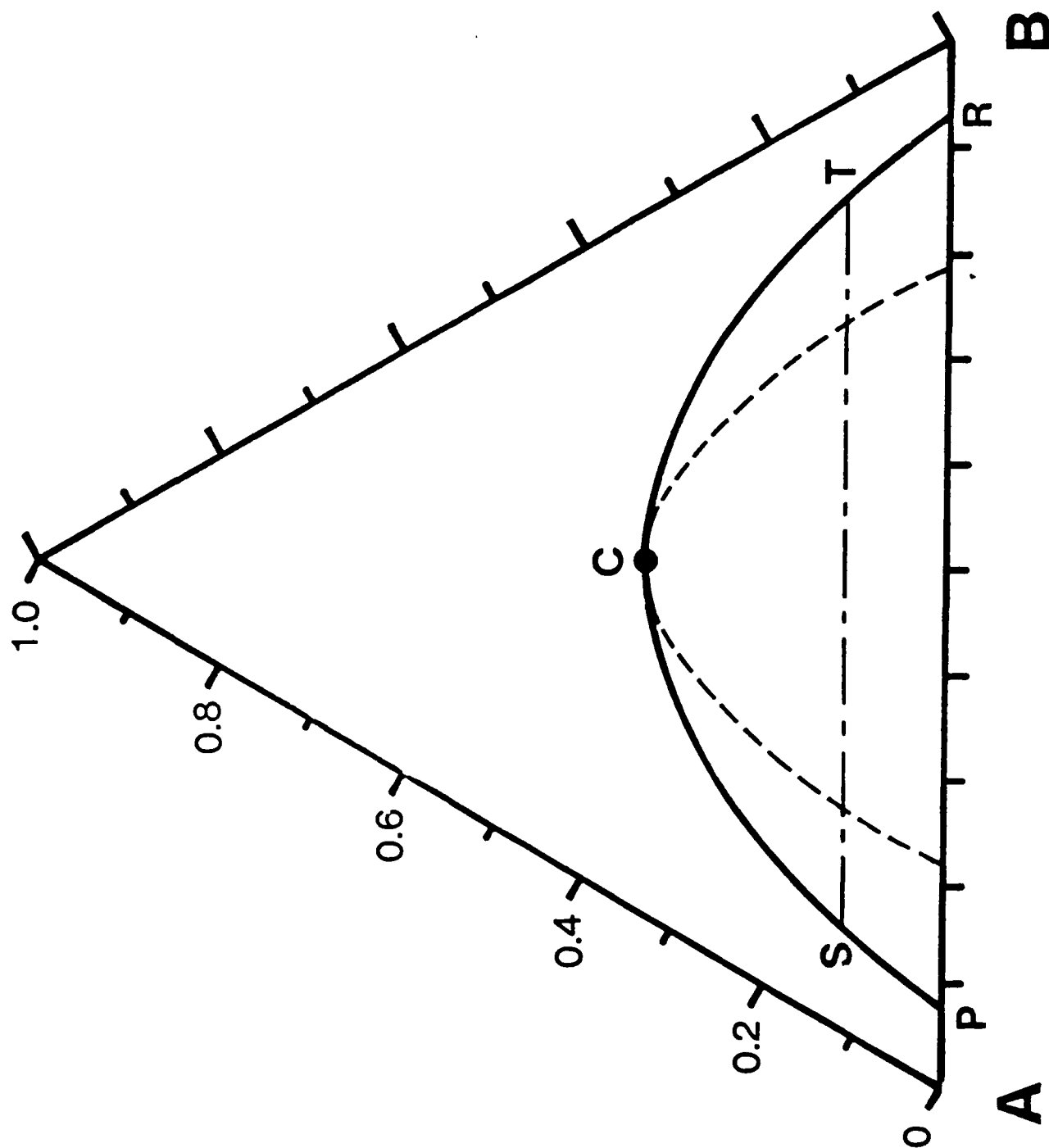
Figure 7B

A-B

FIGURE 7c

Figure 8

FIGURE 9

Figure 10

FIGURE 11

FIGURE 12

FIGURE 13

Figure 14

FIGURE 15

FIGURE 16

Weight Fraction of Polystyrene (M_W 2400)
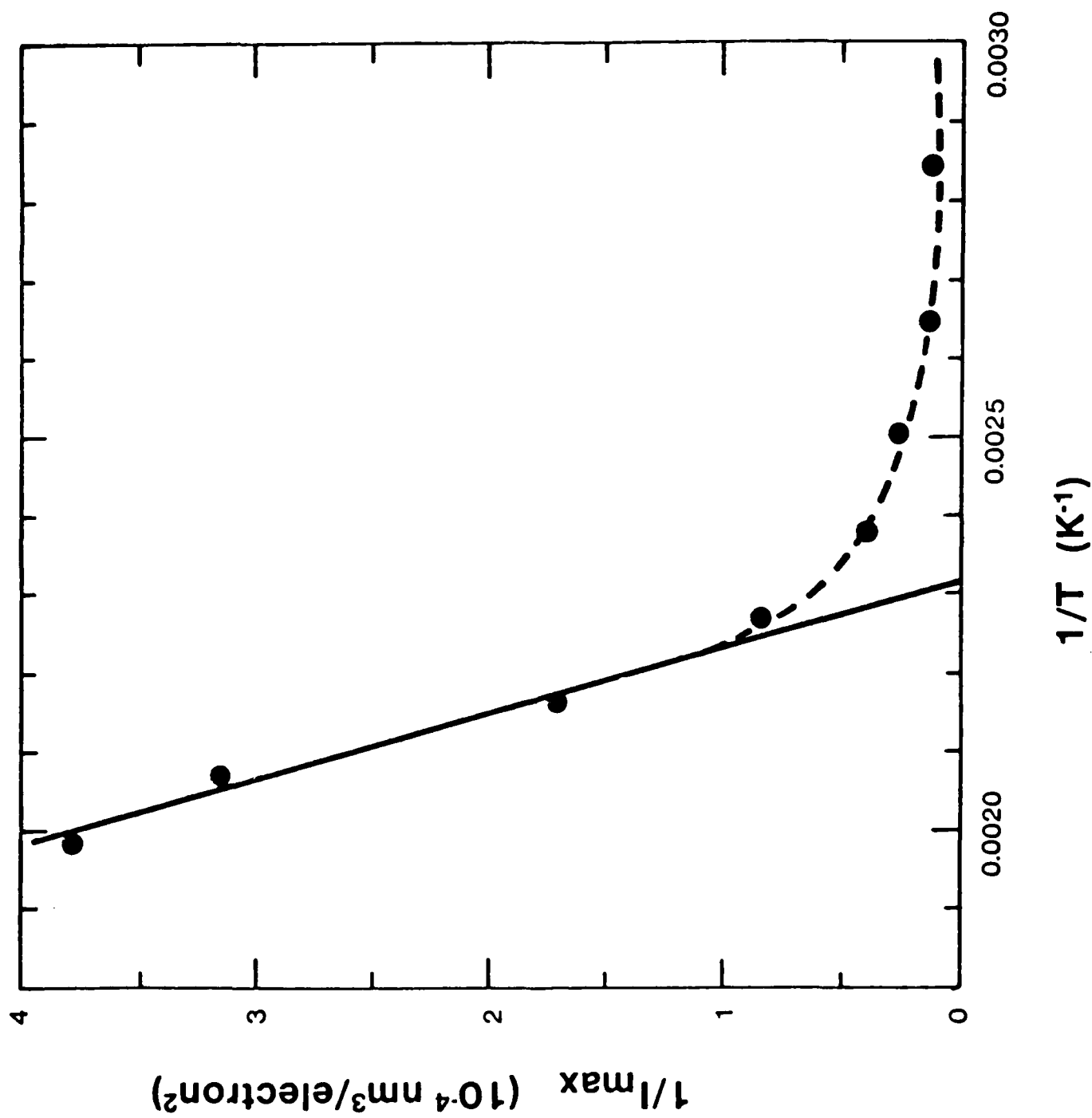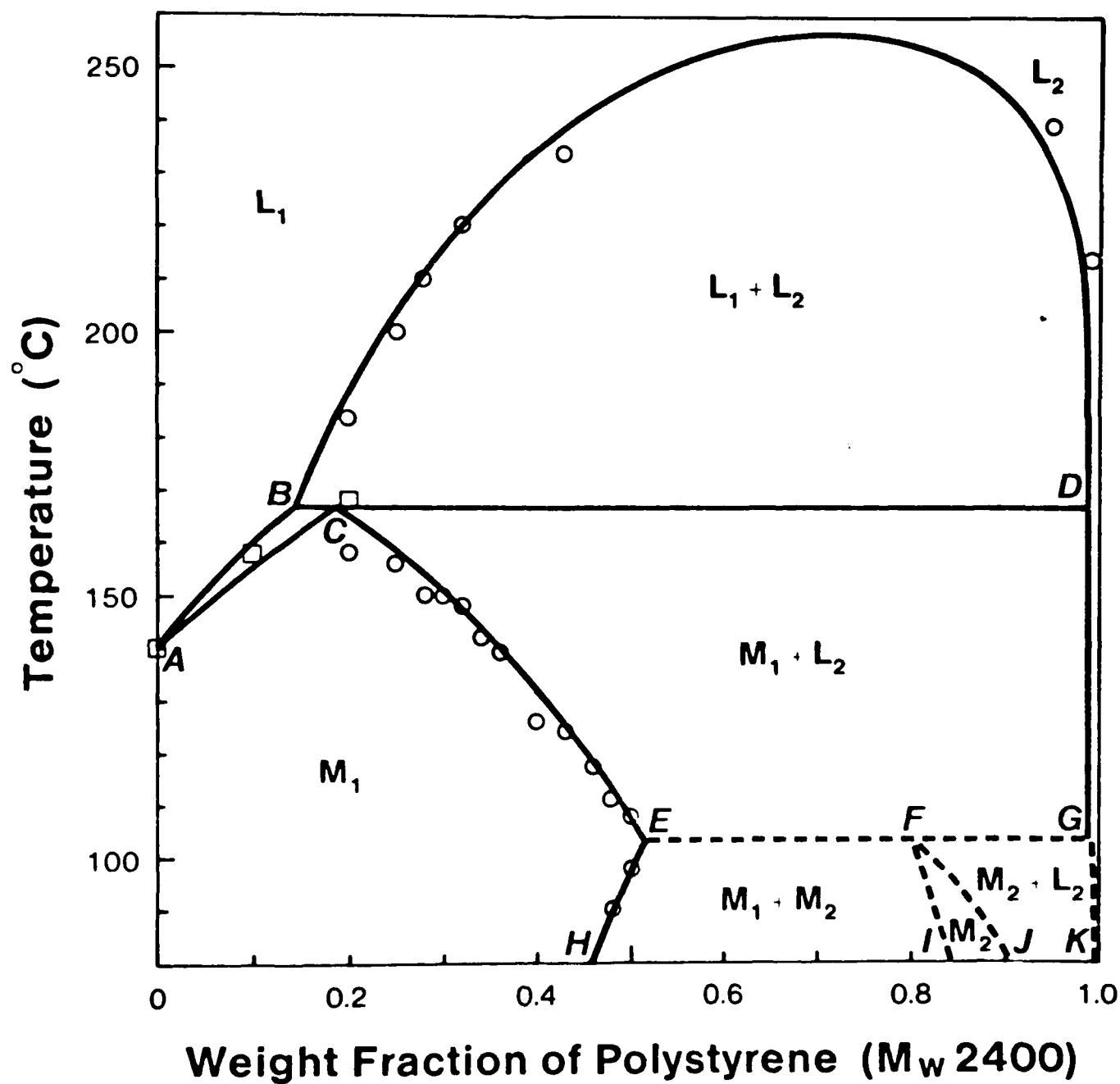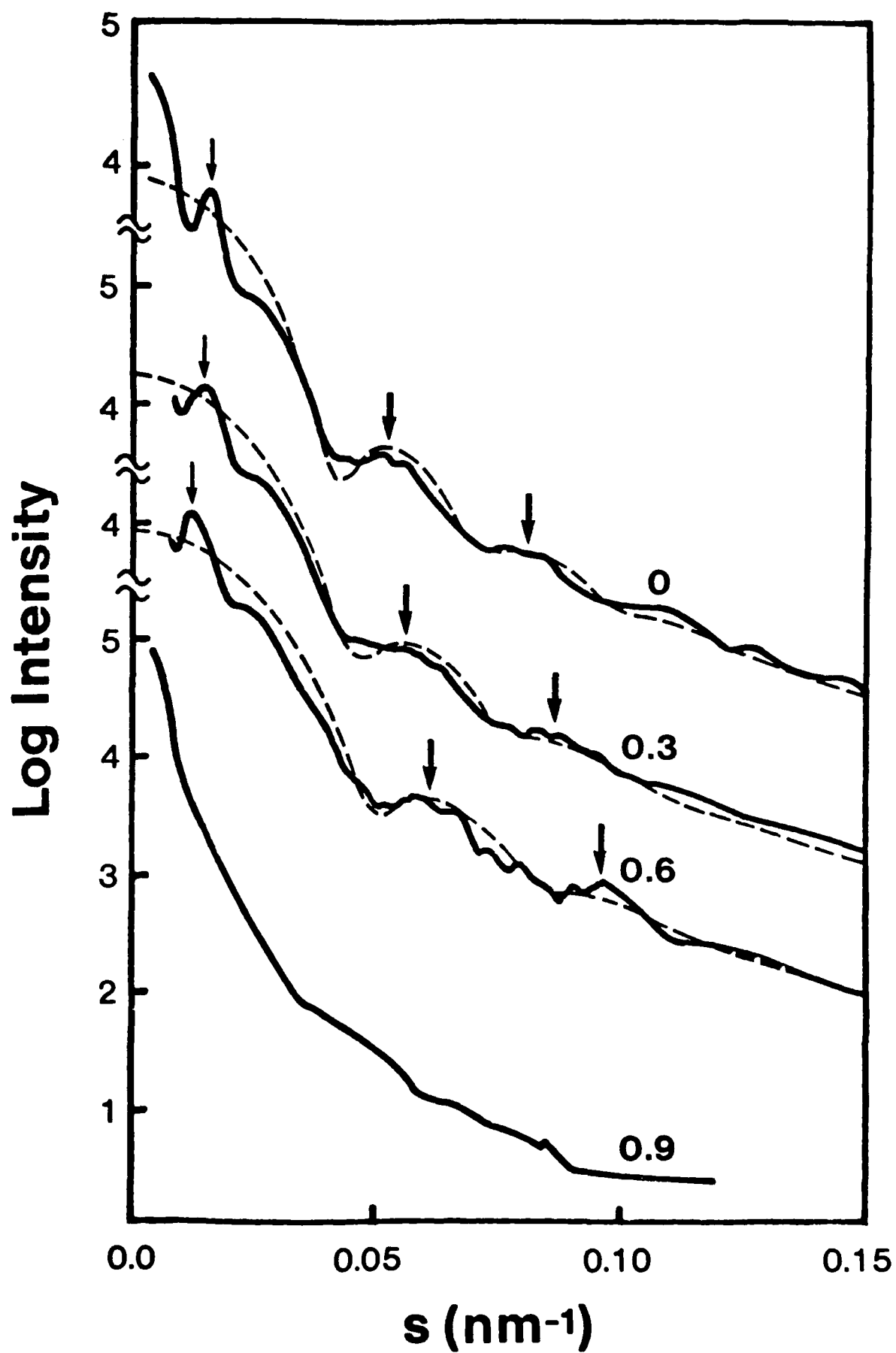
FIGURE 17

FIGURE 18
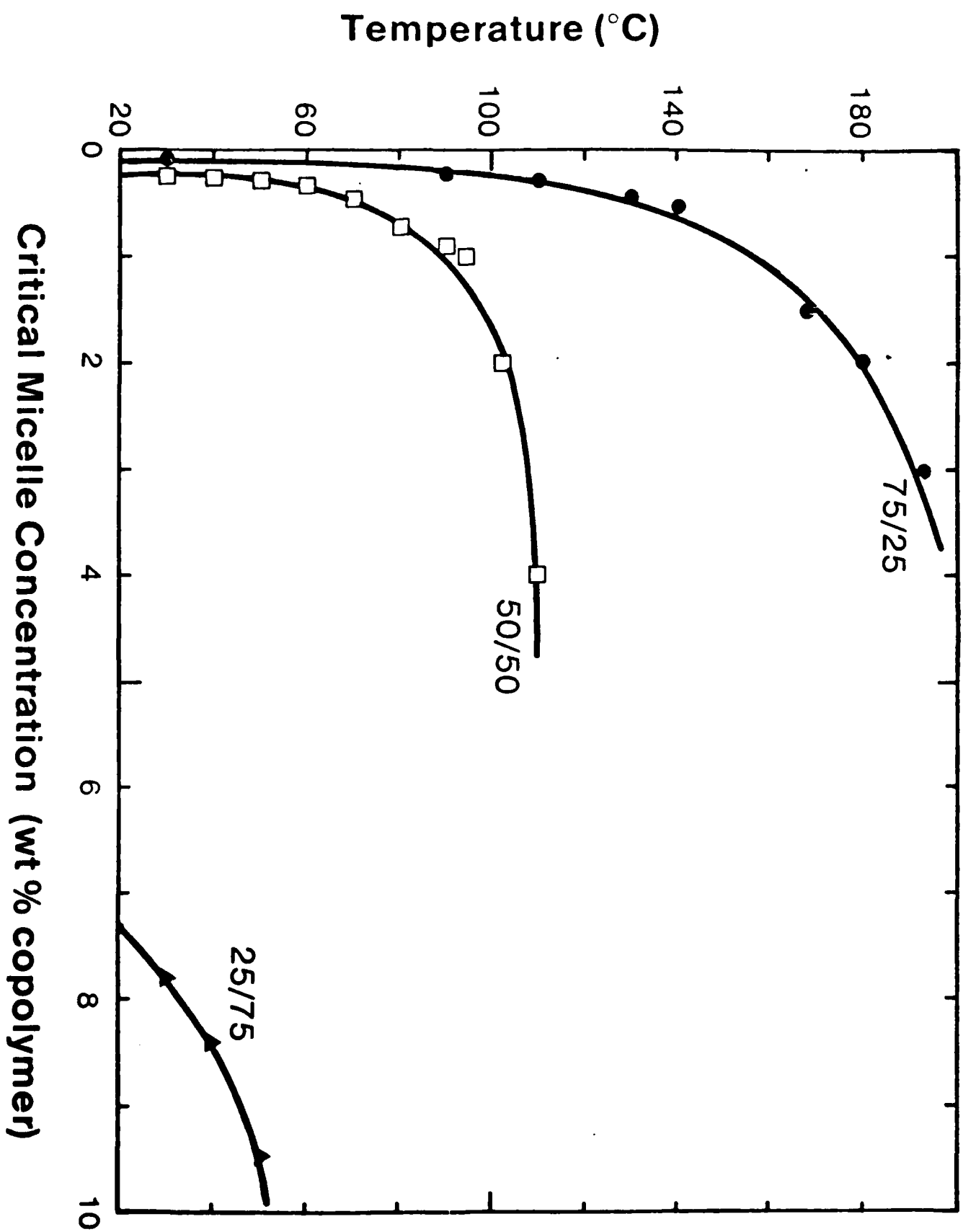
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