Smallangle neutron scattering by partially deuterated polymers and their blends

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Small-angle neutron scattering by partially deuterated polymers and their blends

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Partially deuterated polymers, made by saturating the double bonds of polydienes with deuterium, have been found to produce weak but significant coherent patterns in small-angle neutron scattering (SANS) experiments. The results suggest the presence of slight differences in deuteration levels among the chains. The scattering profiles for such materials and for blends containing them were calculated with the multicomponent random phase approximation (RPA). The coherent intensity for the deuterated component alone is predicted to be proportional to the variance of its scattering length distribution and to have a q dependence corresponding to the pure component structure factor. The SANS data for a variety of partially deuterated polyolefins are shown to be consistent with these predictions. The theory also predicts that the scattering from their blends with an hydrogenous component is enhanced by this scattering length inhomogeneity, that the enhancement is additive, and that the conventional two component RPA may be used to analyze the data after this contribution is subtracted. Experimentally, we find that uncorrected scattering from blends rich in such deuterated components lead to anomalous estimates of chain dimensions and thermodynamic interactions. The anomalies disappear when the proposed correction is applied.

INTRODUCTION

Deuterium labeling is widely used in the study of polymer structure and dynamics by methods such as small-angle neutron scattering (SANS).[1] Labeled components can be prepared by polymerization of deuterated monomers or, less directly but sometimes more conveniently, by adding deuterium to a hydrogenous polymer. Following the latter procedure, we have used partially deuterated components, made by saturating the double bonds of polydienes with deuterium, for SANS studies of the thermodynamic interactions in model polyolefin blends.[2–4]

In the course of this work, we unexpectedly found a weak coherent intensity in experiments conducted with the deuterated component alone. Others have also noted an angle-dependent SANS intensity from deuterated polymers,[5–8] which they usually attribute to voids or particulate impurities such as catalyst residues. However, we found no angular dependence for hydrogenous components, made from the same polydiene precursors and purified identically. We also found that the size obtained by analysis of the deuterated component scattering closely parallels the radius of gyration of the polymer itself. This latter observation suggests the possibility that the labeling level is nonuniform, leading to small but observable SANS contrasts among the various chains that comprise the deuterated component.

Deuterium is introduced by catalytically saturating double bonds with D_2 in the presence of Pd on a $CaCO_3$ substrate.[9] It is well-documented that H–D exchange also takes place,[10] and the amount of exchange might vary with the time each chain spends on the active sites. The level of total deuteration also increases with chain length to some extent,[11,12] presumably related to preferential adsorption on the catalyst sites.[11] It is thus conceivable that even a nearly monodisperse ($M_w/M_n < 1.07$) sample, when fully saturated in this way, consists of chains with a distribution of deuteration levels.

In this paper, we demonstrate that the coherent scattering from such labeled polymers is consistent with labeling inhomogeneity. Our motivation is not simply to explain the effect, however, but also to provide corrections for its influence on the SANS patterns for blends of hydrogenous and deuterated components. In the first section we use the incompressible random phase approximation (RPA) to develop expressions for the coherent SANS intensity of (a) a polymer containing an arbitrary distribution of labeling levels and (b) a blend of that polymer with an arbitrary hydrogenous component. In the second section we present experimental data to test the results and demonstrate their application.

THEORY

The coherent scattering intensity for a single phase, multicomponent polymer blend, $I_c(q)$, can be expressed in terms of the contrast factors, component structure factors, and interactions through the incompressible RPA, as generalized by Akcasu and Tombakoglu[13] and Benoit *et al.*:[14]

$$I_c(q) = \mathbf{B}^T \mathbf{S} \mathbf{B}, \tag{1a}$$

where the structure $\mathbf{S}$ is given by

$$(\mathbf{S})^{-1} = (\mathbf{S}^0)^{-1} + \mathbf{V}. \tag{1b}$$

The matrix $\mathbf{S}^0$ contains the component structure factors in the absence of interactions, the matrix $\mathbf{V}$ contains the interactions between constituent mers, the vector $\mathbf{B}$ specifies the various scattering contrasts, and q is the scattering vector magnitude $(4\pi/\lambda)\sin\theta/2$ (λ = neutron wavelength, θ = scattering angle). We consider a blend of labeled and unlabeled components in which the labeled component consists of n chemically identical species, distinguished only by differences in deuteration level. The Flory–Huggins (FH) equation is used to describe the thermodynamics, the incompressibility constraint is incorporated by methods outlined by Hammouda,[15] and we assign the hydrogenous component as the reference. Under these conditions, $\mathbf{S}^0$ is an $n \times n$ diagonal matrix with components

$$S_{ij}^0 = N_D v_D P_D(q)\phi_i, \quad i=j, \tag{2a}$$

$$=0, \quad i \neq j \tag{2b}$$

and $\mathbf{B}$ has components

$$B_i = \frac{b_i}{v_D} - \frac{b_H}{v_H}. \tag{3}$$

The subscript i refers to the individual species of labeled component, ϕ_i is its volume fraction, and b_i is the mean coherent scattering length of its monomeric units. The subscripts H and D distinguish the polymerization index N, monomeric volume v, and form factor $P(q)$ of the hydrogenous and deuterated components. We further assume that a single FH parameter χ describes all interactions between labeled and unlabeled components and that the interactions among the labeled species themselves are negligible. In this case, all components of $\mathbf{V}$ are identical:

$$V_{ij} = \frac{1}{N_H v_H P_H(q)\phi_H} - \frac{2\chi}{v}, \tag{4}$$

where v is the reference volume. Thus, $\mathbf{S}$ has components

$$(S_{ij})^{-1} = \frac{1}{N_D v_D P_D(q)\phi_i} + \frac{1}{N_H v_H P_H(q)\phi_H} - \frac{2\chi}{v}, \quad i=j \tag{5a}$$

$$= \frac{1}{N_H v_H P_H(q)\phi_H} - \frac{2\chi}{v}, \quad i \neq j. \tag{5b}$$

To complete the solution of Eq. (1) we define a vector $\mathbf{A}$ such that

$$\mathbf{SA} = \mathbf{B} \tag{6}$$

and solve the set of linear equations, term by term, to obtain

$$A_i = \frac{\phi_i}{\phi_D} \frac{B_i + N_D v_D P_D(q)\phi_D(1/N_H v_H P_H(q)\phi_H - 2\chi/v)(B_i - \bar{B})}{1/N_H v_H P_H(q)\phi_H + 1/N_D v_D P_D(q)\phi_D - 2\chi/v} \tag{7}$$

in which the total volume fraction of deuterated component is

$$\phi_D = \sum_{i=1}^{n} \phi_i \tag{8}$$

and the average contrast between deuterated and hydrogenous components is

$$\bar{B} = \frac{\sum_{i=1}^{n}\phi_i B_i}{\sum_{i=1}^{n}\phi_i}. \tag{9}$$

Equation (1) thus reduces to

$$I_c(q) = \mathbf{B}^T \mathbf{A} \tag{10}$$

which is easily evaluated, term by term, to give

$$I_c(q) = \frac{\bar{B}^2}{1/\phi_H N_H v_H P_H(q) + 1/\phi_D N_D v_P P_D(q) - 2\chi/v}$$
$$+ (\overline{B^2} - \bar{B}^2)\phi_D N_D v_D P_D(q), \tag{11}$$

where the average square contrast is

$$\overline{B^2} = \frac{\sum_{i=1}^{n}\phi_i B_i^2}{\sum_{i=1}^{n}\phi_i}. \tag{12}$$

Equation (11) is the main result. The first term is the standard RPA result for binary polymer blends, and the second term vanishes if the scattering length per monomer is the same for all chains of the deuterated component, since in this case $\overline{B^2} = \bar{B}^2$. If the labeling is nonuniform, then $\overline{B^2} > \bar{B}^2$, and the deuterated component alone ($\phi_D = 1$) will generate a coherent scattering signal:

$$I_c'(q) = (\overline{B^2} - \bar{B}^2)N_D v_D P_D(q). \tag{13}$$

Note that the strength of this signal depends only on the variance of the labeling distribution and not its detailed shape. Furthermore, based on Eq. (11), the standard RPA for binary blends can be used to analyze the data after the excess scattering due to labeling nonuniformity is subtracted:

$$[S(q)]_u = \frac{[I_c(q)]_{\text{obs}} - \phi_D I_c'(q)}{\bar{B}^2}, \tag{14}$$

where $[I_c(q)]_{\text{obs}}$ is the coherent intensity of the blend, $I_c'(q)$ is the measured coherent intensity of the deuterated component alone, and $[S(q)]_u$ is the structure factor for a binary blend with uniform labeling in the deuterated component.

The contrast factor for a blend, $\bar{B}^2$, is calculated from the scattering lengths of the constituent atoms in the monomeric units. To a good approximation, $\bar{B}$ is directly pro-

TABLE I. Characteristics of the deuterated polymers.

Sample designation	Degree of polymerization N^a	Average number of deuterium atoms per monomer $\bar{n}_D{}^a$	Glass transition temperature T_g (°C)
D97A	1600	2.79	−22
D97B	865	2.69	−25
D88	1610	2.96	−34
D78	1285	2.37	−42
D66	2030	3.25	−54
D52	1510	2.75	−61
D38	1830	3.03	−62[b]
D32	1720	2.77	−56[c]
DPEP[d]	855	4.69	−60
DPEB[e]	550	3.18	−60
DhhPPA[e]	320	3.97	−24
DhhPPB[e]	910	4.10	−22
DPP[e]	705	3.88	+1

[a]Based on C_4 unit unless otherwise noted.
[b]Partially crystalline, $T_m = 42$ °C.
[c]Partially crystalline, $T_m = 60$ °C.
[d]Based on C_5 unit.
[e]Based on C_6 unit.

portional to $\bar{n}_D$, the average number of deuterium atoms per monomeric unit of the labeled component. As a result,

$$\frac{\overline{B^2} - \bar{B}^2}{\bar{B}^2} = \frac{\overline{n_D^2} - \bar{n}_D^2}{\bar{n}_D^2} \qquad (15)$$

and from Eq. (13), the variance of labeling levels can be inferred from measurements of $I_c'(0)$ if $\bar{n}_D$ is known, e.g., by a density determination. Finally, the q dependence of I_c' depends on the structure factor of the deuterated component, and can therefore be used to estimate its radius of gyration.

EXPERIMENT

The polymers in this study are model polyolefins, synthesized from a variety of polydiene precursors by catalytically saturating their double bonds with either hydrogen or deuterium.[2] All samples were carefully filtered in solution (0.2 μm Anodisc™ filters) before precipitation and final drying. Thirteen polydienes were used to obtain 13 matched pairs of fully saturated samples, one member of each pair being fully hydrogenous (designated H in the first letter of the name) and the other partially deuterated (designated D). All are nearly monodisperse (M_w/M_n < 1.06), and all were extensively characterized by methods described elsewhere.[2–4] Saturated polybutadienes are designated by a number that specifies the percent of vinyl groups in the precursor. The other designations are PEP for a saturated 1,4 polyisoprene (alternating ethylene–propylene copolymer), PEB from a saturated 1,4 polyethylbutadiene (alternating ethylene–butene-1 copolymer), PP for a saturated polymethylpentadiene (atactic polypropylene), and hhPP for two saturated 1,4 polydimethylbutadienes (head-to-head polypropylenes). Polymerization index N, obtained by light scattering, and the mean number of deuterium atoms per monomeric unit $\bar{n}_D$, obtained by density measurements (2), are recorded in Table I. In
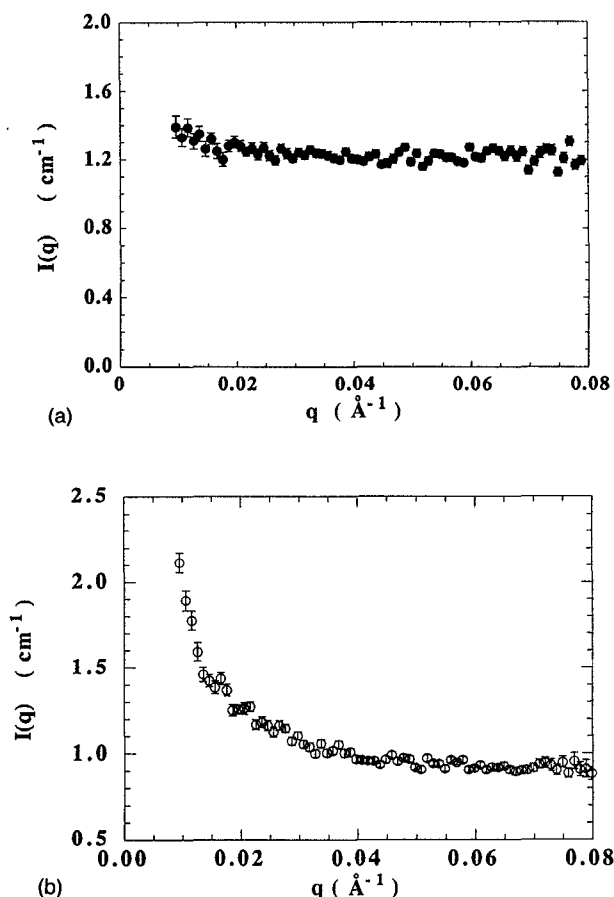

FIG. 1. (a) Total SANS intensity vs q for the hydrogenous polymer H97A. (b) Total SANS intensity vs q for the partially deuterated polymer D97A.

all cases $\bar{n}_D$ exceeds the stoichiometry value of 2.

The SANS experiments were performed at the NIST Cold Neutron Research Facility in Gaithersburg, MD. Data were obtained on the 8 m beam line (NG5) with neutron wavelength $\lambda = 9.0$ Å in the range $0.008 \leqslant q(\text{Å}^{-1}) \leqslant 0.08$. Measurements are reported for all deuterated samples ($\phi_D = 1$), selected hydrogenous samples ($\phi_D = 0$), matched pair mixtures[2] ($\phi_D = 0.50$), and selected blends ($0.1 \leqslant \phi_D \leqslant 0.9$). All are amorphous and single-phase at the temperature of measurement. Sample preparation, procedures to convert count rates to absolute scattering intensity $I(q)$, and subtraction of the incoherent contribution to obtain $I_c(q)$ for each sample are all described elsewhere.[2]

Small-angle x-ray scattering (SAXS) intensities in relative units were obtained with a compact Kratky camera and Braun position-sensitive detector for the range $0.008 \leqslant q(\text{Å}^{-1}) \leqslant 0.10$. The data were collected, reduced, corrected for background scattering, and desmeared, as described elsewhere.[16]

RESULTS AND DISCUSSION

The total SANS intensity profiles for samples H97A and D97A at 27 °C are shown in Fig. 1. Intensities for the fully hydrogenous H97A [Fig. 1(a)] are independent of q,
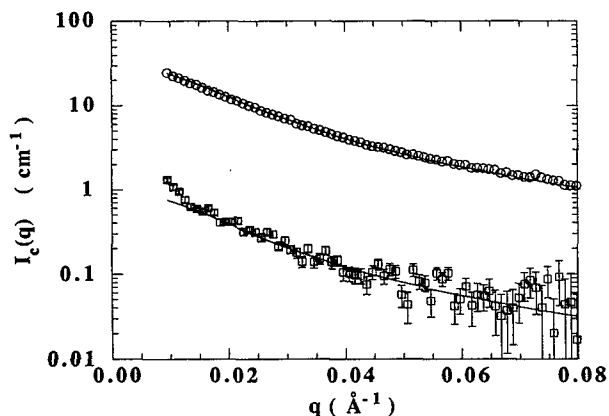
FIG. 2. Coherent SANS intensity for pure $D97A$ ($\phi_D=1$) and the $H97A/$ $D97A$ matched pair mixture ($\phi_D=0.5$). The data are shown as squares for pure $D97A$ and as circles for the matched pair.

as expected, and reflect primarily the incoherent scattering of protons in a molecularly homogeneous liquid. However, the intensities for the partially deuterated $D97A$ [Fig. 1(b)] rise monotonically with decreasing q from a slightly lower incoherent background (reflecting the reduced proton concentration) to values that are well above that background for $q \lesssim 0.03$ Å^{-1}. This behavior is seen for all of the 13 deuterated components.

Figure 2 compares the coherent SANS intensities $[I_c(q)=I(q)-I_{inc}]$ for $D97A$ and the $H97A/D97A$ matched pair ($\phi_D=0.50$). The counting statistics are poorer for $D97A$ alone, and the errors correspondingly larger, particularly at high q. However, the shapes of the patterns are quite similar, which would be expected if our proposed explanation for $I_c'(q)$ is correct. Thus, from Eq. (11), the scattering for a matched pair [$\phi_D=0.5$; $v_H N_H P_H(q) = v_D N_D P_D (q) \equiv vNP(q)$; $\chi_{HD} \sim 0$] is

$$[I_c(q)]_{obs} = \left(\frac{\bar{B}^2}{4} + \frac{\overline{B^2} - \bar{B}^2}{2} \right) vNP(q) \qquad (16)$$

which has the same q dependence as $I_c(q)$ [see Eq. (13)] and differs only in the intensity scale. Each set of data was fitted independently to the Debye function for monodisperse chains:

$$P(q) = \frac{2}{u^2} [e^{-u} - 1 + u], \qquad (17a)$$

$$u = qR_g, \qquad (17b)$$

where R_g is the radius of gyration. From the matched pair data, $[I_c(0)]_{obs}=28.5\pm0.1$ cm^{-1} and $R_g=95.4\pm0.2$ Å; from the deuterated component ($\phi_D=1$) data, $I_c'(0)=1.2$ ±0.2 cm^{-1} and $R_g'=98\pm10$ Å. Uncertainties in molecular weight and absolute calibration are not included in these error bars. The main sources of relative error are estimation of incoherent background for scattering by the deuterated component and the counting statistics. [A 5% blend of $D97A$ in $H97A$ gave $R_g=95.0\pm1$ Å, and matched pair data from the 30 m instrument (NG7) agreed with the values above.] The fits are reasonable, as shown by the curves in Fig. 2, and, within the errors, the sizes from the matched pair and deuterated component scattering are the same. From the theory, the ratio of deuterated component to matched pair intensities depends only on $(\overline{B^2} - \bar{B}^2)/\bar{B}^2$, and, with Eq. (15),

$$\frac{\bar{n}_D^2}{\overline{n_D^2} - \bar{n}_D^2} = 4 \frac{[I_c(0)]_{obs}}{I_c'(0)} - 2. \qquad (18)$$

This gives 0.10_3 as the ratio of standard deviation to mean, $[(\overline{n_D^2} - \bar{n}_D^2)/\bar{n}_D^2]^{1/2}$, for the distribution of deuteration levels among the labeled component chains in $D97A$. For that polymer, $\bar{n}_D=2.79$ deuterium atoms per monomeric (C_4) unit. For the particular example of a Gaussian distribution of deuterium levels about the mean, this corresponds to a range from $n_D=2.67$ to $n_D=2.91$ for the full width at half-maximum (FWHM). We also calculated the variance for a completely random distribution of the deuterium at-

TABLE II. Coherent intensity intercepts and chain dimensions.

Sample	Matched pair ($\phi_D=0.50$)		Deuterated component ($\phi_D=1$)		$\left[\dfrac{\overline{n_D^2} - \bar{n}_D^2}{\bar{n}_D^2} \right]^{1/2}$
	$I_c(0)$ (cm^{-1})	R_g (Å)	$I_c'(0)$ (cm^{-1})	R_g' (Å)	
$D97A$	28.5	95	1.2	98	0.10_5
$D97B$	16.4	63	0.7	73	0.10_5
$D88$	42.2	96	2.2	118	0.11_5
$D78$	18.6	89	3.0	96	0.21_0
$D66$	73.9	123	4.2	254	0.12_0
$D52$	39.1	114	2.4	165	0.12_5
$D38$	63.0	128	2.6	154	0.10_5
$D32$	38.6	127	4.4	138	0.17_5
DPEP	43.3	96	2.7	107	0.12_5
DPEB	10.0	74	1.5	87	0.20_5
DhhPPA	10.1	56	0.8	71	0.14_0
DhhPPB	30.1	101	2.0	121	0.13_0
DPP	17.7	80	1.4	91	0.14_5

oms in excess of the stoichiometric number and obtained $[\overline{(n^2 - \bar{n}^2)/\bar{n}^2}]^{1/2} = 0.01$, which is much smaller than observed.

Similar results were found for the other deuterated components and their matched pairs. The values obtained for $[I_c(0)]_{obs}$, $I'_c(0)$, R_g, and R'_g are given in Table II along with $[(\overline{n_D^2} - \bar{n}_D^2)/\bar{n}_D^2]^{1/2}$, calculated with Eq. (18). All data were obtained for single phase melts at 27 °C except D32 (83 °C) and D38 (51 °C), which were examined at temperatures above their crystalline melting temperatures. In most cases there is reasonable agreement between R_g and R'_g, despite the weakness of scattering by the deuterated component alone. The main exceptions to this are D52 and D66, for which R'_g is much larger than R_g. Note also that a small upturn in intensity at the lowest range of q was always observed in the scattering pattern for deuterated components (see, e.g., Fig. 2). Those last few points were omitted in our fits to determine $I'_c(0)$ and R'_g. Note finally that R'_g was always at least slightly larger than R_g (see Table II). We will return to these observations for further comment in the Concluding Remarks.

To ensure that scattering by the deuterated component alone was not caused by catalyst residues or voids, we performed SAXS measurements on two of the samples, HhhPPA and DhhPPA. This is a reasonably sensitive test because the electron density of both "impurities" should differ substantially from that of the polymers. The results, shown in Fig. 3(a), demonstrate that neither sample produces a q-dependent signal. Over the same range, the SANS data for DhhPPA in Fig. 3(b) displays the usual increase in intensity at low q, and it is clear that particulates or voids cannot account for the behavior.

We turn now to the effect of labeling nonuniformity in the determination of χ for binary blends. Our procedure depends on a comparison of the structure factor for the blend with the matched-pair structure factors for its components.[2] In the course of the analysis we also obtain a second fitting parameter α, which is the ratio of mean R_g in the blend to R_g in the matched pair mixtures.[2] The values of χ and α extracted from the data are both susceptible to systematic errors associated with labeling nonuniformity. The effects are exemplified in Figs. 4(a) and 4(b) by H88/D78 blends at 167 °C. The filled symbols represent values obtained at five blend compositions by the usual analysis, which ignores labeling nonuniformity. The open symbols represent values obtained with the deuterated component contribution subtracted out, according to Eq. (14). As expected, the difference is largest at high concentrations of the deuterated component. The corrected values of α are all near unity and consistent with the results for many other blends.[2,4] The corrected values of χ are more symmetrical with respect to midrange results, and, in particular, the apparent severe upturn at $\phi_D = 0.9$ relative to $\phi_D = 0.1$ is virtually eliminated.

The results at other temperatures and for other blend systems[4] closely parallel those in Figs. 4(a) and 4(b). More reasonable results of α and χ are obtained for $\phi_D \gtrsim 0.75$ when Eq. (14) is used, and the corrections are negligible within the error bounds for matched pairs (ϕ_D
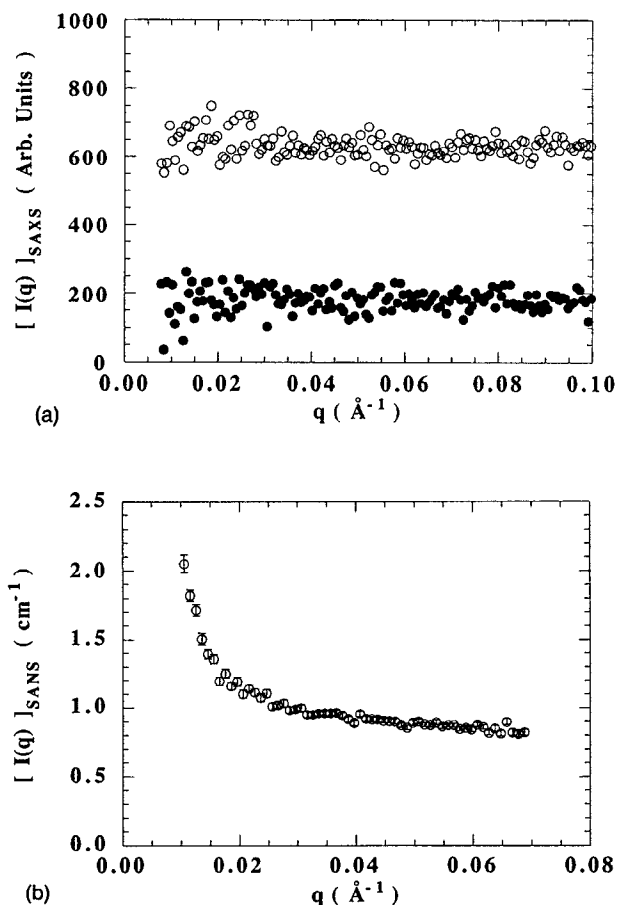

FIG. 3. (a) Total SAXS intensity vs q for pure HhhPPA (filled circles), and pure DhhPPA (open circles). The intensity of DhhPPA was offset by 500 counting units to avoid overlap. (b) Total SANS intensity vs q for pure DhhPPA.

$= 0.5$) and blends with $\phi_D \lesssim 0.5$. All the blend data in Ref. 4 were analyzed with the deuterated component scattering subtracted out [Eq. (14)].

CONCLUDING REMARKS

Although the results agree well with our conjecture of labeling inhomogeneity in the partially deuterated components, there may be other factors that can confer an angular dependence. We examined the SANS intensity for a nearly monodisperse sample of perdeuterated polyisoprene, synthesized with perdeuterated monomer and carefully purified by filtration. The results, shown in Fig. 5, also show a strong increase in $I(q)$ at low q, similar to the result of Bates *et al.*[8] for perdeuterated polybutadiene. Labeling nonuniformity is highly unlikely in either of these cases, so our interpretation is not applicable. Also, the size is inconsistent with the chain dimensions. Thus, the molecular weight of the perdeuterated polyisoprene is 96 000, for which we estimate $R_g = 93$ Å,[17] but the size estimated by forcing the data to fit a Debye function is 250 Å. We also note that angle-dependent SANS intensity from the pure deuterated component observed in this study may not be universal as shown by Tanzer *et al.*[10] and Bates *et al.*[18]
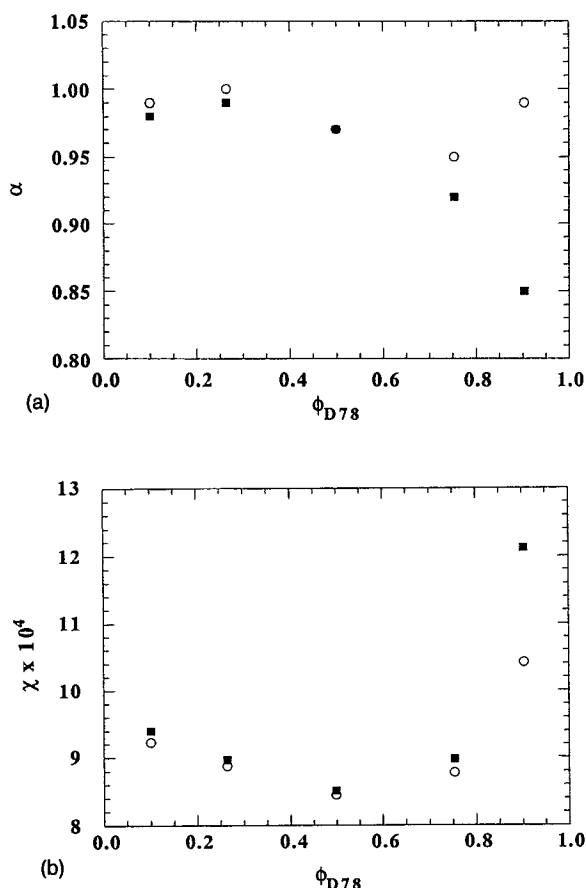
FIG. 4. (a) Chain dimension ratio vs composition for $H88/D78$ blends at 167 °C. Values obtained without correction for the $I_c'(q)$ contribution (■) and with correction, based on Eq. (14) (○), are shown. (b) Flory–Huggins interaction parameter vs composition for $H88/D78$ blends at 167 °C. Values obtained without correction for the $I_c'(q)$ concentration (■) and with correction, based on Eq. (14) (○), are shown.

Earlier we noted small upturns in $I_c'(q)$ at the lowest q for all our partially deuterated components. These may be the result of contributions from whatever mechanism is responsible for coherent scattering by uniformly labeled
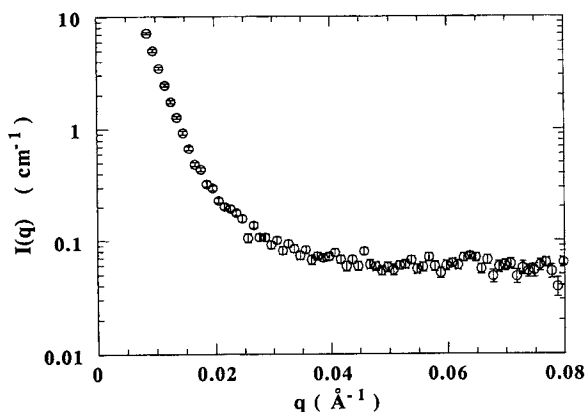
polymers (Fig. 5). The general tendency for R_g' to exceed R_g, and the large discrepancies in the values obtained for $D52$ and $D66$ particularly, may have a similar origin. We also considered a second possibility, suggested in the Introduction, that the $R_g'-R_g$ discrepancy was related to a nonuniformity of labeling with respect to molecular weight. However, a simple model, applied to our polydispersities and tuned to the observed dependence of labeling level on molecular weight, could account for no more than about 1%–2% difference between R_g' and R_g. We are therefore inclined to attribute the differences simply to experimental uncertainties, such as establishment of incoherent base lines for the deuterated component scattering and deletion of the scattering anomalies at very low q.

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FIG. 5. Total SANS intensity vs q for perdeuterated polyisoprene.