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# Measurement of Thermodynamic Interactions in Ternary Polymer Blends by Small-Angle Neutron Scattering

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ABSTRACT: The feasibility of evaluating thermodynamic interactions between polymer species by small-angle neutron scattering (SANS) measurements on ternary blends was investigated. Results were analyzed for two ternary systems of saturated hydrocarbon polymers by means of the multicomponent random phase approximation (RPA) as applied to the Flory−Huggins (FH) model. In one ternary blend—head-to-tail polypropylene, head-to-head polypropylene, and a saturated polyisoprene with 50% 3,4 content—the interaction coefficient $X(T)$ had been determined independently by SANS measurements on binary blends for all three component pair combinations, permitting a direct test of internal consistency for the ternary RPA. The ternary blend data were found to agree well with RPA predictions despite some highly unusual behavior among its binaries, including negative values of $X(T)$ for saturated hydrocarbon pairs. In the other ternary blend—three statistical copolymers of ethylene (E) and 1-butene (B) with different E−B compositions—values of $X(T)$ were available for only two of the binaries, the third pair being immiscible over the range of available temperatures. The SANS data for the ternary blend were used to evaluate the interaction coefficient for the third pair. The interaction coefficients obtained were smaller than values calculated from previously assigned solubility parameters, a result that is disappointing although nonetheless still consistent with results obtained for other strongly interacting pairs.

## Introduction

Over the past few years, we have accumulated a sizable body of data on the thermodynamic interactions between components in blends of saturated hydrocarbon polymers.[1−4] Small-angle neutron scattering (SANS) measurements on binary blends were interpreted through equations based on the random phase approximation (RPA) and the Flory−Huggins (FH) expression for the free energy of mixing

$$\Delta G_{\mathrm{m}} = k_{\mathrm{B}}T\left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2}\right] + X(T)\phi_1\phi_2 \tag{1}$$

in which $\Delta G_{\mathrm{m}}$ is the free energy density of mixing—the free energy change per unit volume—$k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the temperature, and $\phi_i$ and $V_i$ are component volume fractions ($\phi_1 + \phi_2 = 1$) and molecular volumes ($V_i = N_i v_i$ , the $v_i$ and $N_i$ being volume per monomeric unit and number of monomeric units per molecule). The last term is the interaction contribution, and a pair-specific coefficient $X(T)$ that we call the interaction strength,[4] sometimes expressed in dimensionless form as a FH interaction parameter:

$$\chi(T) = \frac{v_{\mathrm{o}}}{k_{\mathrm{B}}T}X(T) \tag{2}$$

The reference volume $v_{\mathrm{o}}$ is arbitrary (we use $v_{\mathrm{o}} = (v_1 v_2)^{1/2}$). Our results so far reveal some interesting trends in interaction strength with the component molecular structures.[4] We are always seeking ways to expand the range of structures and interaction strengths for study; the use of ternary blends offers one such method.

Most species of the saturated hydrocarbon polymer family used previously were obtained by saturating the double bonds of nearly monodisperse polydienes,[5] a route to blend components that confers some significant benefits. The products are structurally well-defined, and they also have narrow molecular weight distribution ($M_{\mathrm{w}}/M_{\mathrm{n}} \le 1.05$), simplifying the analysis. Labeling with deuterium to obtain the necessary SANS contrast is also easily accomplished by using $D_2$ in place of $H_2$ in the saturation step. The interactions in these systems are typically weak ($\chi \sim 10^{-3}$), and at this level the isotopic interaction effects themselves are nonnegligible. However, the availability of structurally-matched, labeled and nonlabeled versions of each component permits “label-switching” experiments to be performed,[6,7] and we were able to show that the desired interaction strength for blends of hydrogenous (nonlabeled) components is given, to a good approximation, by an average of values for the two singly labeled blends (the ones with useful levels of SANS contrast):

$$X \equiv X_{\mathrm{hh}} \approx X_{\mathrm{dd}} \tag{3a}$$

$$X = \frac{({X_{\mathrm{hd}}}^{1/2} + {X_{\mathrm{dh}}}^{1/2})^2}{2} \approx \frac{X_{\mathrm{hd}} + X_{\mathrm{dh}}}{2} \tag{3b}$$

A wide variety of polydienes was employed, but the structures obtainable in this way are still limited—stereoregularity, for example, and linear side chains larger than $C_2$ are effectively unavailable by this

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route. Direct polymerization of olefins offers such structural varieties and others as well. The products in this case are polydisperse, but relatively uniform chain compositions and reasonably well-defined distributions of molecular weight ($M_w/M_n \approx 2$) can be achieved with metallocene polymerization catalysts.[8] The SANS-required labeling would require the polymerization of deuterated monomers, however, and these are expensive and not always available. Also, matched pairs become far more troublesome to achieve than in the polydiene route.

Ternary blends offer an alternative that does not require the polymers to be labeled.[9,10] The following expression is the FH free energy density for blends of three monodisperse components:

$$\Delta G_m = k_B T\left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2} + \frac{\phi_3 \ln \phi_3}{V_3}\right] + X_{12}(T)\phi_1\phi_2 + X_{13}(T)\phi_1\phi_3 + X_{23}(T)\phi_2\phi_3 \quad (4)$$

Here, 1 and 2 referring to the hydrogenous components whose interaction is to be determined and component 3 referring to a deuterated species that forms single-phase binary mixtures with both 1 and 2. The interaction strengths $X_{23}(T)$ and $X_{13}(T)$ can be determined independently from SANS data for the respective binary blends. The coefficient of interest $X_{12}(T)$ is then left as the only fitting parameter to be determined with the SANS data for the ternary blend.

Here we investigate the reliability of the ternary method by using SANS measurements on a ternary blend for which all three interaction coefficients are known from SANS data on the three binaries. We also apply this method to a second ternary system for which one of the three interaction coefficients is unknown because its binary blend is two-phase in the compositional midrange over the accessible range of temperatures. Its purpose is to illustrate how ternaries can expand the practical range for measuring interaction strengths. Handling component polydispersity and application to directly synthesized polyolefins will be described in subsequent papers.

In recent years, the random phase approximation has been expanded to incorporate polymer blends with more than two components.[11] It has been shown that the coherent SANS intensity $I(q)$ is related to the static structure factor matrix of the blend $\mathbf{S}(q)$

$$I(q) = \mathbf{B}^{T}\mathbf{S}(q)\mathbf{B} \quad (5)$$

where $\mathbf{B}$ is a column vector that contains the difference in scattering length densities, $b_i/v_i - b_j/v_j$ $(i \neq j)$ for blend components $i$ and $j$, and

$$\mathbf{S}^{-1}(q) = \mathbf{S}_0^{-1}(q) + \mathbf{V}(q) \quad (6)$$

where $\mathbf{S_0}(q)$ is the structure factor matrix for the bare system, i.e., the same combination of components but without interactions, and $\mathbf{V}(q)$ is the interaction matrix. When applied to a binary system, eq 6 produces the familiar RPA expression for two-component blends

$$\frac{1}{S(q)} = \frac{1}{\phi_1 V_1 P_1(q)} + \frac{1}{\phi_2 V_2 P_2(q)} - 2\frac{X_{12}}{k_B T} \quad (7)$$

$$\mathbf{B} = \frac{b_1}{v_1} - \frac{b_2}{v_2} \quad (8)$$

$$I(q) = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 S(q) \quad (9)$$

where the $P_i(q)$ are normalized form factors. For a ternary system, $\mathbf{S}(q)$ is a 2 × 2 matrix[11]

$$\mathbf{S}^{-1}(q) = \begin{bmatrix} \frac{1}{\phi_1 V_1 P_1(q)} + \frac{1}{\phi_3 V_3 P_3(q)} - \frac{2X_{13}}{k_B T} & \frac{1}{\phi_3 V_3 P_3(q)} + \frac{X_{12} - X_{13} - X_{23}}{k_B T} \\ \frac{1}{\phi_3 V_3 P_3(q)} + \frac{X_{12} - X_{13} - X_{23}}{k_B T} & \frac{1}{\phi_2 V_2 P_2(q)} + \frac{1}{\phi_3 V_3 P_3(q)} - \frac{2X_{23}}{k_B T} \end{bmatrix} \quad (10)$$

and $\mathbf{B}$ is a 2 × 1 matrix

$$\mathbf{B} = \begin{bmatrix} \frac{b_1}{v_1} - \frac{b_3}{v_3} \\ \frac{b_2}{v_2} - \frac{b_3}{v_3} \end{bmatrix} \quad (11)$$

$I(q)$ is given by application of eq 5. Note that if scattering data are available for all three binaries, then the RPA predicts the ternary system scattering without adjustable parameters. Likewise, if data are available for two of the binaries, the interaction coefficient for the third becomes a fitting parameter for the ternary, thus opening a SANS route to interaction coefficients between nonlabeled components.

Scattering data were obtained for two ternary systems to test the validity of three-component RPA. In ternary system A, the components are atactic head-to-tail polypropylene (PP), head-to-head polypropylene (hhPP), and a statistical copolymer made by saturating the double bonds in a polyisoprene from random 1,4 and 3,4 addition (50SPI). The chemical microstructure for each species is given in ref 3. Each binary pair forms single phase blends, so binary SANS data, together with the binary RPA, gives values of each interaction coefficient.[12,13] Therefore, the structure factor matrix $\mathbf{S}$ in eq 10 is completely specified, and the ternary SANS data are predicted by ternary RPA without adjustable parameters.

In ternary system B, the components are hydrogenated polybutadienes (model ethylene/1-butene statistical copolymers) with different compositions—25, 38, and 52 wt % butene, referred to as H25, H38, and H52.[1] Midrange compositions of the H25/H52 blends are phase separated at all accessible temperatures. The addition of H38, which is miscible with both H25 and H52, produces single-phase ternary blends, which can accordingly be analyzed by SANS and the ternary RPA to obtain $X_{H25/H52}$.

## Experimental Section

All materials except PPC (the atactic head-to-tail polypropylene used in this study) have been used in previous binary blend studies.[1-4] Each material is available in both fully

**Table 1. Molecular Characterization of Blend Components**

| sample | degree of polymerization | density at 23 °C (g/cm$^3$) | | final melting temp (°C) | deuterium atoms per monomeric unit in D version | carbon atoms per monomeric unit |
|---|---|---|---|---|---|---|
| | | $\rho_H$ | $\rho_D$ | | | |
| HPPC(DPPC) | 495 | 0.8525 | 0.9137 | | 5.96 | 6 |
| HhhPPA(DhhPPA) | 320 | 0.8726 | 0.9146 | | 3.97 | 6 |
| H50SPI(D50SPI) | 1485 | 0.8631 | 0.9126 | | 4.66 | 5 |
| H25(D25) | 1720 | 0.8798 | 0.9364 | 68 | 3.53 | 4 |
| H38(D38) | 1830 | 0.8598 | 0.9072 | 42 | 3.03 | 4 |
| H52(D52) | 1510 | 0.8604 | 0.9035 | | 2.75 | 4 |

**Table 2. Interaction Coefficients for Binary Blends**

| blend | $X \times 10^2$ (MPa) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $T$ = 27 °C | $T$ = 51 °C | $T$ = 83 °C | $T$ = 108 °C | $T$ = 121 °C | $T$ = 138 °C | $T$ = 167 °C |
| Ternary System A | | | | | | | |
| HPPC/DhhPPA | 5.81 | 4.92 | 4.29 | | 4.05 | | 2.99 |
| DPPC/HhhPPA | 11.6 | 10.3 | 9.02 | | 8.11 | | 7.13 |
| HPPC/D50SPI | −4.83 | −4.89 | −4.68 | | -4.45 | | -4.07 |
| DPPC/H50SPI | −3.25 | −3.03 | −2.90 | | -2.58 | | -2.31 |
| HhhPPA/D50SPI | two phases | 9.90 | 9.58 | | 8.32 | | 7.20 |
| DhhPPA/H50SPI | 8.26 | 7.16 | 6.12 | | 4.87 | | 4.18 |
| Ternary System B | | | | | | | |
| H25/D38 | | | | 5.07 | 4.64 | 4.34 | 3.95 |
| D25/H38 | | | 3.82 | | 2.72 | | 2.43 |
| H38/D52 | | | | 4.63 | | 4.22 | 3.87 |
| D38/H52 | | 4.09 | 3.36 | | 2.87 | | 2.59 |

hydrogenous and partially deuterated form, designated by the prefix H or D. Characterization information, obtained as in previous studies,[5] is summarized in Table 1.

The SANS measurements were conducted on the 8m beamline (NG5) at the NIST Cold Neutron Research Facility in Gaithersburg, MD. Sample preparation, experimental procedures and data reduction were performed as described in previous work;[5] all components are liquids at the experimental temperatures (27−167 °C for system A; 83−167 °C for system B). Equal volume fractions ($\phi = 0.50$) were used for all binary blends. The ternary blends for system A had equal volume fractions of each component ($\phi_i = 0.33$). The volume fractions for system B were 0.15, 0.70, and 0.15 for H25, H38, and H52, respectively, a composition that preliminary estimates indicated would be single phase over the experimental temperature range.

## Results

**Ternary System A: PP/hhPP/50SPI.** Since the interaction strengths associated with this system have been determined from binary blend SANS results, the structure factor matrix $\mathbf{S}(q)$ in eq 10 is completely defined according to the RPA. To determine normalized form factors $P_i(q)$ for the components, SANS measurements were performed on matched pairs according to our usual procedure.[5] Values of $X(T)$ for each two-component combination were determined,[12,13] with results given in Table 2. To account for isotopic labeling effects,[6] "label-switching" experiments were performed with different deuterium labeled components (i.e., HA/DB and DA/HB) for each two-component combination (see Table 2).

A total of six ternary blends were prepared which differ only in deuterium labeling:

| | |
|---|---|
| DPPC/HhhPPA/H50SPI | DPPC/DhhPPA/H50SPI |
| HPPC/DhhPPA/H50SPI | DPPC/HhhPPA/D50SPI |
| HPPC/HhhPPA/D50SPI | HPPC/DhhPPA/D50SPI |

Figure 1 shows SANS intensity comparisons between ternary RPA predictions and experimental data for three system A ternary blends. The agreement was excellent, without adjustable parameters, for each of the six ternary blends. To search for systematic errors, we examined the residual function

$$\Delta(q) = \frac{I_{\mathrm{PRED}}(q)\ I_{\mathrm{OBS}}(q)}{I_{\mathrm{OBS}}(q)} \qquad (12)$$

which is shown in Figure 2 for one of the ternaries. For this and the other ternaries as well, the variance was less than 2% and essentially independent of $q$.

The same data were used to test the sensitivity of the ternary method by making one binary $X$ an unknown, solving for it with the ternary SANS data, and then comparing those results with the results obtained from binary SANS data. Thus, data for the blend H50SPI/HPP/DhhPP were analyzed three times, solving for each $X(T)$ in turn (H50SPI/HPP, HPP/DhhPP, and H50SPI/DhhPP). Figure 3 compares those results with the binary SANS values. The agreement between binary and ternary results is gratifying, and it confirms the validity of the ternary RPA as a means for evaluating the interaction coefficients. It is worth noting that the random phase approximation would seem to impose no special restrictions on the interactions themselves. Thus, the three binaries in this case include negative values of $X$ with LCST behavior as shown in Figure 3 (PP/50SPI), positive $X$ with UCST behavior and "irregular" mixing[12] (PP/hhPP), and finally positive $X$ with UCST behavior and "regular" mixing[12] (50SPI/hhPP).

**Ternary System B: H25/H38/H52.** This system, consisting of three model ethylene/1-butene statistical copolymers, illustrates how one component can "bridge" the interactions between two other components. By addition of sufficient amounts of H38, which is miscible with both H25 and H52, an immiscible binary blend (H25/H52) becomes single-phase and thus accessible to SANS analysis. The ternary RPA SANS results are used here to determine $X_{\mathrm{H25/H52}}$. The interaction coefficients for H25/H38 and H38/H52 blends are known from previous studies[6,7] and are listed in Table 2. Those data were then interpolated to the SANS temperatures for the ternary blends (98, 118, 143, 167 °C) as needed.

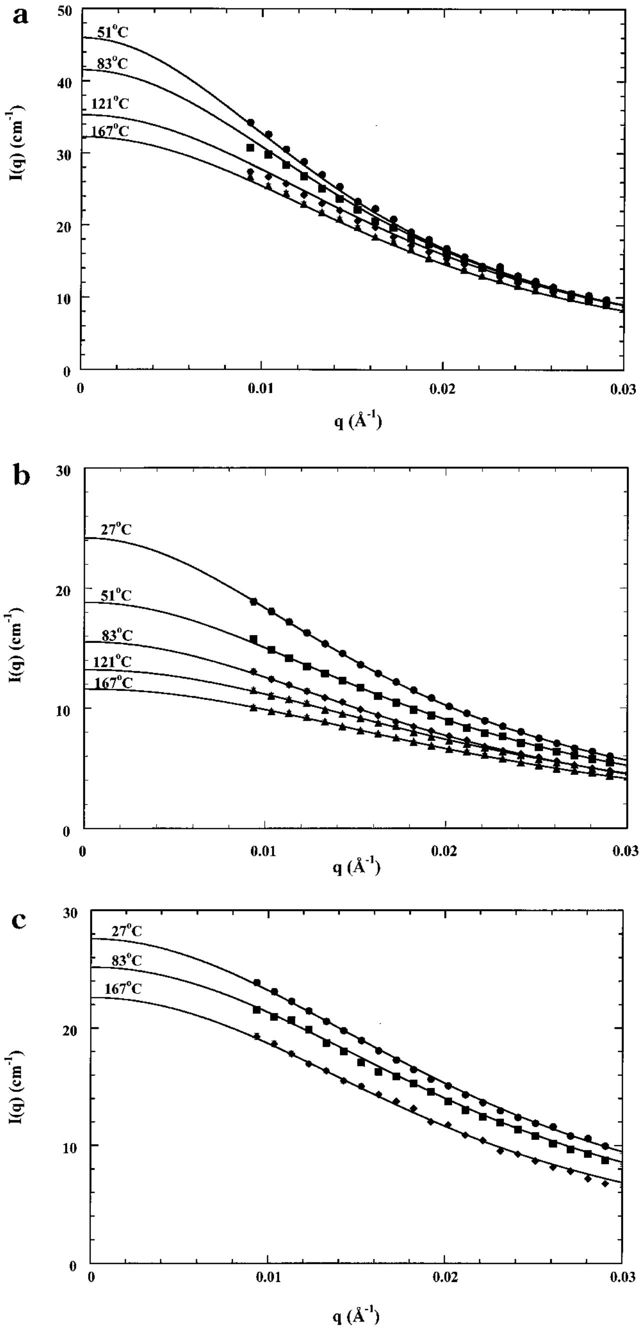

**Figure 1.** Comparison of ternary RPA predictions (solid lines) and ternary blend SANS data at various temperatures for three blends: (a) D50SPI/HPPC/HhhPPA; (b) H50SPI/HPPC/DhhPPA; (c) H50SPI/DPPC/DhhPPA.

Four ternary blends were prepared:

D25/H38/H52
H25/D38/H52
H25/H38/D52
D25/H38/D52

Figure 4a shows the ternary RPA fit of the SANS data at two temperatures for the H25/H38/D52 blend, with $X_{H25/D52}$ as the fitting parameter. Figure 4b shows the sensitivity of ternary RPA to the choice of $X_{H25/D52}$. As expected, the low $q$ data are most sensitive to the interaction strength. Uncertainties appear to be slightly larger than those for binary blends. Interaction coefficients were determined for each combination of isotopic labeling, D25/H52, H25/D52, D25/D52, and H25/H52, the last combination demonstrating how ternary blends may be used to obtain $X(T)$ for hydrogenous components. The results are given in Table 3 and plotted as a function of temperature in Figure 5. Note that $X$ for H25/D52 is consistently larger than $X$ for D25/H52 at each temperature and that the values for H25/H52 and D25/D52 are similar to one another and fall between the other two. These results are consistent with isotopic effects found earlier in binary blends (see eqs 3a and 3b).

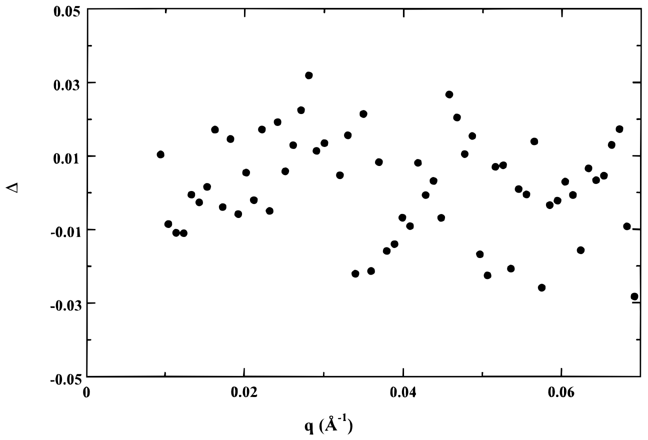

**Figure 2.** Residual function Δ as a function of $q$ for the ternary blend 50SPI/HPPC/HhhPPA at 83 °C.

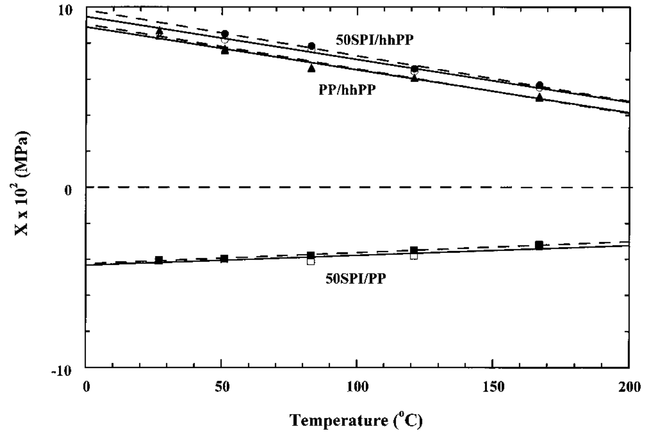

**Figure 3.** Comparison of $X(T)$ from binary and ternary blends (system A) for component pairs using the ternary blend H50SPI/HPP/DhhPP. Filled symbols and dashed lines are values and linear regression from binary blends, while open symbols and solid lines are values and linear regression from ternary blends.

Although $X(T)$ for H25/H52 blends has not been measured previously, it is possible to make an estimate based on a catalog of SANS-assigned solubility parameters for the components.[4] Figure 6 shows both the prediction of $X(T)$ by solubility parameters for H25/H52 and the values obtained from the ternary SANS data by applying eqs 3a and 3b. The temperature dependencies are similar, but the ternary-based values of $X$ are significantly smaller than the predictions. The measured values indicate a favorable mixing irregularity.[12]

There are three other pairs of components involving members of the H*xx* series for which the interactions are weaker than predicted by solubility parameter assignments:

(i) polyethylene/poly(1-butene) (H08 and H100 in our nomenclature); (ii) poly(1-butene)/poly(ethylene-*alt*-propylene) (H100/PEP); (iii) polyethylene/poly (ethylene-*alt*-propylene) (H08/PEP). The interaction strengths are relatively large for all three and were calculated from the order–disorder transition temperature of symmetric

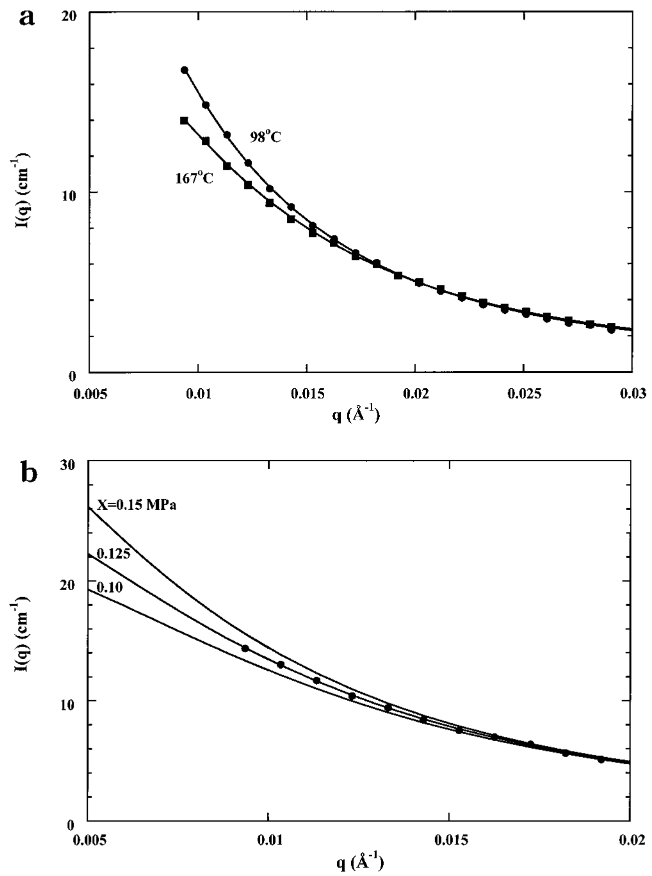

**Figure 4.** Comparison of ternary RPA model fit with ternary blend SANS data: (a) Intensity vs $q$ for the system H25/H38/D52 at various temperatures. The solid line indicates the full range fit using $X_{D25/H52}$ as an unknown. (b) Sensitivity of the RPA model to X. The solid lines indicate the RPA predictions using various $X_{H25/D52}$ values for the ternary blend H25/H38/D52 at 142 °C.

**Table 3. Interaction Coefficients from SANS Data for Ternary Blends**

| | | $X \times 10^2$ (MPa) | | | |
|---|---|---|---|---|---|
| ternary blend | component pair | $T =$ 98 °C | $T =$ 118 °C | $T =$ 142 °C | $T =$ 167 °C |
| D25/H38/H52 | D25/H52 | 10.9 | 8.44 | 6.43 | 6.14 |
| H25/D38/H52 | H25/H52 | 13.3 | 12.3 | 10.8 | 8.78 |
| H25/H38/D52 | H25/D52 | 14.4 | 13.3 | 12.5 | 12.1 |
| D25/H38/D52 | D25/D52 | 12.8 | 12.7 | 10.7 | 8.3 |
| Prediction | H25/H52 | 16.8[a] | 15.6[a] | 14.2[a] | 12.9[a] |

[a] Calculated with the values of $(\delta - \delta_{ref})_{SANS}$ listed in ref 4.

diblock copolymers.[15] The results at 167 °C for these pairs, as well as our ternary-based H25/H52 results, are given in Table 4. The experimental values of $X$ are smaller than the solubility parameter predictions in all cases.

Other examples of enhanced polyolefin blend miscibility are known. Blends with polyisobutylene[12] and with polypropylene[13] have values of $X$ that are less than the solubility parameter predictions, in some cases resulting in negative values of X. However, unlike the pairs listed in Table 4, they have common components (PIB or PP) that seem especially prone to unusual behavior.

That $X(T)$ for H25/H52 determined by the ternary method is significantly smaller than that calculated with the SANS-based solubility parameters still seems surprising to us. Thus, many crosschecks were used in assigning solubility parameters to members of the H*xx* series, and irregularity is in fact relatively rare for blends that contain H*xx* components. Pairs in system A on the other hand show a variety of binary blend irregularities, yet the agreement between those values and the ones obtained by the ternary method is excellent. We considered the possibility that the low concentrations of H25 and H52 ($\phi \approx 0.15$ for each) are somehow responsible, yet the values of $X$ appear to increase somewhat in the concentration extremes[14] and

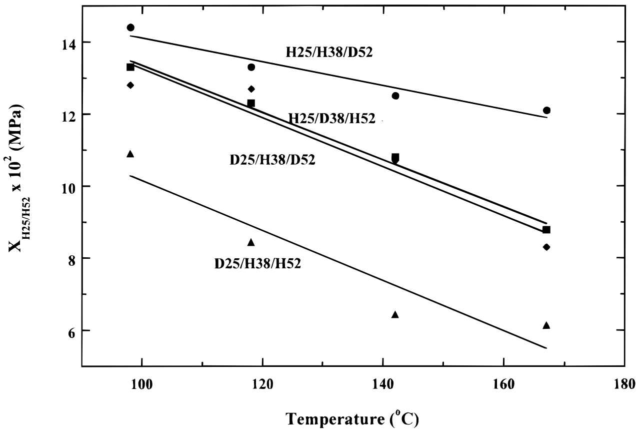

**Figure 5.** Values of $X_{H25/H52}$ from ternary SANS analysis for all system B ternary blends.

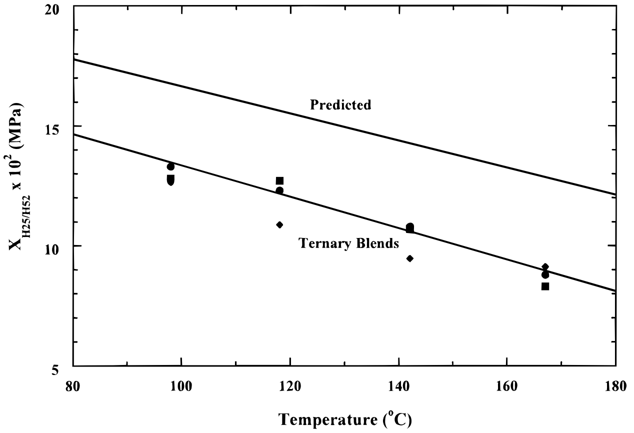

**Figure 6.** Solubility parameter data base predictions and ternary blend SANS results for $\chi_{H25/H52}$. The ternary blend results are displayed as follows: H25/D38/H52 (●), D25/H38/D52 (■), and the average of the $X$ values obtained from H25/H38/D52 and D25/H38/H52 using eq 3b (▲).

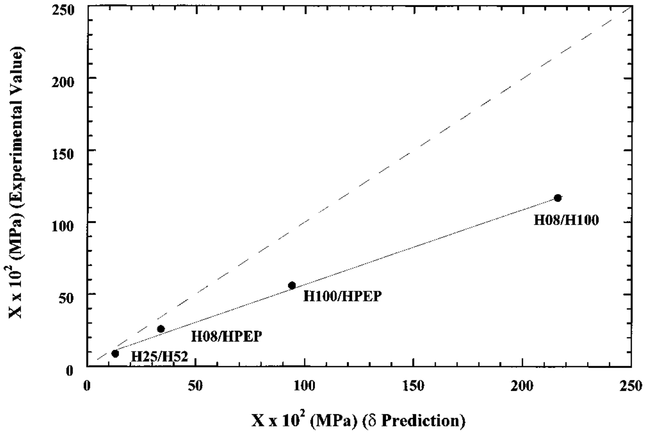

**Figure 7.** Interaction coefficient $X$ from experimental results vs solubility parameter predictions for various polyolefin systems at 167 °C. The solid line is a linear fit to the data, and the dotted line indicates where agreement between experimental results and $\delta$ predictions would occur.

**Table 4. Comparison of Predicted and Observed Interaction Coefficients at 167 °C**

| component pair | $X \times 10^2$ (MPa) predicted | $X \times 10^2$ (MPa) observed |
|---|---|---|
| H08/H100 | 216[a] | 117[b] |
| H100/PEP | 94[a] | 56[b] |
| H08/PEP | 34[a] | 26[b] |
| H25/H52 | 12.9[a] | 8.8[c] |

[a] Calculated with values of $(\delta - \delta_{\mathrm{ref}})_{\mathrm{SANS}}$ for the components. [b] Obtained from block copolymer order−disorder transition temperatures in ref 15. [c] Obtained by SANS for system B ternary blends in this work.

would thereby have produce a discrepancy in the opposite direction to that found.

## Summary

The SANS intensity profiles for ternary A (PP, hhPP, and 50SPI with various labeling configurations) were found to be in excellent agreement with predictions based on the random phase approximation and SANS data for the three binaries. The ternary scattering was sensitive to all three interaction coefficients, being shown to provide values of each in accord with those from the binary scattering. Since a fairly wide range of mixing irregularities were represented in ternary A, there appears to be little restriction on the nature of the interactions themselves. The agreement between binary and ternary results also demonstrates that the interaction coefficients are insensitive to composition ($\phi_i\phi_j = {}^1/_4$ for the binary SANS and ${}^1/_9$ for the ternary). Ternaries evidently offer a reliable method for determining interaction coefficients and would therefore be especially useful for evaluating the interactions for nonlabeled pairs and for pairs that do not form miscible binaries.

The ternary method was applied to ternary B (H25, H38, and H52, with various labeling configurations) to obtain the interaction coefficient for the H25/H52 pair, which does not form miscible binaries. Over the range of temperatures investigated, the interaction coefficient for H25/H52 was positive, as expected, but also significantly smaller than expected from the component solubility parameters. These results, and similar examples within the HPB series, suggest a pattern of repulsion reduction with increasing interaction strength. Thus, solubility parameters are assigned and verified by systems of connected blend sequences, each having relatively weak interactions, but they predict interaction strengths that are too large when applied to blends with relatively strong interactions. There are similar hints of different responses to weak and strong interactions from the pure component *PVT* properties.[4]

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