Neutron Scattering from Polymer Blends Under Pressure

B. HAMMOUDA[1]* and M. BENMOUNA[2]†

[1]National Institute of Standards and Technology, Bldg. 235, Room E151, Gaithersburg, Maryland 20899; [2]Department of Physics, Tulane University, New Orleans, Louisiana 70118 †On leave from: Department of Physics, University of Tlemcen, Tlemcen, Algeria

SYNOPSIS

A procedure is used to analyze small-angle neutron-scattering (SANS) data from a pressurized polymer blend mixture (deuterated polystyrene/polyvinylmethylether). The Lattice-Fluid (LF) equation-of-state model is used along with a compressible random phase approximation (RPA) in order to obtain free volume fractions and intermonomer interaction potentials. Solving the two sets of equations (LF and RPA) self-consistently within the fitting procedure to the SANS data provides an improvement over the familiar incompressible RPA model. In this approach, the free volume fraction is the main varying parameter. Intermonomer interaction potentials were found to depend on pressure (weakly) and temperature (linearly). © 1995 John Wiley & Sons, Inc.

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INTRODUCTION

Recent interest in pressure effects in polymer blends has prompted some experimental and theoretical efforts related to in situ small-angle neutron scattering (SANS). A couple of experiments have been reported[1,2] so far. A procedure for the treatment of SANS data from pressurized polymer blends has also been recently suggested by Bidkar and Sanchez.[3] This procedure is based on using an equation-of-state, the Sanchez-Lacombe lattice fluid (LF) model, and the compressible random phase approximation (RPA) in order to obtain the intermonomer interaction potentials. The purpose of our present investigations is to apply this method to analyze SANS data from deuterated polystyrene/polyvinylmethylether (PSD/PVME) taken at various pressures and temperatures.

A number of equation-of-state models are available to describe free volume effects in polymers. Cell models[4-6] associate a free volume component as part of the monomer volume, lattice fluid models[7] assume that free volume constitutes a separate component, whereas hole models[8] assume a combination of the above two features. A recent article[9] reviews the various equations-of-state and applies them to various polymer systems. Some of these equations-of-state are better at describing pressure-volume-temperature (PVT) data than others.[9]

Since the methods for preparing the PSD/PVME samples and for taking the SANS data have been described elsewhere,[2] we mention briefly the molecular weights (PSD-M_w = 188,000, PVME-M_w = 201,000) used, the PSD weight fractions (10%, 30%, 50%), the temperature range (60–150°C), and pressure range (0.1–81.6 MPa), then proceed directly to the description of the data reduction procedure and of the results obtained.

PROCEDURE FOR ANALYZING SANS DATA FROM POLYMER BLENDS

Following the compressible RPA method[3,10] and the LF equation-of-state, a general procedure is outlined for the treatment of SANS data from a mixture of two homopolymers at various temperatures and pressures. This method was suggested by Bidkar and Sanchez.[3]

Consider the "mixing" polymer fractions for the two polymer components ϕ_1 and ϕ_2 such that $\phi_1 + \phi_2$

= 1. Introduce a free volume fraction f_0 and "new" polymer fractions $f_1 = \phi_1(1 - f_0)$ and $f_2 = \phi_2(1 - f_0)$ such that $f_0 + f_1 + f_2 = 1$. Even though f_0 is not directly measurable, it can be estimated experimentally through precise PVT (density) measurements. Other definitions of standard parameters that describe the blend follow: monomer "hard core" volumes are v_1^* and v_2^*, statistical segment lengths are l_1 and l_2, neutron scattering lengths are b_1 and b_2 and degrees of polymerization are N_1 and N_2.

The Lattice Fluid Equation-of-State

The LF model has been extensively applied to PVT data from single-component polymers. In this approach, it is common to introduce cohesive energy densities (internal pressures) P^* and characteristic temperatures T^* (which are tabulated quantities[9,11]), in order to write down the LF equation-of-state:

$$(1 - f_0)^2 + P/P^*$$
$$+ [\ln(f_0) + 1 - f_0]T/T^* = 0 \quad (1)$$

where the term $1/N = \phi_1/N_1 + \phi_2/N_2$ has been neglected compared to unity.

The polymer blend mixture is a two-component system with internal pressures $P_{ij}^* = -W_{ij}/2v^*$ where W_{ij} is the interaction energy between monomers of kind i and j, v^* is a "reference" volume (often taken to be equal to $(v_1^* v_2^*)^{1/2}$) and $P_{ii}^* = P_i^*$ is understood. With these definitions, the familiar Flory-Huggins interaction parameters are expressed as: $\chi_{ij}k_BT/v^* = -2P_{ij}^* + (P_{ii}^* + P_{jj}^*) = W_{ij}/v^* - (W_{ii} + W_{jj})/2v^*$ where k_B is the Boltzmann constant. Because P_i^*'s are tabulated, one does not even have to define v^*. Following Bidkar and Sanchez,[3] the P^* and T^* for the blend follow the mixing rule:

$$P^* = \phi_1^2 P_1^* + 2\phi_1\phi_2 P_{12}^* + \phi_2^2 P_2^*$$
$$k_BT^* = P^* v_0 \quad (2)$$

and v_0 is the volume of each of the "holes" that constitute the free volume:

$$v_0 = 1/[\phi_1 P_1^*/k_BT_1^* + \phi_2 P_2^*/k_BT_2^*]. \quad (3)$$

The LF equation-of-state can be used to obtain f_0 in terms of the other known parameters which are: ϕ_1, ϕ_2, P_1^*, P_2^*, T_1^*, T_2^* given the measurement pressure and temperature of the blend mixture. Since the unknown parameter P_{12}^* is also needed,

an initial guess at its value $P_{12}^* = (P_1^* P_2^*)^{1/2}$ is used at first.

Sanchez and Panayiotou[11] gave for the deuterated polystyrene/polyvinylmethylether (PSD/PVME) blend system under consideration:

$$\text{PSD:} \quad P_1^* = 355 \text{ MPa}, \; T_1^* = 731 \text{ K},$$

$$\text{PVME:} \quad P_2^* = 353 \text{ MPa}, \; T_2^* = 657 \text{ K}, . \quad (4)$$

Given the initial guess for the intercomponent cohesive energy P_{12}^* we have obtained estimates of the free volume fractions for varying pressure, temperature, and PSD composition.

The Compressible Random Phase Approximation Equations

The RPA equations in their original form were developed for an incompressible polymer blend mixture. Since experimental evidence points to the fact that PSD/PVME blends are compressible,[1,2] the mixture is described as a three-component (polymers as components 1 and 2 and "voids" as component 0) incompressible system (this is also referred to as a two-component compressible system). The RPA equations for a ternary incompressible system are[12-14]:

$$S_{11}(Q) = S_{11}^o(1 + V_{22}S_{22}^o)/$$
$$[(1 + V_{11}S_{11}^o)(1 + V_{22}S_{22}^o) - V_{12}^2 S_{11}^o S_{22}^o]$$
$$S_{22}(Q) = S_{22}^o(1 + V_{11}S_{11}^o)/$$
$$[(1 + V_{11}\dot{S}_{11}^o)(1 + V_{22}S_{22}^o) - V_{12}^2 S_{11}^o S_{22}^o]$$
$$S_{12}(Q) = -S_{11}^o V_{12}S_{22}^o/$$
$$[(1 + V_{11}S_{11}^o)(1 + V_{22}S_{22}^o) - V_{12}^2 S_{11}^o S_{22}^o] \quad (5)$$

where the voids enter only through the "excluded volumes":

$$V_{11} = 1/S_{00}^o - 2P_1^*/k_BT + C_{11}$$
$$V_{22} = 1/S_{00}^o - 2P_2^*/k_BT + C_{22}$$
$$V_{12} = 1/S_{00}^o - 2P_{12}^*/k_BT + C_{12} \quad (6)$$

and the various "ideal" chain structure factors are taken to be:

$$S_{11}^o(Q) = N_1 f_1 v_1^* D_1(Q)$$
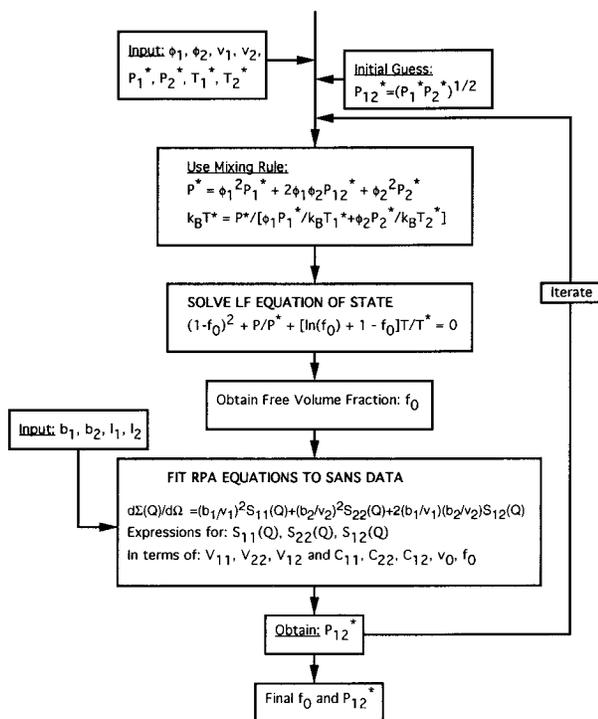$$S_{22}^o(Q) = N_2 f_2 v_2^* D_2(Q)$$
$$S_{00}^o = v_0 f_0$$

Figure 1.   Flow chart of the procedure used to analyze SANS data from pressurized and/or heated polymer blends.

$$D_i(Q) = 2[\exp(-Q^2 R_{gi}^2) - 1 + Q^2 R_{gi}^2]/Q^4 R_{gi}^4. \quad (7)$$

where the radius of gyration R_{gi} is given in terms of the statistical length l_i as $R_{gi} = (N_i l_i^2/6)^{1/2}$.

The C_{ij} coefficients are contributions from the composition dependence of the average void size v_0 and are given by:[3]

$$C_{12} = \{\ln(f_0) + (1 - f_0)\}$$

$$\times (\phi_1 - \phi_2)(P_1^*/k_B T_1^* - P_2^*/k_B T_2^*)/(1 - f_0)^2$$

$$C_{11} = -2\phi_2\{\ln(f_0) + (1 - f_0)\}$$

$$\times (P_1^*/k_B T_1^* - P_2^*/k_B T_2^*)/(1 - f_0)^2$$

$$C_{22} = 2\phi_1\{\ln(f_0) + (1 - f_0)\}$$

$$\times (P_1^*/k_B T_1^* - P_2^*/k_B T_2^*)/(1 - f_0)^2. \quad (8)$$

Finally, the SANS cross-section is given by:

$$d\Sigma(Q)/d\Omega = (b_1/v_1^*)^2 S_{11}(Q) + (b_2/v_2^*)^2 S_{22}(Q)$$

$$+ 2(b_1/v_1^*)(b_2/v_2^*)S_{12}(Q). \quad (9)$$

Using the free volume fraction f_0 obtained from the LF equation-of-state, SANS data from the PSD/

PVME blend at various pressures and temperatures[2] are analyzed using this approach. Nonlinear least-squares fitting of the data yields a value for P_{12}^* in each case which is then fed back into the LF equation-of-state in order to obtain a more realistic value for f_0. This process is repeated until it converges, therefore resulting in a self-consistent solution of the set of LF and RPA equations (see Fig. 1).

DISCUSSION AND RESULTS

Typical SANS data are shown in Figure 2 whereby the scattered intensity $I(Q)$ increases with temperature (as the LCST spinodal temperature is approached). The forward scattered intensity $I(0)$ decreases with pressure (Fig. 3) which points to an upward shift of the spinodal temperature (by as much as $25-30°C/KBar$) as reported before.[1,2]

The other parameters required to analyze the SANS data are:

PSD: $N_1 = 1679$, $b_1 = 1.066 \times 10^{-11}$ cm,

$$v_1^* = 1.6 \times 10^{-22} \text{ cm}^3$$

PVME: $N_2 = 3466$, $b_2 = 3.305 \times 10^{-13}$ cm,

$$\text{and } v_2^* = 8.8 \times 10^{-23} \text{ cm}^3$$

along with the various volume fractions reported in ref. 2. In the fitting to the RPA equations, P_{12}^* and an average segment length l_{av} were floated (the PSD and PVME segment lengths are then obtained as: $l_1 = l_{av}(v_1^*/v^*)^{1/2}$, $l_2 = l_{av}(v_2^*/v^*)^{1/2}$). Solutions of the LF-RPA equations resulted in reasonable values
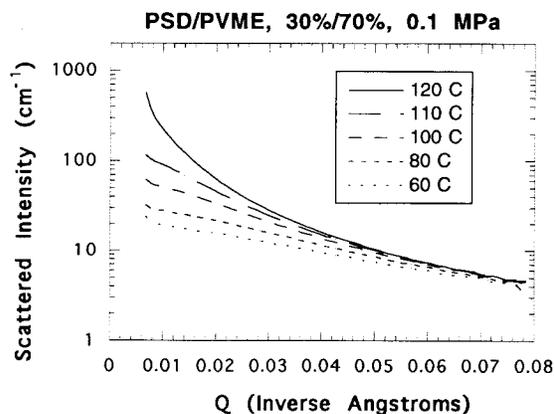

Figure 2.   SANS intensity for a PSD/PVME sample (30/70%) measured for temperatures between 60 and 120°C and atmospheric pressure.
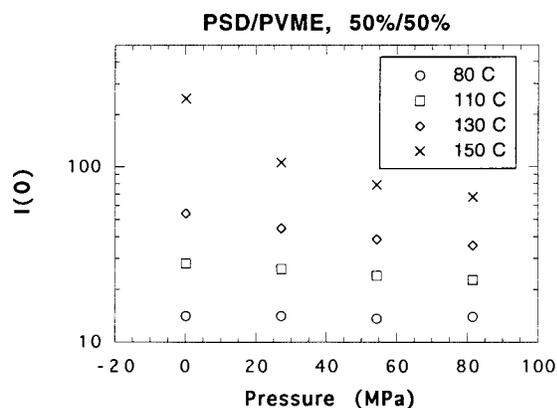
Figure 3. Variation of the forward scattered intensity $I(0)$ (obtained from a Zimm plot) with pressure for the 50/50% PSD/PVME sample at four temperatures.

for the free volume f_0 as shown in Figure 4; f_0 is found to decrease with pressure, increase with temperature, and decrease slightly with PSD composition. These results are in agreement with what limited PVT data have been reported on polystyrene/polyvinylmethylether.[6]

In the RPA approach described here (three-component incompressible or two-component compressible), free volume enters only through the terms $1/v_0 f_0$ and C_{ij}. The two-component incompressible RPA (de Gennes) formula is recovered by taking f_0 to zero. The LF-RPA procedure assumes a main varying parameter (f_0) to describe pressure, temperature, and composition effects. This approach is appropriate to use even when only temperature is varied (pressure term is neglected for atmospheric pressure in the equation-of-state). Fits of the PSD/PVME SANS data to the LF-RPA equations lead to P_{12}^* values that depend on pressure (weakly), temperature (linearly), and composition (Fig. 5). It is interesting to note, however, that the pressure dependence of P_{12}^* is much weaker than that of X_{12} (see ref. 2); the trend of this variation is different in the compressible and incompressible cases ($f_0 \neq 0$ and $f_0 = 0$). The systematic linear temperature variation of P_{12}^* points to the fact that this approach is not accounting for the enthalpic part of the inter-monomer interactions (X_{12}) properly. Actually, Sanchez and Balazs[15] argued for the addition of an entropic contribution to X_{12} when specific interactions are included (as in the case of PSD/PVME). In the same figures (Fig. 5) are also included variations of P_{12}^* corresponding to the incompressible limit ($f_0 \rightarrow 0$). Overall, the LF-RPA approach is a modest improvement over the incompressible RPA
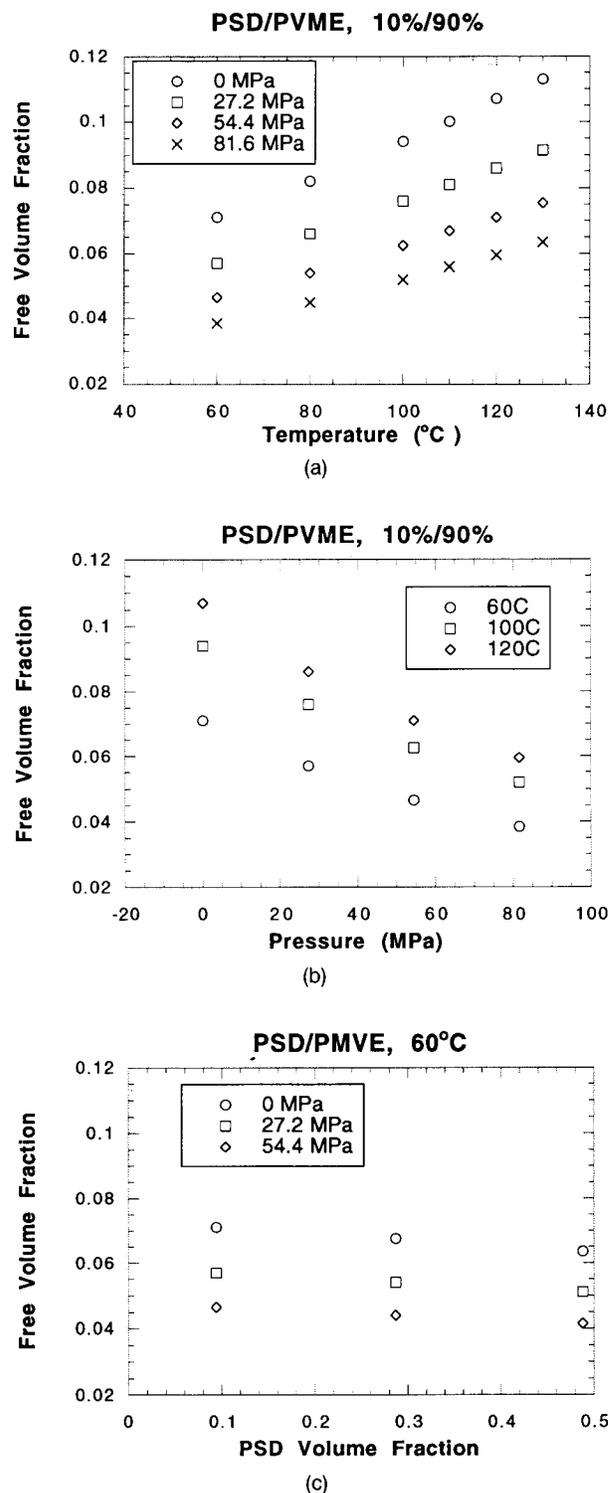

(a)

(b)

(c)

Figure 4. Variations of the free volume fraction f_0 obtained from the self-consistent solution of the lattice fluid equation-of-state for increasing (a) temperature (10%/90%), (b) pressure (10%/90%), and (c) PSD volume fraction (60°C). Note that the PSD volume fractions (9.4, 28.7, and 48.8%) are slightly different from the weight fractions (10, 30, 50%).
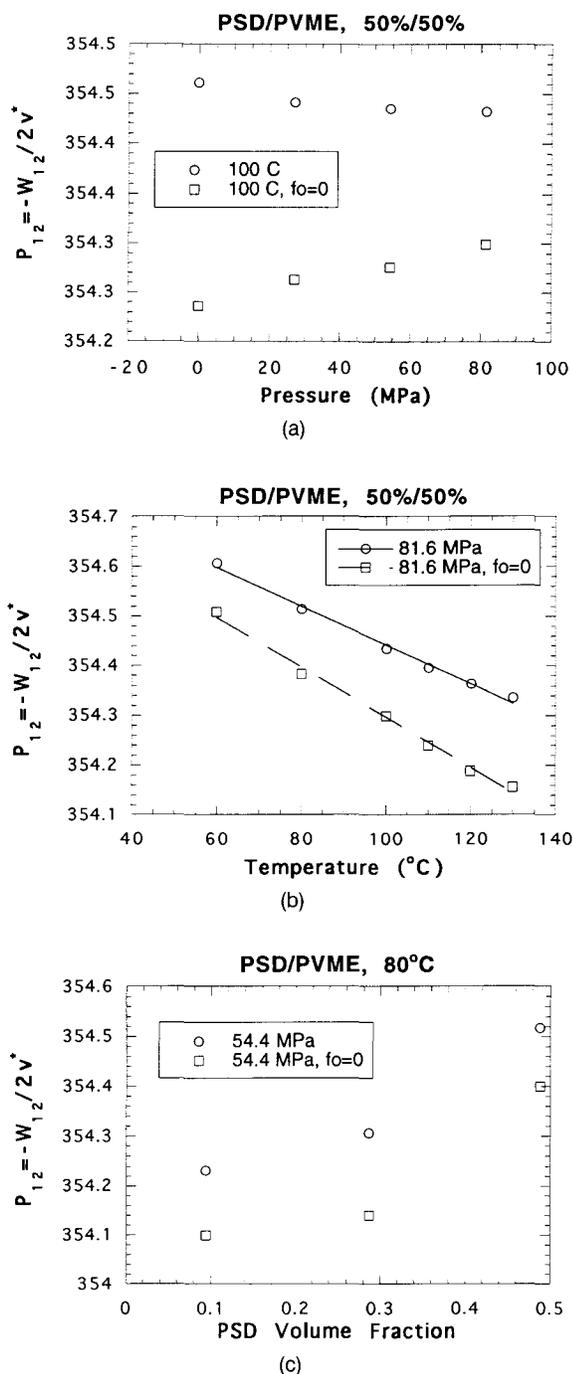
Figure 5. Variations of the intercomponent interaction cohesive energies P_{12}^* obtained from the self-consistent solution of the compressible RPA equations for increasing (a) temperature (50/50%), (b) pressure (50/50%), and (c) PSD volume fraction (temperature of 80°C).

approach (e.g., shows weaker composition dependence). Another approach by Tang and Freed[16] and Dudowicz and Freed[17] analyzes compressibility effects in polymer blend mixtures from a different

perspective (lattice cluster model) and leads to similar observations concerning the variation of intermonomer interactions with temperature, pressure, and composition.

Our results as well as those of Bidkar and Sanchez[3] are showing that this LF-RPA approach is very sensitive to slight variations in pressure and temperature and could potentially be more precise than PVT measurements. The main drawback at this stage is that it uses tabulated values for pure component properties (P_1^*, T_1^*, v_1^*, P_2^*, T_2^*, v_2^*) that were obtained from PVT data. Since the described method is quite sensitive to slight changes in these values, we intend to explore, in the future, the possibility of obtaining even these parameters from SANS measurements as described below.

An alternative approach to obtain pure component characteristics (P_1^*, T_1^*, v_1^*, P_2^*, T_2^*, v_2^* are usually obtained from PVT studies) from SANS measurements is described here. Careful neutron transmission measurements from a pure homopolymer melt (say, PSD or PVME) measured for various sample pressures and temperatures would yield the total macroscopic scattering cross-section as: $\Sigma_s = -\ln(T)/t$ where T is the transmission and t is the sample thickness. This cross-section represents contributions from coherent scattering (small for homopolymer melts) and incoherent scattering and is related to the microscopic cross-sections and the number density of monomers n/V as: $\Sigma_s = (n/V)\sigma_s$. Since σ_s can be calculated for specific monomers based on tabulated values for their constituent nuclei, n/V can therefore be obtained from SANS transmission measurements. The free volume fraction is given by $f_o = 1 - v^*/v_s$ where v^* is the "hardcore" monomer volume and v_s is the specific monomer volume ($v_s = V/n$). The v_s values obtained (from SANS transmission measurements) for each temperature and pressure, can be used in the LF equation-of-state in order to obtain the sought parameters (P^*, T^*, and v^* for each component). Inelasticity corrections (important at long wavelengths) would bring a level of difficulty to this approach. Inserting the obtained values into a two-component incompressible (e.g., PSD plus holes) RPA formula and comparing the calculated and measured SANS scattered intensities ($d\Sigma/d\Omega$) would represent a self-consistency check of the LF-RPA approach.

periments have been performed on the NG3 30 m SANS instrument at NIST. M. Benmouna was supported through a Fullbright Fellowship. Identification of certain equipment or materials does not imply recommendation by the National Institute of Standards and Technology.

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