Macromolecules **1992,** *25,* 5547–5550 **5547**

Correlation of Binary Polyolefin Phase Behavior with Statistical Segment Length Asymmetry

Frank S. Bates,* Mark F. Schulz, and Jeffrey H. Rosedale

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Kristoffer Almdal

Risø National Laboratory, Roskilde, Denmark

Received April 8, 1992
Revised Manuscript Received July 18, 1992

This year marks the 50th anniversary of the landmark statistical theories of Flory[1] and Huggins[2] for polymer–polymer thermodynamics. Their derivations for the binary free energy of mixing, which are usually referred to by the single expression

$$\frac{\Delta F}{k_{\mathrm{B}}T} = \frac{\phi_1}{N_1}\ln \phi_1 + \frac{(1-\phi_1)}{N_2}\ln (1-\phi_1) + \phi_1(1-\phi_1)\chi \qquad (1)$$

survive today as the starting point for almost any polymer mixing theory or experimental analysis. In eq 1, ϕ_1 ($=1-\phi_2$) and N_1 represent the volume fraction and degree of polymerization of species 1, respectively, k_{B} is the Boltzmann constant, and χ accounts for segment–segment interactions. In its original form χ was defined such that $\phi_1(1-\phi_1)\chi$ represented only the enthalpy of mixing while the remaining terms in eq 1 captured the ideal combinatorial entropy of mixing. However, this restricted definition of χ has since been expanded

$$\chi = \chi_0 + \chi_\alpha + \chi_\beta + ... \qquad (2)$$

to accommodate a variety of excess free-energy terms (see below) where

$$\chi_0 = (k_{\mathrm{B}}T)^{-1}\left[\epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22})\right] \qquad (3)$$

represents the original Flory–Huggins segment–segment interaction parameter. In eq 3, ϵ_{12} is detemined by the strength of the (van der Waals) interactions between dissimilar segments.

In spite of its remarkable durability and success, eq 1 is a crude theory that neglects various nonideal aspects of experimental polymer mixtures. For example, the combinatorial entropy calculation neglects intrachain segment contacts and the excluded volume and does not account for the impossibility of chain crossing. (Nevertheless, the basic scaling prediction for the critical segment–segment interaction parameter, $\chi_c \sim N^{-1}$, is supported experimentally as recently shown.[3]) Furthermore, eq 3 rarely accounts for the entire excess free energy of mixing.

The first corrections to Flory–Huggins theory were motivated by the discovery of lower critical solution temperature (LCST) behavior in certain polymer–solvent systems.[4] Flory,[5] and later Sanchez and Lacombe,[6,7] modified the original lattice theory to account for equation-of-state effects such as finite compressibilities and thermal expansivities. More recently, Dudowicz and Freed[8] have made corrections to the lattice theory for differences in segmental shape and compressibility, while Schweizer and Curro[9,10] have adapted an off-lattice liquid state theory, developed for small molecules, to polymer mixtures. To varying degrees these modifications add terms to eq 2, thereby introducing additional temperature, composition, and in some cases molecular weight[9,10] dependencies to χ.

Separating and identifying these excess free-energy contributions experimentally is not trivial. For example, the well-studied system polystyrene–poly(vinyl methyl ether), which exhibits a LCST, has been treated phenomenologically[11] (i.e., $\chi = A(\phi)\ T^{-1} - B(\phi)$), using a modified Flory equation-of-state theory[12] and with a modified lattice theory.[13] Yet none of these treatments directly accounts for the specific interactions that are known to strongly affect the phase behavior of this system.[14]

We have been developing a different approach to studying polymer–polymer phase behavior that began with the elimination of all but the simplest contributions to χ. Isotopic polymer mixtures represent the closest approximation to Flory–Huggins theory that can be achieved experimentally.[15,16] Such systems have provided fresh insights into the applicability[3] and shortcomings[15–17] of the original Flory–Huggins theory. In this paper we present our initial findings for the next level of molecular complexity in polymer mixtures.

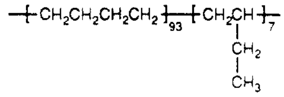
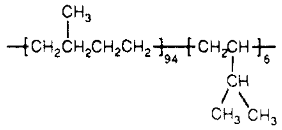
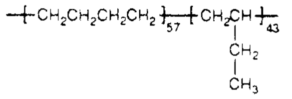
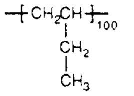
Saturated hydrocarbon polymers, often referred to as polyolefins, are governed by relatively simple van der Waals interactions. Hence we might anticipate that polyolefin mixtures would be closely approximated by regular solution theory. However, the absence of a single dominant thermodynamic factor, as is found in the PVME–PS system,[11] renders these mixtures susceptible to subtle variations in molecular architecture. In a series of ongoing projects we have been investigating the phase behavior and rheological properties of a variety of polyolefin block copolymers and homopolymer mixtures. Recently, we realized that a common factor, the difference (i.e., asymmetry) in the statistical segment lengths, is responsible for a number of unusual properties associateed with these materials, including multiple-ordered phases[18] and selective surface segregation[19] in the block copolymers. We presently extend this analysis to χ and demonstrate a strong correlation between this parameter and phase behavior. In the paper that immediately follows, Liu and Fredrickson[20] provide a theoretical evaluation of this result. To the best of our knowledge, the importance of this effect has not been previously recognized.

Four model polyolefins are considered in this report: polyethylene (PE), poly(ethylenepropylene) (PEP), poly(ethylene/ethylethylene) (PE/PEE, a random copolymer), and poly(ethylethylene) (PEE). The exact microstructures and pertinent physical parameters characterizing these polymers are listed in Table I. These materials were prepared by catalytically hydrogenating anionically polymerized polydienes (isoprene and butadiene) on a calcium carbonate supported palladium catalyst as described elsewhere.[21] Use of appropriate modifiers during the polymerization stage provides control over the product microstructures,[22] which have been verified by ^{1}H and ^{13}C NMR analysis. Diblock copolymers were prepared through the sequential addition of monomers and modifiers to the reaction medium.[23]

PEP, PE/PEE, and PEE homopolymer densities were determined at 23 °C using the density gradient column technique. The density of polyethylene has been reported based on extrapolation from above the melting temperature;[24] the PE melting point occurs at 108 °C. The thermal expansivities for all but the PE/PEE polymer are reported in the literature;[24,25] for PE/PEE we estimate $\partial \ln \rho_{\mathrm{PE/PEE}}/\partial T = 0.43(\partial \ln \rho_{\mathrm{PEE}}/\partial T) + 0.57(\partial \ln \rho_{\mathrm{PE}}/\partial T)$.

0024-9297/92/2225-5547$03.00/0

Table I
Polyolefin Molecular Characteristics

polyolefin	microstructure	ρ(23 °C)[a] (g/cm^3)	$-10^4\partial \ln \rho/\partial T$ (K^{-1})	a(25 °C) (Å)	$10^3\partial \ln a/\partial T$ (K^{-1})
PE (polyethylene)	 $-\!\!\left[\mathrm{CH_2CH_2CH_2CH_2}\right]_{93}\!\left[\mathrm{CH_2CH(CH_2CH_3)}\right]_{7}\!-$	0.855[b]	7.5[c]	8.8[f]	−0.58[h]
PEP [poly(ethylenepropylene)]	 $-\!\!\left[\mathrm{CH_2CH(CH_3)CH_2CH_2}\right]_{94}\!\left[\mathrm{CH_2CH(CH(CH_3)_2)}\right]_{6}\!-$	0.854	7.0[d]	7.2[g]	−0.58[g]
PE/PEE [poly(ethylene/ethylethylene)]	 $-\!\!\left[\mathrm{CH_2CH_2CH_2CH_2}\right]_{57}\!\left[\mathrm{CH_2CH(CH_2CH_3)}\right]_{43}\!-$	0.862	(6.9)[e]	6.9[d]	≈0[i]
PEE [poly(ethylethylene)]	 $-\!\!\left[\mathrm{CH_2CH(CH_2CH_3)}\right]_{100}\!-$	0.869	6.0[d]	5.0[g]	0.2[i]

[a] Density gradient column measurements. [b] Reference 24; extrapolated from above the melt temperature. [c] Reference 24. [d] Reference 25. [e] $0.43(\partial \ln \rho_{\mathrm{PEE}}/\partial T) + 0.57(\partial \ln \rho_{\mathrm{PE}}/\partial T)$. [f] Reference 26; extrapolated from above the melt temperature. [g] Reference 27. [h] Reference 28. [i] Reference 29.

Table II
Polyolefin Homopolymer Mixtures

mixture	$10^{-3}N_{\mathrm{W},1}$	$10^{-3}N_{\mathrm{W},2}$	ϕ	T_c (°C)	ref
PE + PEP	0.42	0.42	0.50	148 ± 1	this work
PEP + PE/PEE	1.63	1.76	0.49	86 ± 2	this work
PEP + PE/PEE	0.42	0.42	0.50	24 ± 2	this work

Table III
Polyolefin Diblock Copolymers

diblock copolymer	$10^{-3}N_{\mathrm{N}}$	f	T_{ODT} (°C)	ref
PE–PEE	0.41	0.50	120 ± 1	43
PE–PEE	0.47	0.47	182 ± 2	43
PEP - PEE	0.79	0.55	16 ± 2	19
PEP–PEE	0.89	0.56	96 ± 1	31
PEP–PEE	0.96	0.55	125 ± 1	31
PEP–PEE	1.45	0.53	291 ± 2	31
PEP–PE	1.43	0.50	120 ± 1	44
PEP–PE	1.79	0.50	139 ± 1	44
PEP–PE	2.14	0.50	159 ± 1	44

The statistical segment length a is of central importance to this paper. It is defined by the unperturbed Gaussian coil radius of gyration

$$R_g = a(N/6)^{1/2} \tag{4}$$

where N is the number of statistical segments per polymer chain. This parameter has been determined for PEE, PE, and PEP in the bulk state by small-angle neutron scattering[16,26,27] and for PE/PEE by intrinsic viscosity measurements at the Θ condition.[25] We must emphasize that the magnitude of a depends on the definition of the statistical segment. The most common definition is based on the monomer repeat unit so that N corresponds to the degree of polymerization. However, we could also choose the Kuhn length, or a single backbone bond, in which case N and a would be scaled up or down such that R_g remains invariant. When dealing with polymer–polymer mixtures, a convenient approach is to choose a single statistical segment volume for both species and then define N and a accordingly. This is equivalent to using a single lattice size in the Flory–Huggins treatment. We have chosen the segment volume

$$V = 1.084 \times 10^{-22} \exp[6.85 \times 10^{-4}(T - 296)] \tag{5}$$

based on the average of the densities and thermal expansivities listed in Table I. All references to N and a in this paper are based on this definition. Gaussian coil thermal expansivities, $\partial \ln a/\partial T$, have been reported for all four polyolefins[27-30] as indicated in Table I.

The weight- and number-average degrees of polymerization, N_{W} and N_{N}, for the homopolymers and diblock copolymers used in this study are listed in Tables II and III, respectively; in all cases $N_{\mathrm{W}}/N_{\mathrm{N}} \lesssim 1.07$. Also given are the homopolymer mixture compositions, $\phi = \phi_c$, where $\phi_c = N_1^{1/2}/(N_1^{1/2} + N_2^{1/2})$ is the critical composition based on eq 1, and the block copolymer composition f. In all cases the systems discussed here are close to the symmetric conditions, $\phi_c = {}^1/_2$ and $f = {}^1/_2$.

Two types of phase transitions are reported in this work, phase separation of single phase binary mixtures and ordering of disordered diblock copolymers. Identification of the phase-separation temperature in the binary mixtures was simplified by using critical compositions. Simple cloud-point measurements led to the critical temperatures, T_c, given in Table II. Order–disorder transition temperatures, T_{ODT}, were determined by low-frequency dynamic mechanical spectroscopy as described elsewhere[31] and are listed in Table III. These phase transition temperatures can be related to χ by making use of the mean-field theories for symmetric binary homopolymer mixtures (eq 1)

$$\chi_c = 2/N \tag{6}$$

and symmetric diblock copolymers[32]

$$\chi_{\mathrm{ODT}} = 10.5/N \tag{7}$$

where N_{W} and N_{N} should be used in eqs 6 and 7, respectively. The results are presented in the conventional form of χ versus T^{-1} in Figure 1. Here we note that the PEP–PE homopolymer mixture and diblock copolymers yield segment–segment interaction parameters that agree within experimental error. From this we can conclude that neglecting fluctuation effects[33,34] (i.e., use of eqs 6 and 7) does not significantly affect our analysis.

As indicated in the introduction, polyolefin mixtures are governed by simple van der Waals interactions. Therefore, we might expect that Flory–Huggins theory, in its original form, would be applicable to such systems.

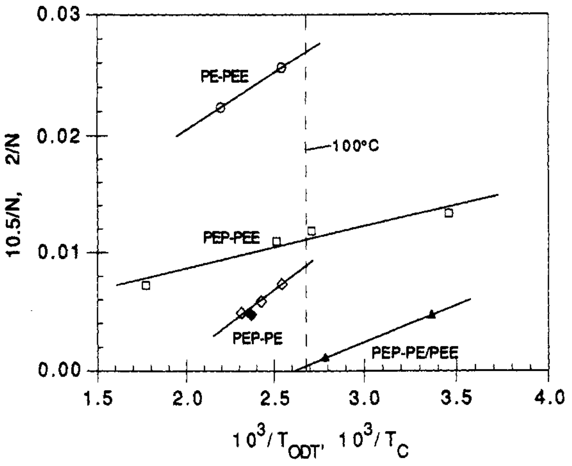


Figure 1. Critical points (filled symbols) and order–disorder transition temperatures (open symbols) for polyolefin binary mixtures and diblock copolymers, respectively, versus χ based on mean-field theories (eqs 6 and 7). Polyolefin molecular structures are given in Table I.

Table IV
Segment–Segment Interaction Parameters at 100 °C

	$10^3\chi$				
	calcd				
system	Small	Hoy	Van Krevelen	exptl	$\Delta a/\bar{a}$
PE–PEE	8.4	13	0.20	28.3	0.50
PEP–PEE	0.05	0.008	0.06	11.6	0.31
PEP–PE	9.8	13	0.01	8.6	0.20
PEP–PE/PEE	5.8	5.8	0.5	0.58	≈0

As a crude test of this possibility we have calculated χ using the solubility parameter approach

$$\chi = \frac{V}{RT}(\delta_1 - \delta_2)^2 \qquad (8)$$

based on three group contribution schemes for estimating δ.[35] The results for T = 100 °C are listed in Table IV, along with the experimental values taken from Figure 1 (dashed line). None of these methods properly predicts the correct sequence of χ values, the magnitude for PE–PEE, or the temperature dependence for PEP–PE and PEP–PE/PEE; these estimates of χ include the temperature dependence of ρ (Table I) and assume no excess volume of mixing. This suggests that factors other than enthalpy of mixing alone are responsible for the phase behavior of polyolefin mixtures.

In separate reports we have demonstrated that the difference in statistical segment lengths in polyolefin block copolymers produces preferential surface segregation[19] and multiple-ordered phases at certain compositions.[18] We now believe that this parameter also plays a significant role in determining the overall phase diagram. Figure 2 illustrates the temperature dependence of a for the four polymers listed in Table I; recall that a is defined using the reference segment volume given by eq 5. Comparison of Figures 1 and 2 reveals a striking correlation. The largest and smallest values of χ correspond to the systems with the largest and smallest difference in statistical segment lengths Δa, and for the PEP–PE/PEE system $\chi \rightarrow 0$ approximately where $|\Delta a| \rightarrow 0$. The two intermediate cases, PEP–PEE and PEP–PE, display intermediate values of χ, although the temperature dependence varies considerably. A comparison of $\Delta a/\bar{a}$ with the experimental χ values at 100 °C is given in Table IV, where $\bar{a} = \phi_1 a_1 + (1 - \phi_1)a_2$. To the best of our knowledge, only Schweizer and Curro[10] have considered this parameter in the context of polymer–polymer thermodynamics. However, they predict an increasingly *negative* χ with increasing Δa based on the RISM theory, opposite to what we find.

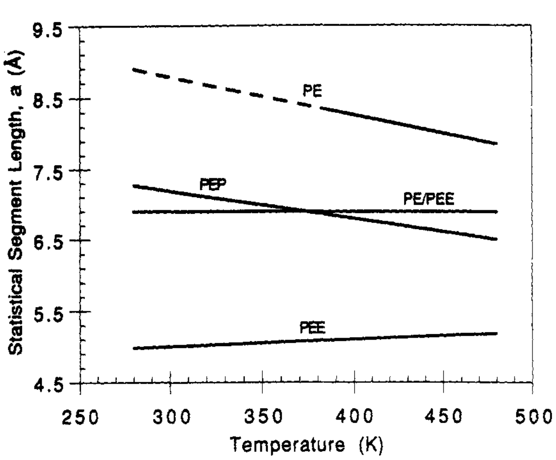


Figure 2. Temperature dependence of the statistical segment length for the polyolefins listed in Table I.

Why should χ increase with increasing Δa? We offer a qualitative explanation here and refer the reader to the paper that immediately follows[20] for a more quantitative derivation. As a conceptual starting point we consider two equal density homopolymer melts consisting of identical molecular weight polymer coils. For simplicity we will assume athermal mixing ($\chi_0 = 0$) and no excess volume of mixing, which is approximated by the polyolefins. However, the two species will have asymmetric statistical segment lengths, $a_1 > a_2$. As indicated in Figure 2 in practice this difference can be quite large, e.g., a_{PE} = 8.3 Å and a_{PEE} = 5.1 Å at 125 °C. The mixing process will be initiated by removing one molecule from each melt and exchanging them. This creates a condition sometimes referred to as frustration. Although the conformational voids created are of equal volume, they are decidedly not of equal size, i.e., R_g. In order for species 1 to occupy the space left by species 2, either it must reduce its size or the conformational void must be rearranged to accommodate it. Similarly, either species 2 must dilate or the void space left by removing species 1 must rearrange in order to effect mixing. To varying degrees this process will be repeated until complete mixing is achieved. These additional conformational adjustments cost entropy, which is not included in Flory–Huggins theory.

Naturally polyolefins will not mix in a strictly athermal ($\chi_0 = 0$), random, or isochoric ($\Delta\rho = 0$) fashion, and accordingly Δa will not be the only factor contributing to χ. When the free energy of mixing is expressed in the Flory–Huggins form, all these effects will lead to the various correction terms appearing in eq 2 and described in part by various theories.[5–10] Presumably this contributes to the variable temperature dependence of χ found in Figure 2. However, as we have demonstrated, when χ_0 becomes small the contribution due to Δa can play a dominant role in determining phase behavior.

There is some additional evidence supporting our Δa hypothesis in certain other nonpolar hydrocarbon polymer mixtures. Balsara and co-workers[36] have recently reported that mixed microstructure polyolefins containing PE and PEE repeat units form binary blends characterized by a χ parameter that appears to scale with the square of the difference in PEE (or PE) content. This result is consistent with our Δa correlation and appears to be qualitatively anticipated by the derivation of Liu and Fredrickson.[20]

Polydienes are somewhat more complex than polyolefins due to the presence of more highly polarizable double bonds. Nevertheless, χ_0 is similar in magnitude to that found in polyolefin mixtures. 1,4-Polyisoprene (1,4-PI; 70% cis-1,4, 20–23% trans-1,4, and 5–7% 3,4) and 1,2-polybutadiene (or high vinyl) (1,2-PB; >99% 1,2) are well-known to form single-phase mixtures over a range of temperatures,[23,37] although we are unaware of a convincing explanation of why this occurs. Using a segment volume of $V = 1.00 \times 10^{-22}$ cm^3, $a_{1,4\text{-PI}} = 5.9$ Å[38] and $a_{1,2\text{-PB}} = 6.0$ Å,[16] and we calculate $\Delta a/\bar{a} = 0.017$ for this system. Therefore, miscibility in 1,4-PI–1,2-PB mixtures is consistent with the statistical segment length correlation. On the basis of a series of block copolymers and homopolymer mixtures, Cohen and Ramos[39] demonstrated that $\chi \approx 1.7 \times 10^{-3}$ (where $V = 1.00 \times 10^{-22}$ cm^3) for 1,4-PI and 1,4-polybutadiene (1,4-PB; 36% cis-1,4, 53% trans-1,4, and 11% 1,2). Since $a_{1,4\text{-PB}} = 6.9$ Å,[40] $\Delta a/\bar{a} = 0.16$, placing this result in qualitative agreement with the polyolefin mixtures (Table IV). However, recently Hasegawa et al.[41] have shown that $\chi = -0.901T^{-1} + 4.17 \times 10^{-3}$ for a 1,4-PI–1,4-DPB mixture containing 47.5% by volume 1,4-DPB (DPB represents deuterated polybutadiene) leading to LCST behavior. This is not anticipated by our correlation with Δa since $\partial \ln a_{1,4\text{-PI}}/\partial T \cong 0.5 \times 10^{-3}$ K^{-1} while $\partial \ln a_{1,4\text{-PB}}/\partial T \cong 0$ K^{-1}.[42] Thus, increasing the temperature should decrease Δa which would mitigate against a LCST. As already stated, the statistical segment length asymmetry is only one of several factors that can influence χ, and we expect polydiene mixtures to be more complicated than polyolefins. Presumably specific van der Waals interactions, nonrandom packing, or excess volume of mixing contributes to this interesting effect. Once χ_0 is sufficiently large, such as with polystyrene–polydiene mixtures, the impact of Δa (and other excess terms in eq 2) will be largely masked and more traditional estimates of χ should be applicable.

In summary, we report the segment–segment interaction parameter χ as a function of temperature for four pairs of polyolefins. These results are not anticipated by the traditional Flory–Huggins heat of mixing. However, a correlation between the magnitude of χ and the statistical segment length asymmetry has been established. We attribute this contribution to χ to the mismatch in polymer conformational size that must be accommodated in order to achieve a homogeneous mixture.

Acknowledgment. Support for this research was provided by the Air Force Office of Scientific Research (AFOSR-90-0207) and by the NSF under a Presidential Young Investigator Grant (DMR-8957386). Lew Fetters has been a constant source of insight and information regarding the characteristics of polymer coil dimensions for which we are most grateful.

References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(2) Huggins, M. *J. Phys. Chem.* **1942**, *46*, 151; *J. Am. Chem. Soc.* **1942**, *64*, 1712.
(3) Gehlsen, M. D.; Rosedale, J. H.; Bates, F. S.; Wignall, G. D.; Hansen, L.; Almdal, K. *Phys. Rev. Lett.* **1992**, *68*, 2452.
(4) Freeman, P. I.; Rawlinson, J. S. *Polymer* **1960**, *1*, 20.
(5) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833; *Discuss. Faraday Soc.* **1970**, *49*, 7.
(6) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352. Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.
(7) Sanchez, I. C. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 1, p 115.
(8) Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5076. Dudowicz, J.; Freed, M. S.; Freed, K. F. *Macromolecules* **1991**, *24*, 5096.
(9) Schweizer, K. S.; Curro, J. G. *Chem. Phys.* **1990**, *60*, 809.
(10) Curro, J. G.; Schweizer, K. S. *Macromolecules* **1990**, *23*, 1402.
(11) Schwahn, D.; Mortensen, K.; Springer, T.; Yee-Medeira, H.; Thomas, R. *J. Chem. Phys.* **1987**, *87*, 6078.
(12) Shiomi, T.; Hamada, F.; Nasako, T.; Yoneda, K.; Imai, K.; Nakajima, A. *Macromolecules* **1990**, *23*, 229.
(13) Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5112.
(14) Ben Cheikh Larbi, F.; Leloup, S.; Halary, J. L.; Monnerie, L. *Polym. Commun.* **1986**, *27*, 23.
(15) Bates, F. S.; Wignall, G. D.; Koehler, W. C. *Phys. Rev. Lett.* **1985**, *55*, 2425. Bates, F. S.; Muthukumar, M.; Wignall, G. D.; Fetters, L. J. *J. Chem. Phys.* **1988**, *89*, 535.
(16) Bates, F. S.; Fetters, L. J.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1086.
(17) Schwahn, D.; Hahn, K.; Streib, J.; Springer, T. *J. Chem. Phys.* **1990**, *93*, 8383.
(18) Almdal, K.; Koppi, K. A.; Bates, F. S.; Mortensen, K. *Macromolecules* **1992**, *25*, 1743.
(19) Foster, M. D.; Sikka, M.; Singh, N.; Bates, F. S.; Satija, S.; Majkrzak, C. F. *J. Chem. Phys.*, in press.
(20) Liu, A. J.-W.; Fredrickson, G. H. *Macromolecules*, following paper in this issue.
(21) Rosedale, J. H.; Bates, F. S. *J. Am. Chem. Soc.* **1988**, *110*, 3542.
(22) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.
(23) Bates, F. S.; Rosedale, J. H.; Bair, H. E.; Russell, T. P. *Macromolecules* **1989**, *21*, 2557.
(24) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1975.
(25) Hattam, P.; Gauntlett, S.; Mays, J. W.; Hadjichristidis, N.; Young, R. N.; Fetters, L. J. *Macromolecules* **1991**, *24*, 6199.
(26) Wignall, G. D. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Grayson, M., Kroschwitz, T. I., Eds.; Wiley: New York, 1987; p 112.
(27) Zirkel, A.; Richter, D.; Pyckhout-Hintzen, W.; Fetters, L. J. *Macromolecules* **1992**, *25*, 954.
(28) Boothroyd, A. T.; Rennie, A. R.; Boothroyd, C. B. *Europhys. Lett.* **1991**, *15*, 715.
(29) Zirkel, A.; Richter, D.; Pyckhout-Hintzen, W.; Fetters, L. J., unpublished results.
(30) Fetters, L. J., personal communication.
(31) Rosedale, J. H.; Bates, F. S. *Macromolecules* **1990**, *23*, 2329.
(32) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(33) Bates, F. S.; Rosedale, J. H.; Stepanek, P.; Lodge, T. P.; Wiltzius, P.; Fredrickson, G. H.; Hjelm, R. P. *Phys. Rev. Lett.* **1990**, *65*, 1893.
(34) Bates, F. S.; Rosedale, J. H.; Fredrickson, G. H. *J. Chem. Phys.* **1990**, *92*, 6255.
(35) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1972.
(36) Balsara, N. P.; Fetters, L. J.; Hadjichristidis, N.; Lohse, D. J.; Han, C. C.; Graessley, W. W.; Krishnamoorti, R., preprint.
(37) Trask, C. A.; Roland, C. M. *Macromolecules* **1989**, *22*, 256.
(38) Mays, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1984**, *17*, 2723.
(39) Cohen, R. E.; Ramos, A. R. *Macromolecules* **1979**, *12*, 131; *Adv. Chem. Soc.* **1979**, No. 176, 237.
(40) Bates, F. S.; Dierker, S. B.; Wignall, G. D. *Macromolecules* **1986**, *19*, 1938.
(41) Hasegawa, H.; Sakurai, S.; Takenaka, M.; Hashimoto, T.; Han, C. C. *Macromolecules* **1991**, *24*, 1813.
(42) Karim, A.; Fetters, L. J.; Bates, F. S., unpublished results.
(43) Rosedale, J. H.; Almdal, K.; Mortensen, K.; Schulz, M. F.; Bates, F. S., in preparation.
(44) Rosedale, J. H.; Almdal, K.; Bates, F. S.; Mortensen, K., in preparation.