Interference of Microstructure and Isotope Labeling Effects in Polymer Blend Compatibility

Andrzej Budkowski,[†,‡] **Jacob Klein,**[*,†] **Erika Eiser,**[†] **Ullrich Steiner,**[†] **and Lewis J. Fetters**[§]

Weizmann Institute of Science, Rehovot 76100, Israel, and Exxon Research and Engineering Company, Annandale, New Jersey 08801

Received November 18, 1992; Revised Manuscript Received March 25, 1993

ABSTRACT: A model is developed which explains a recently-observed asymmetry in the phase-equilibrium behavior of mixtures of statistical ethylene (E)/ethylethylene (EE) copolymers $E_{x_i}EE_{1-x_i}$, with differing microstructure and isotopic substitution levels. A coupling between the isotope and the microstructure contributions to the overall effective segmental interaction parameter χ is predicted, which could enhance or reduce χ depending on the ethylene content of the protonated component relative to that of the deuterated one. From the overall χ, the theory permits the extraction of the bare isotope interaction parameter $\chi_{h/d}$ between hydrogenated and deuterated species and of the parameter $\chi_{E/EE}$ for the E/EE interaction. This is done for the recent data set on coexistence in E/EE mixtures obtained by *Eiser et al.* The parameters thus estimated are compared with available experimental data on similar polyolefinic mixtures.

1. Introduction

In recent years there have been several studies of the thermodynamic properties of mixtures of statistical copolymers of the type A_xB_{1-x}, where monomers of A and B are randomly distributed in the ratio x:$(1 - x)$ along the chain.[1-8] In particular, $A_{x_i}B_{1-x_i}/A_{x_j}B_{1-x_j}$ mixtures, where $x_i \neq x_j$, provide interesting model systems where the components are adjustable between pure A and pure B and have been studied in a number of cases, most notably by Crist and co-workers[7,8] for copolymers of ethylene (C_4H_8, henceforth, E) and 1-butene ($C_2H_3(C_2H_5)$, henceforth, ethylethylene, or EE). Very recently Balsara *et al.* carried out an extensive small-angle neutron scattering (SANS) study[9] on mixing thermodynamics between such random copolymers, where A and B were again E and EE monomers. In related work,[10] following the approach of Budkowski *et al.*,[11] nuclear reaction analysis (NRA) was used[12-14] to determine phase coexistence diagrams in mixtures of E/EE copolymer samples from the same batches as in the Balsara *et al.* study. Deuterium labeling has been used to provide contrast in both the SANS and NRA work: as noted by Sakurai *et al.*[5] and by Rhee and Crist,[8] the isotope and the chemical microstructure effects can combine in a complicated manner to yield the overall measured interaction parameter for the copolymer mixing.

In this connection, an interesting experimental observation has been made in all three studies of E_x/EE_{1-x} blends. The SANS studies of Balsara *et al.*[9] showed that the overall measured interaction parameter for a mixture of a protonated polyolefin with x_i ethylene content (we shall use the abbreviation $hx_i \equiv hE_{x_i}hEE_{1-x_i}$ for such a fully protonated copolymer) and its partially deuterated counterpart with x_j composition ($dx_j \equiv dE_{x_j}dEE_{1-x_j}$), $\chi(hx_i/dx_j)$ is different from the interaction parameter for the same couple but with reversed isotope labeling, $\chi(dx_i/hx_j)$. They found the difference to be in the sense that $\chi(hx_i/dx_j) \leq \chi(dx_i/hx_j)$ whenever $x_j > x_i$; i.e., χ is larger when the component with less ethylene content carries the deuterium label; their light scattering measurements also revealed significantly different phase-separation temperatures for these blends, consistent with the SANS-determined χ values. Similar effects were also observed by Crist,[15] where the difference in the interaction parameters was again in the sense noted above; and the NRA phase-coexistence study by Eiser *et al.*[10] revealed striking differences in the critical temperature T_c, once again in the same sense as noted, when the deuterium labels were exchanged. This is seen in Figure 1 which shows the coexistence curves for the couples (hx_1/dx_2) and (dx_1/hx_2) from the NRA study,[10] where $x_1 = 0.12$ and $x_2 = 0.22$. The degrees of polymerization of the x_1 and x_2 copolymers were $N_1 = 1290$ and $N_2 = 1610$, while the deuteration fractions in the labeled chains—the fraction of protons replaced by deuterium atoms—were $e_1 = 0.296$ and $e_2 = 0.37$, respectively. A difference in the T_c values of some 65 °C is immediately apparent. A fit of the experimental binodal curves to the ones calculated using the Flory–Huggins functional for the mixing free energy,

$$\frac{\Delta F}{k_BT} = (\phi/N_1)\ln\phi + ((1-\phi)/N_2)\ln(1-\phi) + \chi\phi(1-\phi) \quad (1)$$

with the appropriate values of χ yields[10,11] the solid curves appearing in Figure 1, with the following effective interaction parameters

$$\chi(hx_1/dx_2, e_2 = 0.296) = (0.483T^{-1} - 9.6 \times 10^{-7})(1 - 0.6\phi) \quad (2a)$$

$$\chi(dx_1/hx_2, e_1 = 0.37) = (0.664T^{-1} - 1.08 \times 10^{-4})(1 - 0.244\phi) \quad (2b)$$

where ϕ ($=\phi_{x_2}$) is the volume fraction of the x_2 component (i.e., of the copolymer with 0.22 ethylene content).

These observations of the large changes induced in the effective mean segment–segment interactions by exchange of isotopic labeling are puzzling and not accounted for by existing theories.[16] They provide the motivation for the present work in which a very simple model is proposed to account for these effects.

2. Theory

In our treatment we adopt the simplest nontrivial microscopic model for the χ parameter. In this the effective segment–segment interactions in the blend are related to the slight difference in segmental volume between its two components (this makes the reasonable assumption of the absence of dipole or specific interac-

---

[†] Weizmann Institute of Science.

[‡] On leave of absence from Jagellonian University, Cracow, Poland.

[§] Exxon Research and Engineering Co.

0024-9297/93/2226-3858$04.00/0

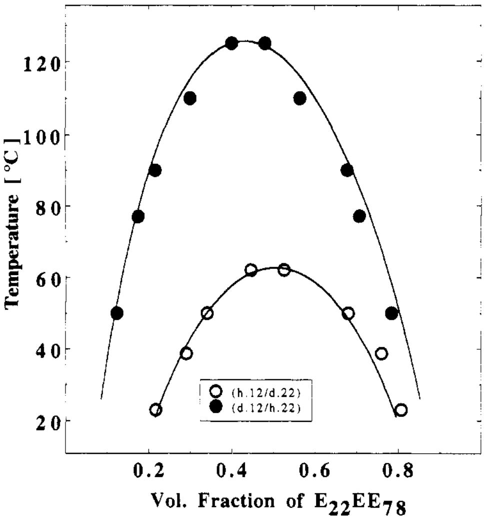

Figure 1. Coexistence curves for ethyl (E)–ethylethylene (EE) copolymer blends (hx_1/dx_2) and (dx_1/hx_2), determined directly by nuclear reaction analysis, taken from ref 10. hx_i (dx_i) is shorthand for a protonated (deuterated) copolymer $E_{x_i}EE_{1-x_i}$. Exchange of the deuterium labels shifts the critical temperature by ca. 65 °C. The solid lines are binodals generated from the Flory–Huggins mixing energy (eq 1) using the effective interaction parameters χ given by eq 2.

tions). This idea was proposed by Buckingham and Hentschel,[17] and extended by Bates and co-workers,[18] for the case of a mixture of a protonated polymer (segmental volume V_h) with its deuterated analogue (V_d). Two volume-related contributions to the effective χ were considered. The first, χ_V, corresponds to the energy associated with adjustment of the segmental volumes of both components V_i (i = h) and V_j (j = d) to the mean segmental volume V of the mixture:

$$\chi_V = \frac{1}{k_BT}\frac{(V_i - V_j)^2}{2\kappa V} \tag{3}$$

where κ is the compressibility of the mixture.

The increase in segmental volume going from deuterated to protonated polymer (from component i to component j) leads to a higher total segment polarizability α_i for the protonated (ith) molecule ($\alpha_i > \alpha_j$). This gives the second, dispersive contribution χ_d to the interaction parameter.[18]

$$\chi_d = \frac{1}{k_BT}\frac{2\pi^2 I(\alpha_i - \alpha_j)^2}{3V^2} \tag{4}$$

where I is the ionization potential.

Assuming a linear relation between the segment polarizability and the segmental volume,[19] we may express these two contributions by a single expression for the effective interaction parameter $\chi_{i/j}$ (i = h, j = d):

$$\chi_{i/j} = \chi_d + \chi_V = C(V_i - V_j)^2 \tag{5}$$

where C is a constant (strictly, C may vary with the relative mixture composition through V, but—as long as V_i and V_j are not too different—this will be a small perturbation).

At the other extreme, of isotopically identical but chemically different segments, we may take the application of these ideas to remain approximately valid as long as one is dealing with purely dispersive interactions and as long as the segmental volumes of the interacting species remain similar. In particular, we apply this in the present case, where the relative difference in segmental volumes for the ethylene (V_E) and ethylethylene (V_{EE}) components is small:[9] $(V_E - V_{EE})/V \approx 1.5\% \ll 1$. Thus we apply the set of eqs 3–5 not only to the evaluation of $\chi_{h/d}$ but also to $\chi_{E/EE}$ and more generally to $\chi(dx_i/hx_j)$, for an E/EE blend with components differing both in chemical microstructure and in isotope composition.

Next, we make the approximation that, in an isotopically homogeneous, random copolymer E_xEE_{1-x}, the mean segment volume $V(E_xEE_{1-x})$ varies linearly with ethylene content x:

$$V(E_xEE_{1-x}) = xV_E + (1-x)V_{EE} \tag{6a}$$

We extend this linear approximation to the relation between the mean segment volume $V(dF_ehF_{1-e})$ and deuteration fraction e for microstructurally identical but isotopically different polyolefins dF_ehF_{1-e}, where $F \equiv E_xEE_{1-x}$:

$$V(dF_ehF_{1-e}) = eV(dF) + (1-e)V(hF) \tag{6b}$$

Using eq 6 we are in a position to evaluate the average segmental volume of a partly deuterated random copolymer $[hE_xhEE_{1-x}]_{1-e}[dE_xdEE_{1-x}]_e$:

$$V([hE_xhEE_{1-x}]_{1-e}[dE_xdEE_{1-x}]_e) = V(hEE) + x[V(hE) - V(hEE)] - e[V(hF) - V(dF)] \tag{7}$$

where volume changes responsible for both microstructural ($V(hE)$-$V(hEE)$) and isotope ($V(hF)$-$V(dF)$) effects are positive. Implicit in eq 7 is the further simplifying approximation that the isotope-induced differences $V(dE)$-$V(hE)$ and $V(dEE)$-$V(hEE)$ are equal.

Finally we calculate the effective segmental interaction parameter $\chi(hx_i/dx_j,e_j)$ in a mixture of a protonated random copolymer $hE_{x_i}hEE_{1-x_i}$ ($=hx_i$) and a partly deuterated copolymer $[hE_{x_j}hEE_{1-x_j}]_{1-e_j}[dE_{x_j}dEE_{1-x_j}]_{e_j}$ ($=dx_j,e_j$). For this purpose we apply eq 5 to the relations between χ and segmental volumes of both components (eqs 6a and 7):

$$\begin{aligned}\chi(hx_i/dx_j,e_j) &= C[V(hx_i) - V(dx_j,e_j)]^2 \\ &= C[(x_i - x_j)[V(hE) - V(hEE)] + e_j[V(hF) - V(dF)]]^2 \\ &= (x_i - x_j)^2\chi_{E/EE} + e_j^2\chi_{h/d} + 2(x_i - x_j)e_j[\chi_{E/EE}\chi_{h/d}]^{1/2}\end{aligned} \tag{8}$$

Equation 8 is the central result of our treatment.[20] The first two terms on the right-hand side may be considered to represent the straightforward additivity of the interactions, symmetric in the composition and extent of isotopic labeling of the components as would be expected (see below) from existing theories of random copolymer mixing. It is the third term, containing the geometrical average of $\chi_{E/EE}$ and $\chi_{h/d}$, that represents the "interference" between isotopic and microstructural effects; this term can enhance or diminish the effective interaction parameter $\chi(hx_i/dx_j,e_j)$ depending on the sign of the difference in compositions ($x_i - x_j$). The effective interaction parameters $\chi(hx_i/dx_j,e_j)$ and $\chi(dx_i/hx_j,e_i)$ of two blends with microstructurally identical components but reversed (and equal, say) deuteration $e_i = e_j = e$ differ, according to eq 8, by $4|x_i-x_j|e(\chi_{E/EE}\chi_{h/d})^{1/2}$. The larger interaction parameter is predicted to occur for a blend where the deuterium labeling is on the component with lower ethylene content ($x_i > x_j$), in line with the experimental observations[9,10,15] in the E/EE system.

It is appropriate to remark that, in principle, eq 8 could also be obtained by extending random copolymer theory.[21] Thus, this theory would describe the effective interaction parameter χ between protonated hx_i and deuterated (to an extent e) dx_j (say) as a function of six segment–segment interaction parameters $\chi_{l,m}$, with l,m = hE, dE, hEE, dEE ($l \neq m$). In order to reduce the number of free parameters further, approximations may be made[7] such that $\chi_{\mathrm{hE/dE}} = \chi_{\mathrm{hEE/dEE}} = \chi_{\mathrm{h/d}}$, $\chi_{\mathrm{hE/hEE}} = \chi_{\mathrm{dE/dEE}} = \chi_{\mathrm{E/EE}}$, and $\chi_{\mathrm{hE/dEE}} = \chi_{\mathrm{dE/hEE}} = \chi_{\mathrm{h/d}} + \chi_{\mathrm{E/EE}}$. This approach leads to the first two terms on the right-hand side of eq 8. We should bear in mind, however, the sequence of inequalities[9,18] in the segmental volumes: $V(\mathrm{hE}) > V(\mathrm{dE}) > V(\mathrm{hEE}) > V(\mathrm{dEE})$. From these we see at once that $V(\mathrm{hE}) - V(\mathrm{dEE}) > V(\mathrm{dE}) - V(\mathrm{hEE})$. Analogous inequalities could be written for the corresponding segmental polarizabilities, from which we conclude that $\chi_{\mathrm{hE/dEE}} \neq \chi_{\mathrm{dE/hEE}}$. The necessary inclusion of an additional parameter describing this difference results in the interference term in the formula expressing the overall effective χ. Finally, the assumption we made about the linear relationship between segment volumes and segmental polarizabilities reduces the number of independent parameters to two and leads to the result of eq 8.[28]

3. Discussion

The effective interaction parameter $\chi(\mathrm{h}x_i/\mathrm{d}x_j,e_j)$ in eq 8 is a function of two unknown parameters, $\chi_{\mathrm{h/d}}$ and $\chi_{\mathrm{E/EE}}$, so that these can be extracted from experimentally determined values of the overall interaction parameter for two different E/EE mixtures. Since the right-hand side of eq 8 is a square, we may write the two relationships as

$$[\chi(\mathrm{h}x_i/\mathrm{d}x_j,e_j)]^{1/2} = |(x_i - x_j)(\chi_{\mathrm{E/EE}})^{1/2} + e_j\,(\chi_{\mathrm{h/d}})^{1/2}| \qquad (i, j = 1, 2; i \neq j) \quad (9)$$

where positive signs of the roots are implicit. These two equations are then readily solved for $\chi_{\mathrm{E/EE}}$ and $\chi_{\mathrm{h/d}}$.

We apply this procedure to the pair of polyolefin blends with reversed isotope labeling ($\mathrm{h}x_1/\mathrm{d}x_2$, e_2) and ($\mathrm{d}x_1/\mathrm{h}x_2$, e_1), whose interaction parameters, obtained from the binodal curves[10] (Figure 1), are given in eq 2. Because these best-fit effective χ values are both T- and ϕ_{x_2}-dependent,[22] the corresponding expressions for $\chi_{\mathrm{h/d}}$ and $\chi_{\mathrm{E/EE}}$ derived by inverting eq 9 also have such a dependence. The calculated values of these interaction parameters as a function of temperature are shown in Figure 2 for two values of the x_2 volume fraction ($\phi_{x_2} = \phi = 0.5, 0.9$).

The "bare" isotope interaction $\chi_{\mathrm{h/d}}$ in Figure 2a increases with ϕ and has a linear T^{-1} dependence. Its values (over the relevant temperature region) are in the range (1–4) × 10^{-4}; this may be compared with values obtained more directly from experiments performed in isotopic mixtures with chemically identical components. The SANS measurements carried out by Balsara *et al.*[9] for *matched* E/EE pairs (i.e., ($\mathrm{h}x_i/\mathrm{d}x_i$) couples in our notation), which would be the most appropriate for purposes of comparison, reveal mean values of χ whose absolute magnitudes are in the range 10^{-4}–10^{-3}, with experimental scatter of order $\pm 10^{-3}$. Thus, while the calculated values of the bare isotope interaction in Figure 2a (solid lines) are certainly within that range, more detailed comparison is precluded.[23] SANS measurements by Bates *et al.*[24] on equimolar mixtures of EE with (perdeuterated) dEE yield a value $\chi_{\mathrm{EE/dEE}} = 7.7 \times 10^{-4}$ at 100 °C, as shown in Figure 2a. This is significantly higher than the predicted $\chi_{\mathrm{h/d}}$, though a substantial spread in the calculated value is possible as a result of small uncertainties in the precise values of the experimentally-determined x and e values.[25]

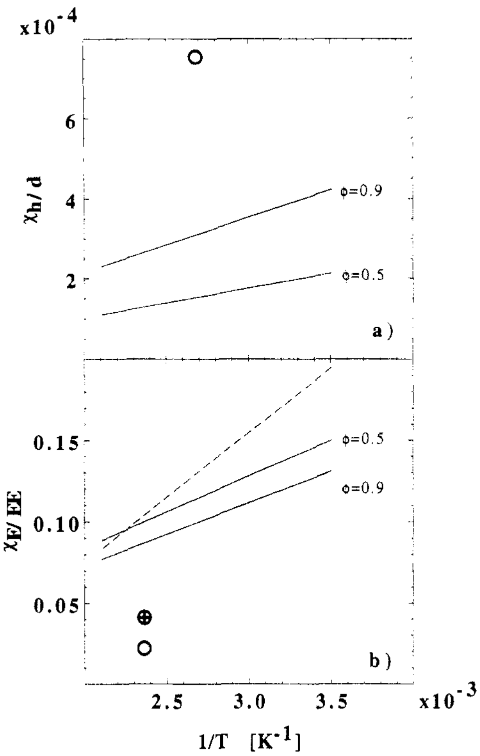

Figure 2. (a) Isotope labeling contribution, $\chi_{\mathrm{h/d}}$, to the overall effective interaction parameter χ, calculated via eq 9 for the set of data presented in Figure 1 and eq 2, as a function of reciprocal temperature T^{-1} (K^{-1}) (solid lines). Calculated interaction parameters for two different volume fractions (ϕ = 0.5 and 0.9) of the $\mathrm{E}_{x_2}\mathrm{EE}_{1-x_2}$ components are shown. The datum point (○) is from SANS for poly(ethylethylene)/perdeuterated poly(ethylethylene) mixtures.[24] (b) The interaction parameter, $\chi_{\mathrm{E/EE}}$, arising from the microstructural difference contribution to the overall effective interaction parameter χ, calculated via eq 9 for the set of data presented in Figure 1 and eq 2, as a function of reciprocal temperature T^{-1} (K^{-1}) (solid lines). The $\chi_{\mathrm{E/EE}}(T)$ dependence for the same pair of mixtures obtained from independent SANS data[9] is plotted as the dashed line. Experimental estimates of $\chi_{\mathrm{E/EE}}$ obtained for a purely protonated blend of $\mathrm{E/E}_x\mathrm{EE}_{1-x}$, with x = 0.69–0.78[8] (○), as well as data scaled from mixtures of n-octane and ethylheptane oligomers[26] (⊕) are shown for comparison.

Figure 2b shows that the bare microstructure interaction $\chi_{\mathrm{E/EE}}$ deduced by applying our model to the data of eq 2 decreases slightly with increasing ϕ but maintains its linearity with T^{-1} (solid lines in Figure 2b). The range of calculated $\chi_{\mathrm{E/EE}}$ values over the relevant temperature range is ca. 0.07–0.17. One investigation with which these values may be compared is that on mixtures of microstructurally-different but isotopically similar (protonated) polyolefins by Rhee and Crist.[8] Their study yields an appreciably lower interaction parameter $\chi_{\mathrm{E/EE}} = 0.022$ at 150 °C than the calculated one, as indicated in Figure 2b. This value was obtained from a variation of the cloud-point method for $\mathrm{hE/hE}_x\mathrm{EE}_{1-x}$ blends with ethylene contents x = 0.69–0.78 in their copolymers, rather higher than in the blends of eq 2 (for which x = 0.12 and 0.22). Another estimate may be made from the measured enthalpy of mixing for oligomers of n-octane and ethylheptane.[26] This leads to $\chi_{\mathrm{E/EE}} = 0.041$ at 150 °C. The SANS data of Balsara *et al.*[9] for the pair of mixtures ($\mathrm{h}x_1/\mathrm{d}x_2$) and ($\mathrm{d}x_1/\mathrm{h}x_2$)—as used in the binodal study (Figure 1)—may also be analyzed using eq 9; this yields a broader range of values $0.08 < \chi_{\mathrm{E/EE}} < 0.20$ (dashed line in Figure 2b), rather close to those calculated from eq 2 (though the corresponding $\chi_{\mathrm{h/d}}$ values extracted are lower by a factor 2 or so than in Figure 2a). The same analysis performed for another pair in their SANS study for ($\mathrm{h}x_i/\mathrm{d}x_j$) mixtures with x_i, x_j = 0.03, 0.12 reveals very similar estimates for $\chi_{\mathrm{E/EE}}$. We may conclude that the evaluations of $\chi_{\mathrm{E/EE}}$ for blends with low ethylene content, based on data from

SANS and NRA independently, are in reasonable accord. They appear, however, to be significantly higher than the $\chi_{E/EE}$ values obtained for olefin copolymers rich in ethylene. This may be because the value of the constant C in eq 5 is dependent on the average blend composition; it may also be related to the recent suggestion[27] that different conditions during the process of copolymerization could lead to different extents of correlations (i.e., introducing a certain amount of "blockiness") along the chains, thereby changing their thermodynamical properties. This would argue that better agreement should be obtained between different studies using polymers from the same batch, as is indeed observed.

Apart from obvious simplifications in our approach, we note that we have throughout ignored the temperature-independent (entropic) part of χ which is not directly related to the dispersive interactions (and which is seen explicitly in our eq 2, for example). It is important to recall these approximations when evaluating the detailed comparison of our two-parameter model with experimental data; though, we note that the magnitude of the asymmetry effect evaluated from our model, given (in eq 8) by the geometric mean of the small isotopic and the much larger microstructural contributions, can indeed account for the large differences in χ (ca. 30%) observed in the relevant experimental studies.

Acknowledgment. We are especially grateful to N. Balsara, W. Graessley, R. Krishnamoorti, D. Lohse, and D. Schulz for extensive discussions and for sharing with us their experimental data prior to publication. Financial support of this work by the German-Israel Foundation, by the U.S.-Israel Binational Science Foundation, and by Minerva is acknowledged with thanks.

References and Notes

(1) Lohse, D. J. *Polym. Eng. Sci.* **1986**, *26*, 1500.

(2) Inaba, N.; Sato, K.; Suzuki, S.; Hashimoto, T. *Macromolecules* **1988**, *21*, 407.

(3) Strobl, G. R.; Bendler, J. T.; Kambour, R. P.; Schultz, A. R. *Macromolecules* **1986**, *19*, 2683.

(4) Izumitani, T.; Takenaka, M.; Hashimoto, T. *J. Chem. Phys.* **1990**, *92*, 3213.

(5) Sakurai, S.; Hasegawa, H.; Hashimoto, T.; Hargis, I. G.; Aggarwal, S. I.; Han, C. C. *Macromolecules* **1990**, *23*, 451.

(6) Schmitt, B. J.; Kirste, R. G.; Jelenic, J. *Makromol. Chem.* **1980**, *181*, 1655.

(7) Nicholson, J. C.; Finerman, T. M.; Crist, B. *Polymer* **1990**, *31*, 2287.

(8) Rhee, J.; Crist, B. *Macromolecules* **1991**, *24*, 5663.

(9) Balsara, N. P.; Fetters, L. J.; Hadjichristidis, N.; Lohse, D. J.; Han, C. C.; Graessley, W. W.; Krishnamoorti, R. *Macromolecules* **1992**, *25*, 6137.

(10) Eiser, E.; Budkowski, A.; Steiner, U.; Klein, J.; Fetters, L. J.; Krishnamoorti, R. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1993**, Aug. See also: Steiner, U.; Klein, J.; Eiser, E.; Budkowski, A.; Fetters, L. J. *Science* **1992**, *258*, 1126.

(11) Budkowski, A.; Steiner, U.; Klein, J.; Schatz, G. *Europhys. Lett.* **1992**, *18*, 705.

(12) Chaturvedi, U. K.; Steiner, U.; Zak, O.; Krausch, G.; Klein, J. *Phys. Rev. Lett.* **1989**, *63*, 616.

(13) Chaturvedi, U. K.; Steiner, U.; Zak, O.; Krausch, G.; Schatz, G.; Klein, J. *Appl. Phys. Lett.* **1990**, *56*, 1228.

(14) Klein, J. *Science* **1990**, *260*, 640.

(15) Crist, B., private communication (ref 43 in Balsara *et al.*[9]).

(16) The effect of the difference in deuteration levels e is too small, by some 3 orders of magnitude, to explain the differences in the overall interaction parameter on exchange of the isotopic labeling as also noted earlier.[9]

(17) Buckingham, A. D.; Hentschel, H.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 853.

(18) Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.

(19) Strictly speaking, such a linear relation applies to Bohr-type spherical atoms. For more complicated molecules the precise relation can still be cast in an equivalent form but the precise prefactors depend on the detailed microstructure. Using a single-valued relation as in eq 5 is equivalent to assuming closely similar microstructures for the different protonated and deuterated species in the copolymers.

(20) More complicated (but still approximate) formulations of χ in terms of microscopic parameters are possible; see, e.g.: Singh, R. R.; Van Hook, W. A. *Macromolecules* **1987**, *20*, 1855. Bates, F. S.; Fetters, L. J.; Wignall, G. (BFW) *Macromolecules* **1988**, *21*, 1086. These have been critically compared in ref 7 with respect to data for E/EE blends. The use of such formulations (e.g., BFW) leads to the same result (eq 8) as obtained with the simpler expression of eq 5.

(21) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.

(22) We note that, in the SANS study,[9] while no systematic ϕ variation of the overall χ was reported, there is some indication (Figure 10 of ref 9) of a trend similar to that appearing in eq 2a for the (hx_1/dx_2) mixture.

(23) Though, it is worth remarking that, within the scatter, there appears to be a systematic decrease of $\chi(hx_1/dx_1)$ with increasing temperature (Table IX of ref 9), as in Figure 2.

(24) Bates, F. S.; Muthukumar, M.; Wignall, G. D.; Fetters, L. J. *J. Chem. Phys.* **1988**, *89*, 535.

(25) For example, an uncertainty of ±2% in the deuteration fractions e implies an uncertainty of ±60% in the calculated χ values in Figure 2.

(26) de St. Romain, P.; Van, H. T.; Patterson, D. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1700.

(27) Fredricson, G. H.; Milner, S. T.; Leibler, L. *Macromolecules* **1992**, *25*, 6341.

(28) Following completion of this work we became aware of two additional studies of the isotope/microstructure interference effect in E/EE mixtures, by J. Rhee and B. Crist (*J. Chem. Phys.*, in press) and by W. W. Graessley, R. Krishnamoorti, N. Balsara, and D. Lohse (*Macromolecules*, in press) in which explanations of the effect are advanced that are similar in spirit to those in the present paper.