(25) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.
(26) Landau, L. D.; Lifshitz, E. M. *Statistical Physics-Part 1*, 3rd ed.; Pergamon Press: New York, 1980.
(27) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(28) Joanny, J. F.; Leibler, L.; Ball, R. *J. Chem. Phys.* **1984**, *81*, 4640.
(29) Broseta, D.; Leibler, L.; Joanny, J. F. *Macromolecules* **1987**, *20*, 1935.
(30) Note that we have only shown $q^*$ to be the most unstable wavenumber for the symmetric case of $f = {}^1/_2$. Justification of this wavenumber for patterns formed by asymmetric systems follows a posteriori by the demonstration that patterns with wavenumbers $q_0 \neq q^*$ have a larger free energy than those characterized by $q^*$.
(31) Leibler, L.; Fredrickson, G. H. Manuscript in preparation.
(32) In the calculations of ref 13 for diblock melts it was assumed (in the spirit of a lattice theory) that $\rho_m = b^{-3}$. This condition, however, is usually not satisfied in experimental systems. Relaxation of the condition leads to the replacement of $N$ by $\bar{N} = Nb^6\rho_m{}^2$ in the fluctuation corrections computed by FRH. It is important to note that $\bar{N}$ does not depend on the definition of a statistical segment, as it can be expressed in terms of observables by $\bar{N} = (6R_g{}^2\rho_c{}^{2/3})^3$. An incorrect expression for $\bar{N}$, different from the ones above, was given in ref 13.
(33) Schafer, L.; Kappeler, Ch. *J. Phys. (Les Ulis, Fr.)* **1985**, *46*, 1853.
(34) Kosmas, M. K. *J. Phys. Lett.* **1984**, *45*, L-889.
(35) Broseta, D.; Leibler, L.; Kaddour, L. O.; Strazielle, C. *J. Chem. Phys.* **1987**, *87*, 7248.
(36) F. Bates, private communication.
(37) de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.
(38) Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996.
(39) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(40) Onuki, A. *J. Chem. Phys.* **1986**, *85*, 1122.
(41) (a) Fredrickson, G. H.; Larson, R. G. *J. Chem. Phys.* **1987**, *86*, 1553. (b) Onuki, A. *J. Chem. Phys.* **1987**, *87*, 3692. (c) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1988**, *89*, 5890.
(42) Fredrickson, G. H. *J. Chem. Phys.* **1986**, *85*, 5306.
(43) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.

# Influence of Star-Core Exclusion on Polymer–Polymer Miscibility

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ABSTRACT: In this study the effect was investigated of the high functionality branch point in the star-shaped polystyrene (PS) molecule on the shape of its phase diagram when mixed with poly(vinyl methyl ether) (PVME). A comparison was made between samples containing a 22-arm star-shaped PS blended with linear PVME and the linear/linear blend comprised of components of the same molecular weight. These materials were characterized by wide-angle light-scattering cloud-point analyses utilizing both ramp and stepwise heating to properly separate thermodynamic and kinetic effects. Although the temperature minima for the cloud-point curves of both the star/linear blend and the linear/linear blend are the same, the curve for the star/linear system is shifted to the polystyrene-rich side of the composition axis. From this shift, a value of 0.27 is determined as the fraction of the star sterically hindered from interacting with neighboring molecules.

## Introduction

Recently it has been increasingly noted that the phase behavior of multicomponent polymers can be changed not only by varying their intercomponent interaction and their molecular weights but also by modifying the molecular design of the molecules. Factors such as copolymer block length, degree of branching or cross-linking, chain stiffness, and overall copolymer architecture affect the morphology and phase behavior of a material.

A star molecule is a good model system to study exclusion due to multiple functionality branching in polymers. The role of steric hindrance resulting from a multiple junction may be studied by analyzing the phase diagram of a blend containing star-shaped molecules. By substitution of a star polymer in place of a linear one of the same type and molecular weight, the changes which result in the phase diagram can be utilized to obtain information concerning the exclusion exhibited in the core region.

In this study, the phase behavior of the poly(vinyl methyl ether) (PVME)/polystyrene (PS) blend system was characterized. Wide-angle light-scattering cloud-point analysis was used to determine the miscibility limit of this blend system. Binary mixtures of polystyrene and poly(vinyl methyl ether) were among the first blends to be studied and were investigated by a number of techniques, including optical and electron microscopy, differential scanning calorimetry (DSC), light and neutron scattering, NMR and IR spectroscopy, and excimer fluorescence.[1-9] Special attention has been devoted to this blend because it possesses an experimentally accessible LCST, below which it exhibits complete miscibility. Thus it serves as an excellent system in which to study the phase-separation behavior of polymers.

The cloud-point curve allows the practical determination of the binodal and can be detected by optical microscopy or by wide-angle light scattering. The cloud-point curve is established by measuring the temperatures at which clear (miscible) blends become turbid. This method can be used when the refractive indices of the two components are significantly different with the assumption that phase separation in the blend is sufficiently rapid to allow an accurate determination of the demixing temperature.

According to the thermodynamics of mixtures, the most influential factors which determine whether or not an LCST is exhibited in a polymer–polymer mixture are the interaction between components and the thermal expansion parameters.[10] The precise position of the phase-sep-

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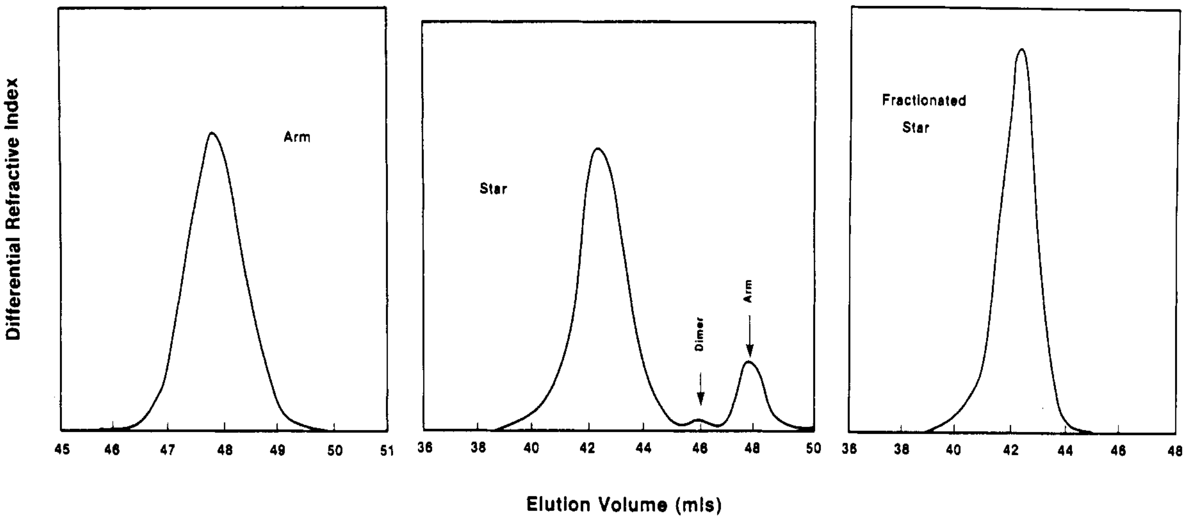

**Figure 1.** SEC chromatograms of the linear "parent" material and the star products before and after fractionation. Low molecular weight components are not detected by SEC after fractionation.

aration curve is then determined primarily by the molecular weight and somewhat by the molecular weight distribution.

The experimental dependence of the cloud point on molecular weight, for blends of high molecular weight PS in PVME, has been described by Nishi and Kwei.[11] When they blended PS with PVME of molecular weight 100 000, Nishi and Kwei observed a decrease of cloud-point temperatures with increasing PS molecular weight until it reached a value of 200 000. As the molecular weight of the PS component is further increased, the effect of this parameter levels off and even reverses. This change in the cloud point temperature as molecular weight increases is caused by a kinetic effect due to the manner in which the cloud point is generally obtained.

A very broad molecular weight distribution for either component may modify the entropy term and therefore affect the phase diagram. Theory predicts that the composition of the critical point shifts very little from the critical point of the blend of uniform molecular weight distribution as long as both components possess approximately the same relative molecular weight distribution.[12,13]

If the heating rate is sufficiently slow and the molecular weight is not too high, the cloud-point curve represents, to a good approximation, the binodal, i.e., the thermodynamic limit of miscibility, although this assumption is not strictly valid due to the distribution of molecular weights exhibited by the blend components and the activation energy associated with the phase-separation process.[13-15]

## Experimental Section

In order to systematically study the effects of molecular architecture on the PS/PVME phase diagram and minimize the effects of the other factors (molecular weight, molecular weight distribution, distribution of arms), a series of star PS and linear PS samples of matched molecular weight were utilized. These samples both exhibit a narrow molecular weight distribution and, in the case of the star a narrow distribution of the number of arms. Although star-shaped PS is commercially available (from Polysciences, Inc.), the characterization of these materials indicates that they contain large fractions of linear arms and thus are not suitable for study without extensive prior fractionation.[16] The star-shaped polystyrene employed in this study possessed an arm molecular weight of 57 000 and a functionality of 22, as determined by low-angle laser light scattering (LALLS).

High-vacuum conditions and reactors with break-seals were utilized for all polymer preparations. These procedures are described in previous publications.[16,17] Styrene was purified by stirring and degassing on the vacuum line over $CaH_2$, followed by distillation over *n*-butyl-/*sec*-butylmagnesium. Benzene was stirred over concentrated sulfuric acid for 2 weeks. It was then transferred to a vacuum line where it was stirred, dried, degassed, and stored over polystyryllithium until used. Divinylbenzene (DVB) from Monomer Polymer Laboratories, a commercial mixture of DVB and ethylvinylbenzene (EVB) isomers, was purified by the same procedure used for styrene. The initiator for polymerization was *sec*-butyllithium in cyclohexane (12%, Lithium Corp.). This material was used as received.

The linear precursor was prepared by initiating polymerization of styrene with *sec*-butyllithium in benzene. After 48 h, the polymerization was completed. The star was made by adding purified DVB to the solution of living polystyrene. A darkening of the orange poly(styryllithium) solution to light red was noted as the DVB was added to the chain ends. The reactor was then stirred at room temperature overnight to facilitate linking. The reaction was terminated by previously degassed methanol. The final product was a mixture of 80–85% star with unreacted arm and a small amount of dimer. The functionality of the star was controlled by the amount of DVB that was added (DVB/Li = 11).

Solvent/nonsolvent fractionation was used to separate the star from residual lower molecular weight components. A 1% solution of the polymer was prepared in toluene. Methanol was slowly added with stirring until a distinct turbidity appeared. The solution was heated until the turbidity disappeared (5–10 °C above room temperature). It was then poured into a warm separatory funnel. The solution was left overnight to allow the formation of two phases. The precipitated phase (star) was removed and subjected to a second fractionation. After two fractionations, no residual arm was detected (Figure 1) by size-exclusion chromatography (SEC),[18] and $M_W/M_n$ was found to equal 1.11.

The molecular weight of the linear PS (Toyo Soda Type F-128) was 1 260 000 ($M_W/M_n < 1.1$) and the 22-arm star had a molecular weight of 1 280 000 as determined by LALLS. The PVME ($M_W$ = 99 000; $M_W/M_n$ = 2.1) was obtained from Scientific Polymer Products, Inc. The casting solvent was spectrometric grade toluene, which was obtained from Aldrich Chemical Co.

The PVME was dehydrated at 60 °C under vacuum for 24 h to remove all water from the as-received material. Toluene solutions were prepared by varying the PS weight ratio in the range 0.02–0.6. The concentration was 3 g of solid polymer in 100 mL of toluene. The PS/PVME mixtures of various weight ratios were cast onto glass slides and placed in a vacuum oven. The solvent was evaporated at room temperature for a few hours and then under vacuum for at least 24 h at 75 °C. Homogeneous films were obtained by this method. As a precautionary measure, the cloud-point experiments were performed within 2 weeks after sample preparation to prevent any effect of slow phase separation which may occur if room temperature is below a possible UCST for the blend.

Phase behavior was determined by measuring the intensity of light scattered from the sample. The blend films on glass slides were inserted in a Mettler FP-82 hot stage. A 2-mW helium-neon

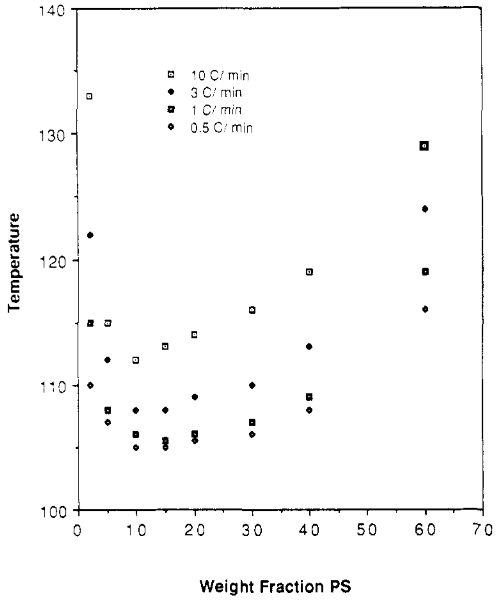

**Figure 2.** Cloud-point curves at different heating rates for star polystyrene in poly(vinyl methyl ether).

laser beam of wavelength 632.8 nm was focused onto the sample and the intensity of the light scattered out the end of the slide was measured by using a RCA 4840 photomultiplier tube.

The measured intensity of the scattered light versus temperature was plotted on a chart recorder. A Mettler controller allows the heating of the blends at different heating rates with a manufacturer specified accuracy of ±0.5 °C. This compares with a value of ±0.4 °C obtained in a calibration using different melting point standards.

The cloud-point curve was determined from the increase in wide-angle ligth-scattering intensity as the polymer blend is heated from the one-phase region into the two-phase region. Upon heating, the initially miscible polymer blend undergoes demixing, giving rise to small domains of phase-separated polymer which scatter visible light.

The cloud points were determined on the plot of light-scattering intensity versus temperature from the intersection of the base line with a straight-line approximation of the scattering intensity as it increases with temperature. The complete cloud-point curve is then determined by analyzing blends which span the entire range of composition.

In order to minimize inaccuracy in the cloud-point determination due to kinetic effects, an attempt was made to extrapolate the cloud-point values measured to an infinitely slow heating rate. As this procedure proved to be rather difficult, cloud-point measurements were then carried out under isothermal conditions. Waiting at least 45 min for phase separation to occur, the temperature was increased by steps of 0.5 °C and any change in the intensity of scattered light was measured. This method permits detection of the earliest stages of phase separation and suitable for the determination of the phase boundary with an error no greater than ±1.0 °C.

## Results and Discussion

The cloud-point curves for the PVME/star PS and the PVME/linear PS blend systems were determined at heating rates of 10, 3, 1, and 0.5 °C/min and are presented in Figures 2 and 3, respectively. The cloud-point curves depend significantly on the heating rate, even around the minimum of the phase diagram, where phase separation occurs primarily by spinodal decomposition. In cloud-point determinations of lower molecular weight blends ($M_W$ < 200 000), if only modest heating rates are employed, the concentration fluctuations would be expected to develop quickly enough not to cause any sizeable kinetic effect. On the other hand, in high molecular weight systems, such as those in this study, concentration fluctuations develop more slowly and therefore an appreciable heating rate dependence is observed. This is especially the case in the composition regions far from the minimum of the cloud-point curves in which nucleation growth is the predominant initial mechanism of phase separation. The composition of the minimum of the cloud-point curves, however, appears to be independent of the heating rate and in the past has been found only to be dependent on the molecular weight of the blend components and the relative molecular weight distributions.[12,13]

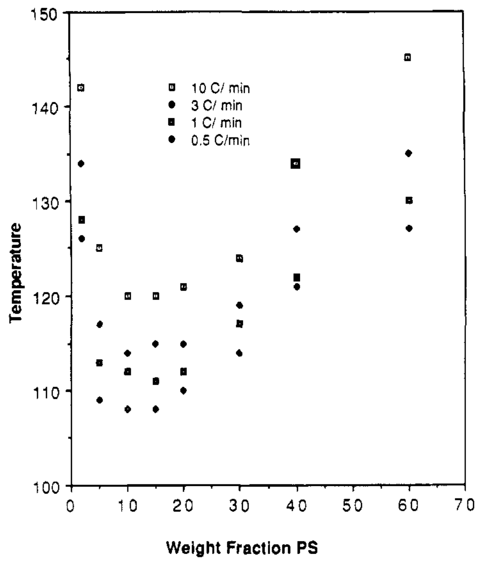

**Figure 3.** Cloud-point curves at different heating rates for linear polystyrene in poly(vinyl methyl ether).

It is also quite evident that the heating rate dependence is stronger for the linear/linear system than the star/linear system. This is most likely the case because the star molecules have a much smaller radius of gyration than the linear molecules of equivalent molecular weight and thus diffuse faster than their linear counterparts.[19] Furthermore, entanglements are believed to be less pronounced for the star/linear blend because of the core steric hindrance. The linear/linear blend is therefore expected to phase separate more slowly during the cloud point determination than the star/linear blend. To experimentally account for differences due to kinetic effects between the cloud-point determinations for the star/linear and the linear/linear blends, an attempt was made to extrapolate to an infinitely slow heating rate. It is quite evident in Figure 4 that it is difficult to know with what functional form an accurate extrapolation of a 0 °C/min rate could be carried out.

Therefore, although quite time consuming, isothermal measurements were utilized to determine the cloud-point curves (which could be compared with each other) for the star/linear and the linear/linear blends of PS and PVME (Figure 5). The isothermal data for the star/linear blend were very close (about 1 °C) to the data obtained at 0.5 °C/min (Figure 6); however, for the linear/linear blend system, the difference between the temperature at which phase separation is detected at 0.5 °C/min and that of isothermal conditions was very large and varied from 5 °C for the 15% PS composition to 11 °C at 60% PS.

The isothermal experiments which were carried out can be regarded as a very good approximation of the equilibrium boundary between the single and the two-phase region. It is thus very clear from the isothermal curves that the substitution of a star-branched polymer does not appreciably alter the phase behavior of the blend. In spite of the fact that the phase diagram of a polymer blend is

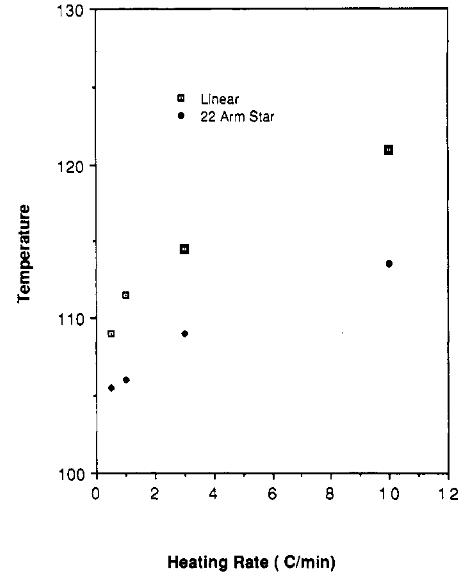

**Figure 4.** Cloud point as a function of heating rate for 20/80 (w/w) blends of polystyrene/poly(vinyl methyl ether).

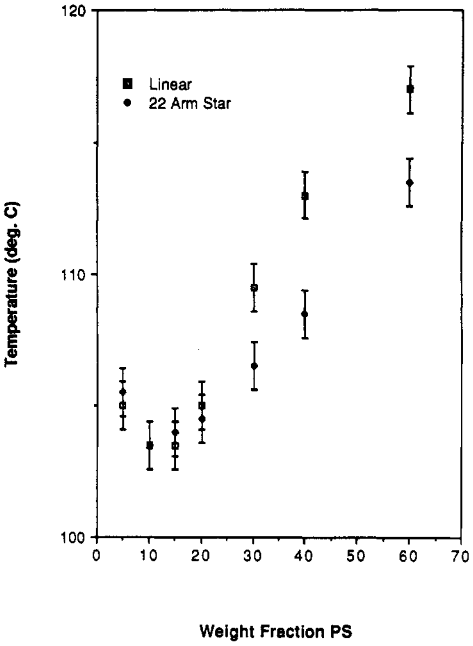

**Figure 5.** "Isothermal" cloud-point obtained by stepwise heating for both star/linear and linear/linear blends of polystyrene/poly(vinyl methyl ether).

extremely sensitive to small changes made to the system (as Yang et al. demonstrated in obtaining a 40 °C shift merely be substituting PS-$d_8$ for PS[5]), the cloud-point curve minimum occurs at the same temperature for the star/linear and linear/linear blends.

Thus, to a first approximation, the substitution of star-shaped molecules into the blend PS/PVME does not affect the phase diagram. These results should not be totally surprising as there are several reasons that the binodal curves for the two blend systems should not greatly differ. The blends containing star polymers do not possess an interaction parameter which differs from that of the blends comprised only of linear polymers. The enthalpic interaction between the PS and PVME should be almost exactly the same before and after substitution of star polymers since no change was made in the overall concentration of chemical groups present. The combinatorial entropy, in addition to being a minor effect for these materials, is expected to be very similar in both types of blends since equal molecular weight components are compared. In the star molecules utilized, the effect of additional end groups due to the branched structure of the molecules should be negligible.

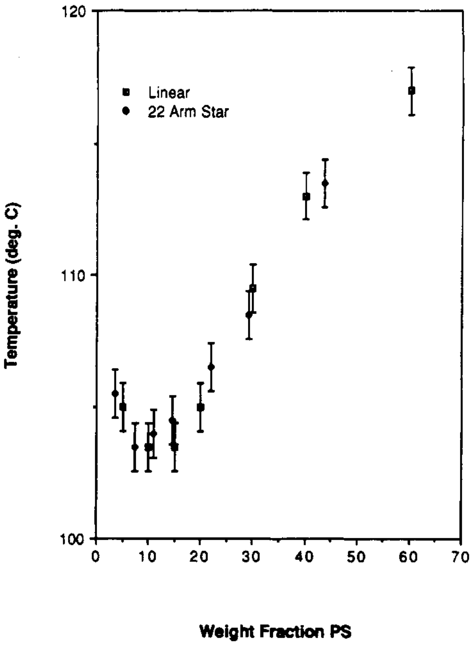

**Figure 6.** Cloud-point curve of the star/linear blend with the abscissa multiplied by $(1 - k)$ being compared with the cloud-point curve for the linear/linear blend. The parameter "$k$" represents the fraction of the star-shaped molecule which is excluded from interacting with neighboring molecules in the blend.

The primary effect which is noticeable with star substitution is a small compositional shift in the cloud-point curve toward the star-rich side. Since the monomer concentration is very high in the core of the 22-arm star, the neighboring molecules will not be able to penetrate into the star center. This shielding effect in the core would then naturally cause the phase diagram to deviate toward the PS-rich side, since a certain fraction of the star PS is not interacting with the other molecules. The extent of this deviation would be expected to vary with the number and length of the star arms.

The exclusion of these molecules from the dense core of the star can be quantified by a screening factor that represents the fraction of PS material that does not interact with neighboring molecules. The multiplication of the star curve abscissae by a factor $k$ allows the superposition of both linear/linear and star/linear curves (Figure 6). Thus a fraction, $1 - k$, of the star molecules is screened from interacting with neighboring PVME and PS molecules. The fraction of screening in the 22-arm star, calculated from the isothermal cloud-point curves, was 0.27.

The screening can be attributed in part to the DVB/EVB microgel center which makes up 4% of the star by weight. PVME would be completely excluded from this region. The Daoud–Cotton blob model[20] proposes that additional screening should also arise from two interior "regions" of stars. In the core area near the microgel center the arms possess extended configurations, which should be impenetrable to neighboring macromolecules. An intermediate ("unswollen") region between the core and star exterior is also proposed.[20] In this region, neighboring chains would not be totally excluded, but they should experience difficulty in penetrating into this area. For either a higher functionality or shorter arm length, a greater percentage of screening would be expected, consistent with the fact that the effect of crowding in the core is more pronounced when the functionality is increased. Daoud and Cotton[20] calculated a law of proportionality between the screening factor and the square root of the functionality of a star-shaped molecule in the melt. For our star, the core and intermediate regions make up only a very small portion of the star and can account for only a few percent screening.

Miyake and Freed[21] and Croxton[22] have criticized the Daoud–Cotton model and stressed the need for considering geometrical packing effects in the interior regions of high-functionality stars. These effects were ignored by Daoud and Cotton[20] but have recently been studied by Huber et al.[23] for simulated 12-arm polymethylene stars. The failure of the Daoud–Cotton model to take packing into account may, at least in part, explain the greater screening factor derived from the isothermal cloud-point curves.

Upon comparing the cloud-point curves of the linear PS blend ($M_W = 1\,260\,000$) with that of the 22-arm star-shaped PS ($M_W = 1\,280\,000$) at a heating rate of 0.5 °C/min, a 4 °C difference was observed between the minima of the cloud-point curves for the star/linear and the linear/linear blend systems (Figure 6). This difference was shown, by the isothermal experiments, to be mainly due to kinetic factors.

Two additional effects are expected as a result of blending polystyrene stars with linear polymers. In mixtures of linear and star-shaped polymers, the linear polymer is expected to exhibit a slightly contracted radius of gyration and the star polymer a slightly expanded radius of gyration compared to the unperturbed configurations of these molecules. The star molecule should expand somewhat into the region occupied by the linear molecule due to the fact that a star not only excludes neighboring molecules from the core region and also from the ends of its own arms. Likewise, when the linear molecule is turned back from the vicinity of the star, its radius of gyration will be lessened. Neutron scattering is being employed to determine whether or not these effects are sizable. Since these opposite effects would compensate for each other, and thus would not be expected to appreciably alter the phase diagram of the blend, it is not surprizing that they were not observed in this study.

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**Registry No.** PVME, 9003-09-2; PS, 9003-53-6; (S)(DVB) (copolymer), 9003-70-7.

## References and Notes

(1) Bank, M.; Leffingwell, J.; Thies, C. *J. Polym. Sci. Polym. Phys. Ed.* **1972**, *10*, 1097.
(2) Nishi, T.; Wang, T. T.; Kwei, T. K. *Macromolecule* **1975**, *8*, 227.
(3) Davis, D. D.; Kwei, T. K. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2337.
(4) Kwei, T. K.; Nishi, T.; Roberts, R. G. *Macromolecules* **1974**, *7*, 667.
(5) Yang, H.; Hadziioannou, G.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 159.
(6) Jelenic, J.; Kirste, R. G.; Oberthur, R. C.; Schmitt-Strecker, S.; Schmitt, B. J. *Makromol. Chem.* **1984**, *185*, 129.
(7) Gelles, R.; Frank, C. W. *Macromolecules* **1983**, *16*, 1448.
(8) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 1486.
(9) Snyder, H. L.; Meakin, P.; Reich, S. *J. Chem. Phys.* **1982**, *78*, 3334.
(10) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(11) Nishi, T.; Kwei, T. K. *Polymer* **1975**, *16*, 285.
(12) Roe, R. J.; Lu, L. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 917.
(13) McMaster, L. P. *Macromolecules* **1973**, *6*, 760.
(14) Koningsveld, R.; Staverman, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 349.
(15) Koningsveld, R.; Staverman, A. J. *J. Polym. Sci., Part C* **1967**, *16*, 1775.
(16) Mays, J. W.; Hadjichristidis, N.; Fetters, L. J. *Polymer* **1988**, *29*, 680.
(17) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(18) SEC analyses were carried out by Dr. L. J. Fetters using the methods described in ref 16.
(19) This is true only so long as the branch lengths of the star are not too long. For longer branches large enhancements of viscosity are observed: Graessley, W. W. In *Physical Properties of Polymers*, Mark, J. E., et al., Eds.; American Chemical Society: Washington, DC, **1984**; Chapter 3.
(20) Daoud, M.; Cotton, J. P. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 531.
(21) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228.
(22) Croxton, C. A. *Polym. Commun.* **1988**, *29*, 2.
(23) Huber, K.; Burchard, W.; Bantle, S.; Fetters, L. J. *Polymer* **1987**, *28*, 1990, 1997.