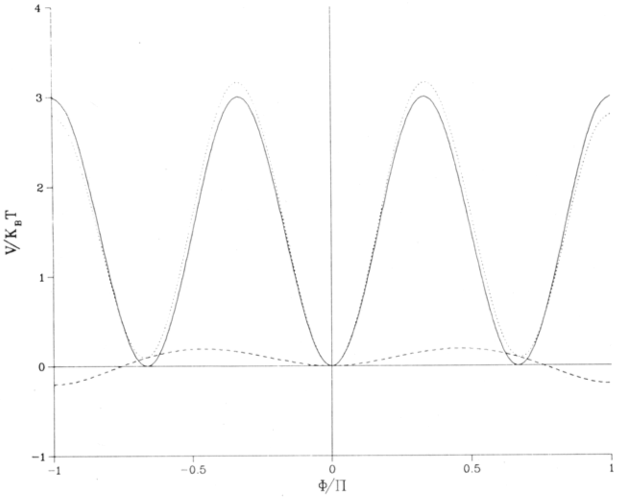

Figure 7. Potential about bond b_2 (in units of k_BT) vs. ϕ. The solid line represents the bare torsional potential v_ϕ defined in eq 2.3, the dashed line is the Fixman potential given by eq 2.4, and the dotted line is the torsional-plus-Fixman potential.

friction limit (overdamped), the dynamics of rigid and flexible models of *n*-butane do not differ significantly. Secondly, in the low-friction limit (underdamped) where the dynamics do differ (although only slightly), the addition of the Fixman potential is of no help. Since the overdamped case is the physically realistic situation, we conclude that the dynamics of rigid and flexible models of *n*-butane are essentially equivalent.

Unfortunately, one cannot automatically generalize from the case of *n*-butane to longer chains. The reason is that butane, because of its single dihedral angle, has only one long time scale associated with it (except for overall rotation and translation). Long chains, on the other hand, will have many different time scales because of the larger number of soft modes. It is not clear whether the rigid model will accurately reproduce the flexible model in these cases. Such a study is the subject of future work.

Acknowledgment. This work was suppprted in part by a grant from the National Science Foundation Polymer Program (Grant DMR-8303197) and from the Biophysical Program (Grant PCM-8212404). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the research. We thank Gene Helfand for his very helpful discussions and suggestions.

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Measurement of the Correlation Hole in Homogeneous Block Copolymer Melts

Frank S. Bates†

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. Received August 10, 1984

ABSTRACT: Homogeneous block copolymer melts are predicted to exhibit a decrease in interchain segment correlation (a "correlation hole") at wavevectors corresponding to a polymer coil radius. Small-angle neutron scattering data are presented which demonstrate this effect in two 1,4-polybutadiene–1,2-polybutadiene diblock copolymers. These results are quantitatively predicted by the mean–field theory of Leibler, thereby providing a new method for determining the Flory interaction parameter χ in binary polymer blends. χ was found to be dependent on sample composition, which can be attributed to equation-of-state contributions to the mixing free energy.

Introduction

A system of undiluted, amorphous homopolymers of sufficiently high index of polymerization ($N \gg 1$) is composed of ideal (Gaussian) chains, for which the mean squared radius of gyration, $R^2 = Na^2/6$, is defined in terms of an effective segment (Kuhn) length, a. In the case where every chain contains a block of labeled and a block of unlabeled segments, the probability of bringing like segments from separate chains into the same vicinity is reduced, since molten polymers are nearly incompressible. This depletion of interchain segment–segment correlation is called the correlation hole[1] and results in a peak in the measured correlation function, $S(Q)$, at a scattering wavevector of $QR \sim 1$. Small-angle neutron scattering (SANS) measurements of polystyrene samples containing blocks of deuterium-labeled segments have confirmed the prediction of the correlation hole for noninteracting chains.[2] Homogeneous block copolymers containing blocks of chemically different segments between which there exists a nonzero energy of interaction, typically defined in terms of the Flory parameter χ, have not been so examined. Leibler[3] has expanded on the concept of the correlation hole in noninteracting chains and calculated the correlation function for diblock copolymers in the

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† Present address: Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.

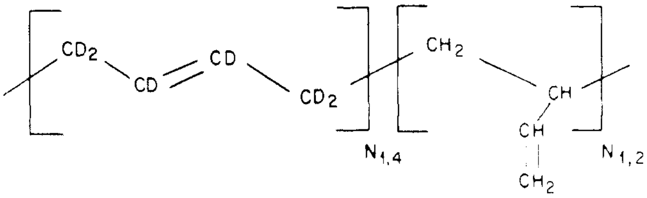

Figure 1. Chemical structure of the polybutadiene diblock copolymers where the 1,4 block is composed of a mixture of 89% 1,4 (mixed cis and trans) and 11% 1,2 segments. D and H refer to deuterium and hydrogen, respectively.

Table I
Polybutadiene Molecular Characteristics

	N_N	Φ	N_W/N_N
sample	number-average degree of polymerization	fraction 1,4 block	polydispersity index
BB1	470	0.47	1.05
BB3	580	0.18	1.04
B1	890	0	1.02

homogeneous melt state. This initial report demonstrates that this correlation function both accurately predicts the SANS results obtained from a diblock copolymer and provides a new sensitive method for measuring χ, which is presently shown to be dependent on the sample composition.

Experimental Section

Two 1,4-polybutadiene–1,2-polybutadiene diblock copolymers were prepared by anionic polymerization, employing perdeuteriobutadiene for the 1,4 block and protiobutadiene for the 1,2 block, thereby providing the required contrast for the SANS experiments. The microstructure of these diblock copolymers is depicted in Figure 1. The number-average degree of polymerization, N_N, composition, $\Phi = N_{1,4}/N$ ($N_{1,4} + N_{1,2} = N$), and polydispersity index, N_W/N_N (N_W is the weight-average degree of polymerization) were determined by membrane osmometry, infrared absorption, and high-pressure size exclusion chromatography, respectively. These results are given in Table I. A complete description of the synthesis and characterization procedures employed can be found elsewhere.[4]

Scattering experiments were conducted at the National Bureau of Standards (NBS) small-angle neutron scattering facility near Washington, DC, employing an incident wavelength of 8.5 Å and a sample-to-detector distance of 3.6 m. A detailed description of the NBS SANS instrument has previously been reported by Glinka.[5] Background and detector sensitivity corrected data were converted to an absolute differential scattering cross section per unit solid angle (cm^{-1}) using neutron calibration constants obtained from a secondary standard (sample B1)[6] by the method of Jacrot[7] and from the scattering of vanadium. The reported intensities are subject to an error of ±20%.

Results and Discussion

Neutron scattering results, in units of absolute intensity, are presented in Figure 2, and the data from samples BB1 and BB3 corrected for incoherent scattering based on the incoherent scattering from sample B1, are replotted in Figures 3 and 4.

According to Leibler[3] the correlation function for a homogeneous block copolymer melt is given by

$$S(Q) = N/(F(Q) - 2\chi N) \qquad (1)$$

where

$$F(Q) = \frac{g_1(R)}{g_1(R_1)g_1(R_2) - \frac{1}{4}[g_1(R) - g_1(R_1) - g_1(R_2)]^2}$$

$$g_1(x) = 2[Q^2x^2 + \exp(-Q^2x^2) - 1]/R^4Q^4$$

$$R^2 = R_1{}^2 + R_2{}^2$$

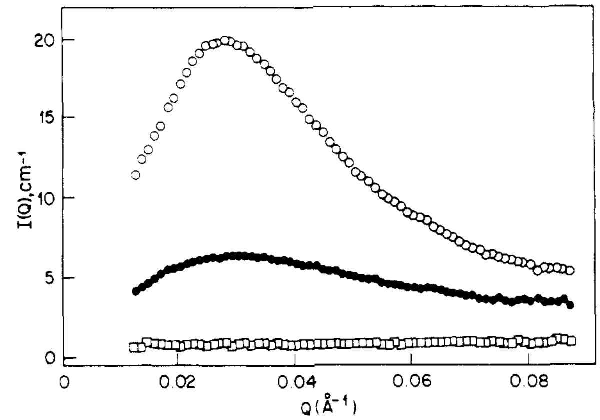

Figure 2. Small-angle neutron scattering (total intensity in absolute units) from two diblock copolymers, BB1 (open circles) and BB3 (filled circles), and a homopolymer, B1 (squares). The peaks derive from the correlation hole effect while the homopolymer intensity results from incoherent scattering.

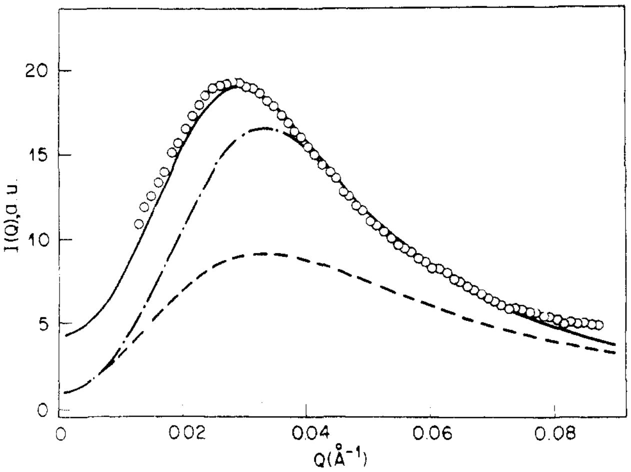

Figure 3. Calculated vs. experimental coherent scattering intensity (absolute units) for sample BB1 (composition = 0.47) as a function of the interaction parameter, χ, and chain polydispersity, N_W/N_N. The solid curve is based solely on experimentally determined parameters. Dashed curve, $\chi = 0$, $N_W/N_N = 1$; dash–dot curve, $\chi = 9.5 \times 10^{-3}$, $N_W/N_N = 1$; solid curve, $\chi = 9.5 \times 10^{-3}$, $N_W/N_N = 1.05$.

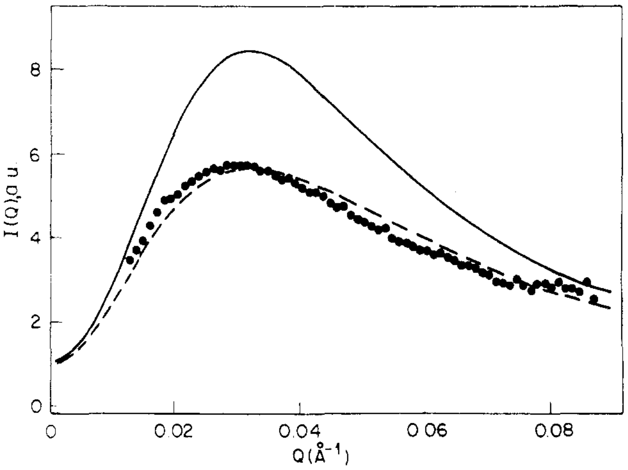

Figure 4. Calculated vs. experimental coherent scattering intensity (absolute units) for sample BB3 (composition = 0.18) as a function of the interaction parameter χ. Both calculated curves have been corrected for chain polydispersity. Solid curve, $\chi = 9.5 \times 10^{-3}$; dashed curve, $\chi = -2 \times 10^{-3}$.

$g_1(x)$ is the correlation function for Gaussian chains,[1] where R_1 and R_2 are the radii of gyration of each block of the diblock copolymer molecule. For $\chi = 0$, eq 1 reduces to the case of noninteracting chains. Increasing χ (or increasing N for $\chi > 0$) deepens the correlation hole and increases the magnitude of the correlation peak; at the spinodal point, $(\chi N)_s$, $S(Q)$ diverges. This behavior is analogous to what has been predicted,[1] and recently observed,[8] in miscible blends of homopolymers, where the divergence occurs at $Q = 0$. With the exception of the critical point, this divergence in $S(Q)$ is preceded by the development of an ordered phase, at the microphase separation transition (MST), occurring just below $(\chi N)_s$.[3] Leibler predicts a critical point at $(\chi N)_{\text{crit}} = 10.5$ and $N_1 = N_2$. Thus, for typical values of N (>100), homogeneity is contingent on a very weak (or attractive) interaction between polymer blocks.

The parameters appearing in eq 1 have either been measured or estimated from literature data. In a polydisperse system, N is replaced by N_W,[1] which can be obtained from N_N and N_W/N_N (Table I). Individual block lengths are directly related to N through the composition. Averaging the various reported values of a for 1,4-polybutadiene[9] yields $a_{1,4} = 6.7$ Å. Although a for 1,2-polybutadiene has not been reported, the value for 3,4-polyisoprene, a closely related molecule, has been measured.[10] Since 1,4-polyisoprene and 1,4-polybutadiene exhibit the same a values[9] it is reasonable to assume that the vinyl isomers of each will also be similar in magnitude. Therefore, the Kuhn length for 1,2-polybutadiene is assumed to be $a_{1,2} = 5.9$ Å. On the basis of these physical parameters, the calculated scattering intensity

$$I(Q) = \frac{N_A}{V}[b_{1,4} - b_{1,2}]^2 S(Q) \tag{2}$$

for noninteracting blocks ($\chi = 0$) is plotted with the SANS data in Figure 3 (dashed curve), where V is the segment molar volume ($V_{1,4} \simeq V_{1,2}$), b the segment coherent scattering length, and N_A is Avogadro's number. Included in this calculation is a minor correction[11] for a small, measured amount (~5%) of homopolymer, which accounts for the nonzero intercept at $Q = 0$. Clearly, this prediction does not match the experimental results.

In order to independently determine χ, a series of 1,4-polybutadiene–1,2-polybutadiene diblock copolymers near the critical point ($N\chi \sim (N\chi)_{\text{crit}}$) were examined rheologically.[13] The disorder-to-order transition in these materials is accompanied by a dramatic increase in the low-frequency modulus and dynamic viscosity. By varying N near the critical composition and monitoring these properties, the critical degree of polymerization for this system at 20 °C has been estimated to be $N_{\text{W,crit}} = 1.1 \times 10^3$. According to eq 1, this requires χ to equal 9.5×10^{-3}. Adding this interaction term to $S(Q)$ brings the prediction for $Q > 0.04$ Å^{-1} into good agreement with the data (dash–dot curve, Figure 3). The disagreement with the SANS results for $Q < 0.04$ Å^{-1} is a consequence of neglecting the effects of polydispersity.

Leibler and Benoit[11] have calculated that a small amount of polydispersity in a partly labeled polymer melt of noninteracting blocks should have a large effect on the correlation hole measurement. Their approach to modifying $S(Q)$ in order to account for polydispersity is presently applied to the case of interacting blocks. Polydispersity arises mainly through the polymerization kinetics, which predicts a Poisson distribution, and in the present case can be modeled with a Schultz–Zimm distribution

$$\Theta(N) = (k/N_N)^{k+1} N^k \exp\{-(k/N_N)N\}/\Gamma(k+1) \tag{3}$$

where $k = (N_W/N_N - 1)^{-1}$ and Γ denotes the gamma function. Therefore, $g_1(x)$ in eq 1 has been replaced by $\overline{g_1(x)}$, where

$$\overline{g_1(x)} = \frac{1}{N_W}\int_0^\infty \int_0^\infty (N_1 + N_2) g_1(x) \Theta(N_1) \Theta(N_2)\, dN_1\, dN_2 \tag{4}$$

The measured polydispersity, k, is related to that of each block by[14] $k^{-1} = k_1^{-1}\Phi^2 + k_2^{-1}(1 - \Phi)^2$. Since k_1 and k_2 cannot be determined separately, I have made the reasonable assumption that $k_1 = k_2$; calculations indicate that the predicted $S(Q)$ is relatively insensitive to this assumption. As demonstrated in Figure 3 (solid curve) this polydispersity correction, within experimental error, accounts for all the previous discrepancy between theory and experiment. It should be noted that the intensity measurements are subject to an error of ±20%, placing the following limits on the SANS-determined interaction parameter at $\Phi = 0.47$, $8 \times 10^{-3} \leq \chi \leq 1.2 \times 10^{-2}$.

The prediction for sample BB3 ($\Phi = 0.18$), based on the interaction parameter measured near the critical composition, $\chi = 9.5 \times 10^3$, clearly does not agree with the experimental results, as shown in Figure 4 (solid curve). Instead, a best fit to the data is obtained with $\chi = -2 \times 10^{-3}$ as given by the dashed curve. Because sample BB3 lies further from the spinodal curve than BB1, the predicted scattering intensity is considerably less sensitive to changes in χ than in the previous case; the precision of the SANS measurements sets an upper limit of $\chi \leq 6 \times 10^{-3}$ at $\Phi = 0.18$. Since both sets of measurements are subject to the same relative error, it can be concluded that $\chi(\Phi = 0.18) \leq 0.5\chi(\Phi = 0.47)$. This finding is in disagreement with the typical assumption of a composition-independent interaction parameter.[1]

These results demonstrate that the mean-field calculation of $S(Q)$ given by Leibler[3] accurately represents the spatial distribution of segments in homogeneous diblock copolymer melts. The Q location of the correlation hole appears to be accurately predicted by ideal chain statistics. Both the location and intensity of the correlation peak are strongly, but predictably, influenced by chain polydispersity.

An important finding of this work is that χ is strongly composition dependent in miscible polymer blends where χ is very small. Recently, several other investigators have obtained similar results from SANS studies of homopolymer blends.[8,16] In particular, Herkt-Maetzky and Schelten[8] have found variations in χ, near $\chi = 0$, for poly(vinyl methyl ether)–deuteriopolystyrene blends which are similar in magnitude to that presently reported.

The assumption of a composition independent interaction parameter originates with regular solution thermodynamics,[15] which predicts an upper critical solution temperature (UCST) for polymer–polymer blends. Experimentally, lower critical solution temperature (LCST) behavior has been found to be the rule. Such results led Flory[17] to develop the so-called "equation-of-state" thermodynamics for polymers, which attempts to take into account changes in local liquid structure upon mixing. This theory has been qualitatively successful in predicting an LCST for polymer blends.[18] In terms of the presently measured χ, equation-of-state contributions to the mixing free energy are manifested as a composition-dependent interaction parameter. In the past, such differences in χ have been virtually impossible to measure in polymer–polymer blends. SANS analysis of the correlation hole in block copolymers provides a sensitive method of investigating these effects, and the thermodynamics of polymer blends in general. Future reports will address these issues in more detail.

Acknowledgment. Charles Glinka and Charles Han of NBS kindly provided the author with the opportunity for, and assistance in, obtaining the SANS data. Mark Hartney aided in the preparation of the samples. I have also benefited from numerous discussions with Dean Douglass.

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General Treatment of Equilibrium Copolymerization of Two or More Comonomers Deduced from the Initial State of the System

Michael Szwarc* and Charles L. Perrin

Department of Chemistry, University of California, San Diego, La Jolla, California 92093.

Received July 2, 1984

ABSTRACT: A mathematical approach was developed to account for equilibrium copolymerization, a process involving the pertinent propagation and cross-propagation steps, as well as their respective depropagations, but free of termination and chain transfers. The treatment leads to the determination of the equilibrium concentrations of the comonomers, the molecular weight distribution of the resulting copolymers, the average composition of *n*-mers as a function of *n*, the probability of having a specified comonomer at *m*-th segments of *n*-mers, etc. This information is deduced from the knowledge of the initial state of the system and the required equilibrium constants. The treatment applies to low as well as to high molecular weight polymers and is designed to handle any number of comonomers.

The problem of monomer–polymer equilibrium was explored initially by Dainton and Ivin.[1] Such an equilibrium is of considerable interest when one deals with living polymer systems[2] since the permanent capacity of those polymers to grow is coupled with their capacity to degrade. Consequently, living polymers eventually have to be in equilibrium with their monomers. The treatment of such an equilibrium in living homopolymers was outlined by Tobolsky and Eisenberg[3] and later by Wheeler et al.[4]

A reversible copolymerization was studied less thoroughly. Calculation of the free energy of conversion of two infinitely long homopolymers, ...AA... and ...BB..., into an infinitely long copolymer of a desired composition was reported by Sawada[5] and later by Theil.[6] Kinetics of copolymerizations involving propagation and depropagation was developed by Lowry,[7] and similar treatments were discussed by other investigators.[8-12] The complexity of the problem, set in conventional kinetic form, limits this approach to copolymerizations involving a reversible addition of only one comonomer.

The stochastic approach, developed by O'Driscoll and his associates,[13] permits handling copolymerizations with all four basic steps reversible, i.e.

$$\text{-A}^* + \text{A} \underset{b_{11}}{\overset{k_{11}}{\rightleftharpoons}} \text{- AA}^*$$

$$\text{-A}^* + \text{B} \underset{b_{12}}{\overset{k_{12}}{\rightleftharpoons}} \text{-AB}^*$$

$$\text{-B}^* + \text{A} \underset{b_{21}}{\overset{k_{21}}{\rightleftharpoons}} \text{-BA}^*$$

$$\text{-B}^* + \text{B} \underset{b_{22}}{\overset{k_{22}}{\rightleftharpoons}} \text{-BB}^*$$

In such schemes the propagation rate is assumed to be determined by the nature of the last unit of the growing polymers and the monomer's nature, while the rate of depropagation is determined by the nature of the last two units.[18] This treatment, in common with the previous ones, deals with copolymerizations proceeding at constant, although arbitrary, concentrations of the comonomers. Under such conditions the distribution of the monomeric segments in the copolymer chains becomes virtually constant as their length becomes sufficiently long, approaching the limiting distribution of infinitely long chains. Such a distribution obeys the first-order Markov statistics; i.e., probabilities of finding the segments A or B at any location in the chain, as well as the respective conditional probabilities of A being preceded by A or B preceded by B, all become constant, independent of location. Let it be stressed that the steady-state conditions result in constant probabilities of finding A or B at the *ends* of growing polymers; howowever, these probabilities are, on the whole, different from those determining the chances of having these units at any other arbitrary location in the chain.

Let us summarize the important achievements gained through this work. The composition of long copolymers

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