

# Temperature, composition and molecular-weight dependence of the binary interaction parameter of polystyrene/poly(vinyl methyl ether) blends

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The binary interaction parameter  $\chi_{\text{eff}}$  has been obtained for deuterated polystyrene/poly(vinyl methyl ether) blends as a function of temperature, composition and molecular weight from small-angle neutron scattering experiments. The consistency of the correlation length  $\xi$ , the zero-wavenumber scattering intensity  $S(0)$  and the  $\chi_{\text{eff}}$  parameter with the mean-field prediction has been demonstrated by the  $q$  dependence of the static structure factor  $S(q)$  and the  $1/T$  dependence of  $\xi^{-2}$ ,  $S(0)^{-1}$  and  $\chi_{\text{eff}}$ . The effective interaction parameter  $\chi_{\text{eff}}$  can be related to the Flory–Huggins interaction parameter  $\chi_F$ . The free-energy function as well as the spinodal curve and cloud-point curve have been constructed.

**(Keywords: interaction parameter; polystyrene; poly(vinyl methyl ether); blends)**

## INTRODUCTION

The technical importance of polymer blends has been well recognized in recent years<sup>1</sup>. Making polymers miscible through chemical structure modification is a very important topic, but miscibility may not be the ultimate characteristic one is looking for. This is because synergistic effects which enhance the property of a phase-separated material mainly come from molecular alignment, reinforcement, phase domain size and morphology.

In order to understand and possibly control the domain sizes and morphology due to phase decomposition, one has to understand thermodynamics (statics) as well as phase-separation kinetics (dynamics). We understand that statics and dynamics are inseparable subjects if we wish to talk about phase behaviour of even a simple binary system. The most important quantity needed in both static and dynamic characterization is the free energy (of mixing) of the system as a function of temperature and composition. For the case of polymer systems, we also need to know the molecular-weight dependence of the free-energy function.

Small-angle neutron scattering (SANS) has been used<sup>2–4</sup> to measure the effective or scattering binary interaction parameter  $\chi_{\text{eff}}$  (for convenience, we will drop the subscript 'effective' or 'scattering' throughout this

paper and define  $\chi_{\text{eff}} = \chi_{\text{scatt}} = \chi$ ) for a deuterated polystyrene/poly(vinyl methyl ether) (PSD/PVME) system. This technique offers a rather simple, fast and accurate method of obtaining the  $\chi$  parameter. Therefore, a systematic study of this  $\chi$  parameter as a function of composition ( $\phi$ ), temperature ( $T$ ) and molecular weight ( $MW$ ) is possible.

The extraction of the  $\chi$  parameter from SANS measurements depends on the mean-field nature of the polymer system and the random-phase approximation (RPA) calculation. Nevertheless, within our measurement error, we have found this procedure quite satisfactory. Furthermore, we should point out that the  $\chi$  parameter extracted from this procedure is different from the  $\chi_F$  parameter in the Flory–Huggins free-energy function as long as the  $\chi_F$  parameter is allowed to be compositionally dependent. The exact origin of this compositional dependence of  $\chi_F$  is not certain. It could be caused by residual entropic effects of monomer size difference between the two components, by the local packing orientations, by the chain-end effect, etc.<sup>5–8</sup>. We shall discuss the relationship between  $\chi$ , which is measured in our experiment, and  $\chi_F$ , which is used in the free-energy function of Flory–Huggins type later. We should point out that we have allowed the  $\chi_F$  to be compositionally dependent, which is different from the original definition of the Flory–Huggins  $\chi$  parameter. Essentially, we have incorporated all residual compositional dependence into  $\chi_F$ . But, as long as the interaction between the two types of monomer can be described by a single  $q$ -independent potential function  $U(\phi, T)$  at a given  $\phi$  and  $T$ , the RPA calculation will provide a general scattering factor  $S(q)$ , which allows the extraction of the effective interaction parameter  $\chi$  from

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the scattering experiment. Then, through the compositional dependence of  $\chi$ , the free-energy function can be constructed according to the calculation by Sanchez<sup>9</sup>, which will be demonstrated later.

In this paper, we present a systematic study of the effective  $\chi$  parameter as a function of  $\phi$ ,  $T$  and  $MW$  for high-molecular-weight and narrow-molecular-weight-distribution deuterated polystyrene/poly(vinyl methyl ether) systems by the SANS technique. The free-energy function has then been constructed numerically from these measurements.

## THEORETICAL BACKGROUND

It has been shown by de Gennes<sup>10</sup> and later by Binder<sup>11</sup> that for a non-interacting polymer system, the random-phase approximation calculation gives an inverse additivity of the scattering structure factor  $S(q)$ . In other words, the inverse of the total scattering structure factor  $S(q)$  equals the sum of the inverse of the individual structure factor  $S_A(q)$  and  $S_B(q)$  for a binary polymer system:

$$\frac{1}{S(q)} = \frac{1}{N_A \phi_A S_A(q)} + \frac{1}{N_B \phi_B S_B(q)} \quad (1)$$

On the other hand, for an interacting system with a mean-field potential  $U$ , the total structure factor can be represented as:

$$\frac{1}{S(q)} = \frac{1}{N_A \phi_A S_A(q)} + \frac{1}{N_B \phi_B S_B(q)} - 2\chi \quad (2)$$

By putting in the scattering lengths and other constants, equation (2) can be written as<sup>4</sup>:

$$\frac{k_N}{S(q)} = \frac{1}{\phi_A N_A v_A S_D(U_A)} + \frac{1}{\phi_B N_B v_B S_D(U_B)} - \frac{2\chi}{v_0} \quad (3)$$

where

$$k_N = N_0 \left( \frac{a_A}{v_A} - \frac{a_B}{v_B} \right)^2$$

with  $N_0$  being the Avogadro number,  $a_i$  being the scattering length per mole of monomer  $i$ ,  $v_0$  and  $v_i$  being the molar volumes of a reference unit cell and of the  $i$ th segment respectively. The single-chain structure factor  $S_D(U_i)$  may be represented by the Debye function:

$$S_D(U_i) = \frac{2}{U_i^2} [\exp(-U_i) - 1 + U_i] \quad (4)$$

with  $U_i = q^2 R_{g,i}^2 / 3$  and  $q$  is the magnitude of the scattering wavevector:

$$q \equiv |\mathbf{q}| = (4\pi/\lambda) \sin(\theta/2)$$

$\lambda$  is the wavelength of the incident beam and  $\theta$  is the scattering angle.  $R_{g,i}$ ,  $N_i$  and  $\phi_i$  are the radius of gyration, the degree of polymerization and the volume fraction of polymer  $i$ , respectively. The  $\chi$  parameter obtained is related to the mean-field potential  $U$  for a given composition and temperature as:

$$U = v_A v_B \chi / v_0^2 \quad (5)$$

By the expansion of the Debye function and dropping all terms higher than the second moment, equation (3) can be written in the Ornstein-Zernike form:

$$S(q) = S(q=0) / [1 + \xi^2(T, \phi) q^2] \quad (6)$$

with

$$\xi^2(T, \phi) = \frac{\bar{b}^2}{36} [\phi_A \phi_B (\chi_s - \chi)]^{-1} \quad (7)$$

and

$$\frac{\bar{b}^2}{v_0} = \phi_A \phi_B \left( \frac{b_A^2}{v_A \phi_A} + \frac{b_B^2}{v_B \phi_B} \right) \quad (8)$$

where  $\xi(T, \phi)$  is the correlation length at temperature  $T$  and composition  $\phi = \phi_A$ ,  $b_i$  is the statistical segment length of the  $i$ th component and  $\chi_s$  is the effective  $\chi$  parameter at the spinodal point:

$$\frac{\chi_s}{v_0} = \frac{1}{2} \left( \frac{1}{v_A \phi_A N_A} + \frac{1}{v_B \phi_B N_B} \right) \quad (9)$$

In the vicinity of the phase separation temperature, both  $S(q=T, \phi)$  and  $\xi(T, \phi)$  may have scaling forms as often observed in critical fluctuation phenomena:

$$S(q=0, T, \phi) = S_0(\phi) \varepsilon^{-\nu} \quad (10)$$

$$\xi(T, \phi) = \xi_0(\phi) \varepsilon^{-\gamma} \quad (11)$$

where

$$\varepsilon = \left| \frac{T - T_c}{T_c} \right| \quad (12)$$

If a binary polymer system can be described by the mean-field model<sup>12,13</sup>, then  $\nu$  and  $\gamma$  should have values of 1/2 and 1 respectively. One should notice that  $\chi$  has a unit of energy per  $k_B T$ ; the  $1/T$  dependence of  $\chi$  together with equations (3) and (7) predict that in the vicinity of the critical temperature  $T_c$ :

$$S(0, T, \phi) \propto |T - T_c|^{-1} \quad (13)$$

and

$$\xi(\phi) \propto |T - T_c|^{-1/2} \quad (14)$$

These are consistent with the mean-field exponents of  $\nu$  and  $\gamma$ . However, this is a result which should be expected because the RPA calculation itself is a mean-field calculation. Therefore, a check on the  $1/T$  dependence of  $\chi$  or a check on equations (13) and (14) are equivalent to a check on the mean-field exponents  $\nu$  and  $\gamma$ . We shall discuss this point again in the discussion section.

## EXPERIMENTAL

### Materials

Poly(styrene- $d_8$ ) (PSD) was prepared by anionic polymerization of styrene- $d_8$  in benzene with

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