$(p^{-2})$ . Therefore, the former rotation makes a significant contribution to  $[\eta]$  for  $p \lesssim 10$ . (The numerical solutions<sup>3</sup> show that the two contributions are of the same order of magnitude at p = 2.) Thus it follows that  $[\eta]$  with the slip boundary condition may be appreciably smaller than that with the stick boundary condition only for  $p \lesssim$ 10, while the effects on it may be regarded as negligibly small for larger p.

#### Conclusion

We have examined various possible sources of the disagreement between the diameters estimated from different transport coefficients by the use of our equations for them for cylinder models. The most probable source seems to be the replacement of rough surfaces of real macromolecular chains by smooth surfaces; the trend of disagreement may be interpreted by this effect. The possible breakdown of the stick boundary condition on the rough surfaces is immaterial. Then there arises the question: Why is the diameter from crystallographic data close to that from  $\bar{s}$  for some cases and to that from  $[\eta]$  for others? Probably the answer is that it depends on the degree of solvation. As seen from eq 5, the diameter from crystallographic data may be closer to that from  $\bar{s}$  or from  $[\eta]$  as the degree of solvation is small or large. Of course, there are not few cases for which the good agreement between the diameters is found. A typical example is a triple helix of Schizophyllum commune polysaccharide.29 The cylinder model is a good approximation to them.

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# Chain Dimensions and Interaction Parameters in Neutron Scattering from Polymer Blends with a Labeled Component

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ABSTRACT: A short derivation is presented of the scattering laws for a two-component polymer blend in which one component contains some deuterated molecules. It is shown that the scattering can be separated into two terms, one arising from the single-chain contribution of the deuterated molecules and the other arising from concentration fluctuations within the blend. This second term contains the interaction parameter. The application of this scattering law in interpreting results from real systems is discussed and its use demonstrated on data from two low molecular weight polymer blends.

## 1. Introduction

It has recently become clear that the best way of observing single-chain properties in small-angle neutron scattering from polymer blends is by deuterating a reasonably high fraction (c) of a component, labeled 1, rather than only small fractions and then letting  $c \rightarrow 0$  in a Zimm analysis (the usual way<sup>2</sup> of seeing single-chain properties in a dense environment).

Another aspect of investigations of blends is the recognition by de Gennes<sup>3</sup> that the random phase approximation (RPA) can be applied in such dense systems of chains

to calculate the response functions and thus the scattering cross sections.

We present here a short derivation of the general scattering law for a two-component blend (with a fraction c of the component 1 deuterated) which has been referred to in a series of papers by Summerfield and Akcasu<sup>1</sup> but not explicitly derived. We use this derivation as a vehicle for discussing what the apparent "single-particle" law actually means. This is all clarified (by a simple extension of the de Gennes results to the case where the monomer volumes  $v_1$  and  $v_2$  of the components are not the same)

when an explicit form of the interaction is introduced. For a dense system it is clear that the Flory interaction parameter U, described interactions between monomers, is more appropriate in the scattering function than the use of a second virial coefficient  $A_2$ . Indeed scattering, via a formula to be presented, is a way of extracting the interaction parameter in order that it can be compared with its value used in thermodynamic investigations of blends. In the second part of the paper we demonstrate the practical aspects by applying the derived formulas to analyses of small-angle neutron scattering results for two blend systems.

#### 2. Neutron Scattering of Two-Component Blends

Let the two components have monomer volumes  $v_1$  and  $v_2$  (let  $\beta = v_1/v_2$ ) and have scattering lengths, per monomer, a and b, respectively. The scattering length of component 2 will appear in a form (b') scaled by the relative volumes of the species; that is,  $b' = \beta b$ . Let a fraction (c) of species 1 be deuterated and denote the scattering lengths of the deuterated and protonated monomers of this species by d and h, respectively. We will use, on deuteration, an average value of a  $(\bar{a})$  defined by

$$\bar{a} = cd + (1 - c)h$$

In solid polymer mixtures the scattering from the compositional fluctuations of long, connected objects is huge compared with that from the density fluctuations. Thus in the de Gennes picture we consider polymer blends to be locally and globally incompressible. If the concentration of monomers is  $\phi$ , with

$$\phi(\mathbf{r}) = \phi_1(\mathbf{r}) + \phi_2(\mathbf{r})$$

then there exist mean concentrations

$$\bar{\phi} = \bar{\phi}_1 + \bar{\phi}_2$$

with compositional fluctuations  $\delta \phi_i(\mathbf{r})$  from the mean values,  $\bar{\phi}_i$ , such that

$$\phi_i(\mathbf{r}) = \bar{\phi}_i + \delta\phi_i(\mathbf{r})$$

The condition of incompressibility is expressed by the relation

$$\delta\phi_2(\mathbf{r}) = -(v_1/v_2)\delta\phi_1(\mathbf{r}) \tag{2.1}$$

The scattering cross section  $S(\mathbf{q})$  of neutrons from the compositional fluctuations in the blend will be simply derived below and yields

$$S(\mathbf{q}) = c(1-c)(d-h)^2 \chi_{1s}(\mathbf{q}) + (\bar{a} - b')^2 \chi_1(\mathbf{q})$$
 (2.2)

Here,  $\chi_{1s}(\mathbf{q})$  and  $\chi_1(\mathbf{q})$  are correlation functions for the 1 component of the system, the former being for *self*-correlations (within a single chain) and the latter involving cross terms between chains as well as the intrachain correlations. Thus  $\chi_1(\mathbf{q})$  is given by

$$\chi_1(\mathbf{q}) = \langle \delta \phi_1(\mathbf{q}) \delta \phi_2(-\mathbf{q}) \rangle \tag{2.3}$$

The derivation of (2.2) proceeds by noting that a fluctuation in scattering length density  $\delta\omega(\mathbf{q})$  is

$$\delta\omega(\mathbf{q}) = d\delta\phi_d + h\delta\phi_h - b'(\delta\phi_d + \delta\phi_h) \tag{2.4}$$

(employing (2.1)). Thus for  $S(\mathbf{q})$  we have

$$S(\mathbf{q}) = \langle \delta\omega(\mathbf{q})\delta\omega(-\mathbf{q}) \rangle = (d - b')^2 \langle \delta\phi_d(\mathbf{q})\delta\phi_d(-\mathbf{q}) \rangle + (h - b')^2 \langle \delta\phi_h(\mathbf{q})\delta\phi_h(-\mathbf{q}) \rangle + 2(d - b')(h - b') \langle \delta\phi_d\delta\phi_h \rangle$$
(2.5)

Let  $F_s(\mathbf{q})$  and  $F_x(\mathbf{q})$  denote the correlations between monomers within one chain and cross terms between chains, respectively. We then have for n chains in unit volume

$$\langle \delta \phi_d \delta \phi_d \rangle = cn F_s(\mathbf{q}) + (cn)^2 F_x(\mathbf{q})$$

$$\langle \delta \phi_h \delta \phi_h \rangle = (1 - c) n F_s(\mathbf{q}) + (1 - c)^2 n^2 F_x(\mathbf{q})$$

$$\langle \delta \phi_d \delta \phi_h \rangle = c(1 - c) n^2 F_x(\mathbf{q})$$
 (2.6)

The last of (2.6) lacks the intramolecular term since it involves d-h correlations, and thus it is clear that a combination of all three terms will give  $F_{\rm s}({\bf q})$  explicitly. Noting that for correlations within a chain

$$nF_{\rm s}(\mathbf{q}) \equiv \chi_{1\rm s}(\mathbf{q})$$

and that for total correlations

$$nF_{\rm s}(\mathbf{q}) + n^2F_{\rm x}(\mathbf{q}) \equiv \chi_1(\mathbf{q})$$

then substitution of (2.6) into (2.5) yields the desired expression (2.2).

Inspection of (2.2) shows that there are two idependent modes of fluctuation. Compositional fluctuations between species 1 and 2 weighted by an effective contrast factor  $(\bar{a} - b')^2$ , will give the interactions between 1 and 2. Isotopic fluctuations within 1 give intrachain correlations and eventually single-chain characteristics such as radii of gyration  $R_{g}$ . We perform below an RPA analysis of the three-component system which confirms (a) the independence of the modes of fluctuation, (b) the de Gennes prescription for extracting the interaction parameter U between different species (of different monomer volumes  $v_1 \neq v_2$ ), and (c) that, in the presence of interaction, additional correlations depending of the size of species 2 are not induced into  $\chi_{1s}(\mathbf{q})$  and hence that single-chain properties of the species 1 such as the chain radius of gyration,  $R_{\rm g}^{-1}$ , can be extracted unambiguously. A simple Zimm analysis will be incorrect (see eq 3.11).

#### 3. Extension of the de Gennes Analysis<sup>3</sup>

The interaction between monomers in a dense system of polymers of species 1 and 2 contributes

$$F_{\rm int} = \frac{1}{2}U \int d\mathbf{r} \ \phi_1(\mathbf{r})\phi_2(\mathbf{r}) \tag{3.1}$$

to the free energy. U is effectively the Flory interaction parameter<sup>4</sup> but with dimensions of a segment volume. The response of the system concentrations  $(\delta\phi_d,\,\delta\phi_h,\,$  and  $\delta\phi_2)$  to applied fields  $(\delta\psi_d,\,\delta\psi_h,\,$  and  $\delta\psi_2)$  coupling to the concentrations is, from linear response theory, given by the density correlation functions  $\chi$ . Thus we get, using mean field theory

$$\delta\phi_d = \chi_d^{\ 0}\delta\psi_d - U\chi_d^{\ 0}\delta\phi_2 + \chi_d^{\ 0}\upsilon_1\delta\Psi$$

$$\delta\phi_h = \chi_h^{\ 0}\delta\psi_h - U\chi_h^{\ 0}\delta\phi_2 + \chi_h^{\ 0}\upsilon_1\delta\Psi \qquad (3.2)$$

$$\delta\phi_2 = \chi_2^{\ 0}\delta\psi_2 - U\chi_2^{\ 0}(\delta\phi_d + \delta\phi_h) + \chi_2^{\ 0}\upsilon_2\delta\Psi$$

where  $\delta\Psi$  is a Lagrange multiplier expressing the system incompressibility. The  $\chi_i^0$  are the bare response functions for chains with no interactions; i.e., they are

$$\chi_i^0(\mathbf{q}) = \langle \delta \phi_i(\mathbf{q}) \delta \phi_i(-\mathbf{q}) \rangle_0 = \bar{\phi}_i N_i f_D[(q R_g^i)^2]$$
 (3.3)

where  $R_{\rm g}^{\ i}$  is the radius of gyration,  $N_i$  is the number of monomers in chains of the *i*th component (d or h for the first component),  $f_{\rm D}$  is the Debye function for ideal polymers

$$f_{\rm D}(x) = \frac{2}{x^2}(x - 1 + e^{-x})$$
 (3.4)

Equation 3.3 is expressed per unit volume. Thus, subsequently in the use of  $\chi^0$  in scattering cross sections (e.g., (3.9)), these too should be normalized by the scattering

volume, in the manner of, for example, Higgins.<sup>5</sup>

The Lagrange multiplier  $\delta\Psi$  is determined by solving (3.2) simultaneously for  $\delta\phi_d$ ,  $\delta\phi_h$ ,  $\delta\phi_2$  in terms of the  $\delta\psi_i$  and substituting the resulting expressions in the incompressibility condition

$$v_1(\delta\phi_d + \delta\phi_h) + v_2\delta\phi_2 = 0 \tag{3.5}$$

The result for  $\delta\Psi$  is then resubstituted in the expressions for the  $\{\delta\phi_i\}$ . The equations for  $\{\delta\phi_i\}$  are now of the form

$$(\delta \phi_d, \delta \phi_h, \delta \phi_2) = \chi \begin{pmatrix} \delta \psi_d \\ \delta \psi_h \\ \delta \psi_2 \end{pmatrix}$$
 (3.6)

with the response matrix  $\chi$  thus defined in the solution giving all the possible correlations:

$$\chi_{ij} = \langle \delta \phi_i \delta \phi_j \rangle \tag{3.7}$$

Knowledge of these correlations gives, via the easily derived relation

$$S(\mathbf{q}) = a_i \chi_{ij}(\mathbf{q}) a_j$$

$$\equiv (d, h, b) \chi \begin{pmatrix} d \\ h \\ b \end{pmatrix}$$
(3.8)

the final expression for the cross section

$$S(\mathbf{q}) = \frac{\chi_1^0 \chi_2^0 (\bar{a} - b')^2}{\beta^2 \chi_1^0 + \chi_2^0 - 2\beta U \chi_1^0 \chi_2^0} + c(1 - c)(d - h)^2 \chi_1^0$$
(3.9)

where the  $\chi_d^0$  and  $\chi_h^0$  of (3.2) are related to  $\chi_1^0$ , the response of the 1 component as a whole, by  $\chi_d^0 = c\chi_1^0$ ,  $\chi_h^0 = (1-c)\chi_1^0$ . Relation 3.9 indeed confirms the separation of  $S(\mathbf{q})$  into a "self term" and another term. It is now explicitly clear that only the  $\chi_1$  term of (2.2) (involving interchain correlations contributing to  $\delta\phi_1\delta\phi_1$ ) has the structure of the 2 chains induced into it by incompressibility (de Gennes' correlation hole). However, the "self term" is unambiguously independent of the structure of the 2 chains.

The interaction parameter U can be extracted from the first term  $S_1(\mathbf{q})$  of (3.9)

$$S_1^{-1}(\mathbf{q}) = \frac{1}{(\bar{a} - b')^2} \{ (\chi_1^0)^{-1} + \beta^2 (\chi_2^0)^{-1} - 2\beta U \}$$
 (3.10)

with care being taken to correct for differences in monomer specific volumes ( $\beta \neq 1$ ). When the sole interest is in such thermodynamic quantities, information at q = 0 will suffice. The above are then accessible from conventional mean field theory of the Flory-Huggins<sup>4</sup> type.

Finally, we comment that (3.9) should be exploited in the high-deuteration ( $c \sim 0.5$ ) region to optimize the coherent intensity as compared with the incoherent background, the  $(\bar{a}-b')^2$  term being explicitly adjusted for as a function of c. In fact, a straightforward Zimm analysis to get  $R_{\rm g}^{\, 1}$  will yield an apparent variation of  $R_{\rm g}^{\, 1}$  with the relative concentration of component 1 in 2:

$$R_g^{1}(\text{apparent}) = R_g^{1}(1 + \epsilon(1 - f)(1 - f + \alpha f))^{1/2}$$
 (3.11)

where f is the volume fraction of 1

$$\phi_1 = f\phi$$

$$\bar{\phi}_2 = (1 - f)\bar{\phi}$$

and  $\epsilon$  is the combination of scattering lengths

$$\epsilon = \frac{2dh - (d-h)b}{(d-h)^2}$$

The expression (3.10) for the variation of the apparent value of  $R_{\rm g}^{\, \rm l}$  with composition was calculated for the simple case of  $N_1=N_2$ ,  $v_1=v_2$ , and a ratio of the actual radii of gyration  $(R_{\rm g}^{\, 2}/R_{\rm g}^{\, \rm l})^2=\alpha$ .

## 4. Use of the Scattering Law Formula

Examination of eq 3.9 suggests some straightforward manipulation of the scattering data to yield values of  $R_{\rm g}^{-1}$  and of the interaction parameter, U.

**Determination of Chain Dimensions.** Measurements at two values of c and a weighted subtraction

$$S_{c1} - \left\{ \frac{(c_1d + (1 - c_1)h - b')^2}{(c_2d + (1 - c_2)h - b')^2} \right\} S_{c2}$$

will yield

$$[c_1(1-c_1)-c_2(1-c_2)](d-h)^2\chi_1^0$$

From this  $R_{\rm g}^{\, 1}$  can now be obtained from a conventional Zimm plot, together with  $N_1$ , which gives a useful check on the subtraction procedures since it must agree with values from other measurements.

Such subtractions have been proposed by Wignall<sup>6</sup> and applied to some blend systems by Stein et al.<sup>7,8</sup> There are, however, some practical difficulties that arise with this "head-on" approach.

The principal difficulty arises because the incoherent background (and all other backgrounds (e.g., cell scattering)) must be exactly subtracted before the weighted subtraction is applied. This incoherent background may be measured at high q, where the coherent scattering is no longer important. However, extrapolation back to the q range of the experiments is often nontrivial since the two measurements may have to be made at different times, using different apparatus.

Alternatively, the incoherent cross section might be calculated from the known bound-atom cross sections. However, these bound-atom cross sections are not well-known for nuclei bound to polymer molecules, and the observations that the transmissions of polymeric samples can be strongly temperature dependent indicates that the effects of molecular motions are not negligible. Probably the best method is to determine the incoherent scattering from the two polymers separately and construct a background for the blend by a suitable addition. There are still objections to this method because there may be structural features in the polymers (e.g., crystallinity) not reproduced in the blend or the molecular mobility and hence the relevant bound-atom cross sections may be altered in the blend.

Two maneuvers for minimizing there difficulties are possible. In the first the concentration of deuterated material is chosen so that the coefficient of the first term in eq 3.9 is identical with its value in a purely hydrogenous blend. Under these conditions the concentration  $\hat{c}$  is defined by

$$(\hat{c}d + (1 - \hat{c})h - b')^2 = (h - b')^2 \tag{4.1}$$

Ignoring the trivial  $\hat{c} = 0$  root, we obtain

$$\hat{c} = 2(b'-h)/(d-h) \tag{4.2}$$

which is positive where b' is greater than h.

Values of  $\hat{c}$  satisfying this expression are normally low so that the amount of deuterated material present is small and the incoherent scattering differs by only a few percent in the labeled and hydrogenous samples. The errors consequent on using this incoherent background without correction for the deuterium are negligible compared to

Table  $I^a$ 

	PPGM wt fraction = 0.3				PPGM wt fraction = 1.0	
c	$\frac{\operatorname{coeff} S_1}{\times 10^{24} \ \mathrm{cm}^2}$	$\begin{array}{c} \operatorname{coeff} \chi_1^{\ 0} \\ \times \ 10^{24} \ \mathrm{cm}^2 \end{array}$	R <sub>g</sub> , A (±5%)	$M_{ m W} \ (\pm 10\%)$	R <sub>g</sub> , A (±5%)	M <sub>W</sub> (±10%)
0	0.06	0		<del></del>	<del></del>	
0.07	0.02	0.76	12.3	2125	13.7	2025
0.44	4.7	2.88	20.1	2880		

<sup>a</sup> PPGM = polymer 1 and PEGM = polymer 2; T = 45 °C.

these discussed already. Thus a subtraction of the two signals will yield directly the single-chain term.

An alternative approach is to prepare a copolymer of polymer consisting of hydrogenous and deuterated materials in the same ratio as the chosen c. The blend of the this copolymer with polymer 2 then forms the background. In this case the incoherent scattering, void and density fluctuations, and the concentration signal are all subtracted out, leaving a bare single-chain term.

Examples of each of these maneuvers are given in section 5.

**Determination of the Interaction Parameter.** Again the direct approach is weighted subtraction of two measurements

$$S_{c_1} - \frac{c_1(1-c_1)}{c_2(1-c_2)}S_{c_2}$$

yielding now the first term in eq 3.9. If this is extrapolated to zero q we obtain

$$S_{1}(0) = \left[ (c_{1}d + (1 - c_{1})h - b')^{2} - \left\{ c_{1}(1 - c_{1})/c_{2}(1 - c_{2}) \right\} \times (c_{2}d + (1 - c_{2})h - b')^{2} \right] / \left[ (N_{1}\phi_{1})^{-1} + \beta^{2}(N_{2}\phi_{2})^{-1} - 2\beta U \right]$$

$$(4.3)$$

Assuming  $N_1$  and  $N_2$  are separately determined, U may be obtained. It should be noted, however, that as the spinodal is approached the denominator in eq 4.3 tends to zero. The intensity off the fluctuation term increases dramatically (critical scattering) but the value of U obtained will depend crucially on the accuracy of the values of  $N_1$  and  $N_2$  used. Alternatively, if the scattering from a sample with relatively small deuterated fraction c is corrected for incoherent scattering by subtracting the scattering from a sample with c=0 and extrapolated to zero q, then we have

$$S_{1}(0) = \frac{(cd + (1 - c)h - b')^{2} - (h - b')^{2}}{(N_{1}\phi_{1})^{-1} + \beta^{2}(N_{2}\phi_{2})^{-1} - 2\beta U} + c(1 - c)\phi_{1}N_{1}(d - h)^{2}$$

$$(4.4)$$

and knowing  $N_1$ , one can separate out the fluctuation term to yield U as before.

#### 5. Application to Two Blend Systems

We show how the above discussion works in practice by taking examples from data obtained for two different low molecular weight blend systems. The details of the experiments and the implications of the results as regards the thermodynamic aspects of the systems will be discussed elsewhere. The neutron scattering data were all obtained with the D17 spectrometer at the Institut Laue-Langevin. Laue-Langevin.

Methoxylated Poly(ethylene glycol) (PEGM) with Methoxylated Poly(propylene glycol) (PPGM). For low molecular weights and at elevated temperatures these two polymers are partially compatible, phase separating as the temperature is lowered. For the pair used here with molecular weights  $M_{\rm PEGM} = 600$  and  $M_{\rm PPGM} = 2000$ ,

the upper critical solution temperature (UCST) is about 36 °C for a 50/50 mixture. The effect of deuteration of the PPGM component on this value is negligible.

For this system b' is greater than h so that eq 4.2 may be applied. This has enabled us to obtain the chain dimensions as a function of blend concentration. Results are reported elsewhere, 10 and here we concentrate on a 30 wt % mixture of PPGM in PEGM to demonstrate the effect of eq 3.9. The experiments were carried out at 45 °C, i.e., well above the phase boundary. For this blend concentration, eq 4.2 yields a value of  $\hat{c} = 0.08$ . Table I gives values of the radius of gyration and molecular weight (from the q = 0 intercept) obtained by analyzing the signal for a sample with a value of c close to this "null point" and one far away from this value, in both cases simply subtracting the scattering of the purely hydrogenous (c = 0)mixture. For the concentration close to  $\hat{c}$  the coefficient of  $S_1(\mathbf{q})$  is close to that for c=0 (in both cases here very small) and analysis of the data for  $S_c - S_0$  yields the correct molecular weight for the PPGM molecules and a value of  $R_g$  somewhat smaller than that in a PPGM melt. For c $\gg \hat{c}$  the  $S_1(\mathbf{q})$  coefficient becomes larger than that for the single-chain term. Now the  $S_c - S_0$  signal yields a manifestly incorrect apparent molecular weight and a much larger apparent radius of gyration.

Analysis of the apparent molecular weight in terms of eq 4.4 leads to a value of U=0.0707. The analysis of heats of mixing data<sup>13</sup> gives U=0.12 at 50 °C. The positive value of U still allows mixing of these low molecular weight species because the entropy term is relatively large. We believe the discrepancy between the two values of U is revealing and this will be discussed in a future publication.<sup>10</sup>

**Polystyrene with Polybutadiene.** Low molecular weight samples of these polymers are again compatible at elevated temperatures. Polystyrene, M = 3400, with polybutadiene, M = 960, shows a UCST at about 110 °C. For this system b' = h so we cannot apply the same approach as for PPGM/PEGM. Moreover, in this case deuteration of either component shifts the phase boundary by about 20 °C (data for the phase boundary after deuteration of the PB component have been published, <sup>14</sup> and the similar effect of deuterating the PS component has been observed at one blend concentration only by the present authors).

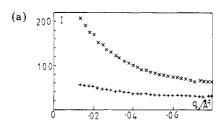
In this case the approach of using a copolymer background where the d/h ratio = c has obvious advantages. To a first approximation the thermodynamic status of the blend should be the same for the PS copolymer/PB blend as for the PSd/PSh/PB blend.

Figure 1a compares the scattering from a blend with c=0.23 with one where c=0. Figure 1b shows the result of analyzing the subtracted intensities was a plot of  $I^{-1}$  vs.  $q^2$ . The radius of gyration and molecular weight taken from the straight part of the curve and listed in Table II are far larger than for the PSd molecules in a PSh melt. Figure 2a compares the scattering for the same value of c with scattering from a similar blend containing a PSd/PSh copolymer with d/h=c. The importance of the fluctuation signal is clearly seen. Now the  $R_{\rm g}$  and mo-

Table IIa

PPS wt fraction = 0.43					PPS wt fraction = 1.0	
${{ m coeff} \ S_{_1}} \times 10^{_{24}} \ { m cm}^2$	$\begin{array}{c} \operatorname{coeff} \chi_{\scriptscriptstyle 1}{}^{\scriptscriptstyle 0} \\ \times \ 10^{\scriptscriptstyle 24} \ \mathrm{cm}^{\scriptscriptstyle 2} \end{array}$	$R_{ m g}, { m \AA} \ (\pm5\%)$	M <sub>w</sub> (±10%)	R <sub>g</sub> , Å (±5%)	M <sub>w</sub> (±10%)	
2.71	0	······································	······································			
12.68	0					
12.68	5.27	(c-a) 32	8000	14.4	3600	
	$ \begin{array}{c} \text{coeff } S_1 \\ \times 10^{24} \text{ cm}^2 \end{array} $ 2.71 12.68	$ \begin{array}{cccc}  & \text{coeff } S_1 & \text{coeff } \chi_1^{\ 0} \\  & \times 10^{2^4} \text{ cm}^2 & \times 10^{24} \text{ cm}^2 \end{array} $ $ \begin{array}{ccccc}  & 2.71 & 0 \\  & 12.68 & 0 \end{array} $	$egin{array}{cccccc} { m coeff}  S_1 & { m coeff}  \chi_1^{\ 0} & R_{ m g},  { m \AA} \  imes 10^{ 24}  { m cm}^2 &  imes 10^{ 24}  { m cm}^2 & (\pm 5\%) \ \hline 2.71 & 0 \ 12.68 & 0 \ \end{array}$	$egin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

<sup>a</sup>Polystyrene = polymer 1 and polybutadiene = polymer 2; T = 135 °C.



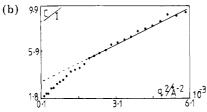
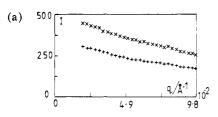


Figure 1. (a) Scattering from a blend containing 57% polybutadiene, 10% polystyrene- $d_8$ , and 33% polystyrene- $h_8$  (×) compared to that from a blend of 57% polybutadiene and 43% polystyrene- $h_8$  (+). (b) Inverse scattered intensity against  $q^2$  for the signal obtained by subtracting the curves in (a).



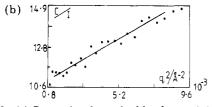


Figure 2. (a) Scattering from the blend containing 10% polystyrene- $d_8$  as in Figure 1a (×) compared to a blend of 57% polybutadiene with 43% of a copolymer of styrene- $d_8$  and styrene- $h_8$  (+). (b) Inverse scattered intensity against  $q^2$  for the signal obtained by subtracting the curves in (a).

lecular weight values in Table II agree much better with the value for PSd in a melt of PSh. The residual differences in the molecular weight values are outside experimental error in the measurement. They may reflect differences in the fluctuation signal in the two blends arising from imperfect temperature control or from the thermodynamic differences between the d/h copolymer and the mixed h and d polystyrene.

## 6. Conclusions

We have shown that the single-chain dimensions and the interaction parameter may be unambiguously determined from the small-angle neutron scattering signals of polymer blends in which one component contains a deuterated fraction.

Application to practical systems demonstrates the importance of the interaction term, which must be carefully removed before values of  $R_g$  can be reliably determined.

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Registry No. PEGM, 9004-74-4; PPGM, 37286-64-9; polystyrene, 9003-53-6; polybutadiene, 9003-17-2; polystyrene- $d_8$ , 27732-42-9; neutron, 12586-31-1.

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