Chain dimensions of crystallizable polymers in the solid and melt states

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Small angle neutron scattering (SANS) data were obtained on hydrogenated polybutadiene, a crystallizable polymer ($\alpha_c \approx 0.4$), which is equivalent in chemical microstructure to polyethylene with *ca.* 18 ethyl groups per 1000 main chain carbon atoms. One linear sample ($M = 62\,400$) and one 3-arm star ($M = 104\,400$) were used; labelled species were prepared by deuteration of the parent polybutadienes. Scattering curves were obtained in both the solid state and the melt with mixtures containing up to 30% of the labelled species. The results indicated random mixing in the melt and the rapidly crystallized solid, and only a very slight amount of segregation in the slowly crystallized solid. The scattering curves conformed to predictions for random coil molecules over a wide range of scattering vectors. The radius of gyration obtained was the same in the solid and melt states, and in close agreement with θ solvent values for polyethylene.

Keywords Polyethylene; deuteration; neutron scattering; chain dimensions; branching; crystallization

INTRODUCTION

We report here information obtained by small angle neutron scattering (SANS) on crystallizable polymers with well defined molecular structure. The polymers were prepared by the hydrogenation or deuteration of polybutadiene. They closely resemble polyethylene, and several features make them especially attractive for SANS studies. They have very narrow molecular weight distributions ($M_w/M_n < 1.1$). Hydrogenated and deuterated versions can be prepared from the same parent polymer: they differ structurally only in deuterium content. Both linear and star-branched species can be made, so the effects of large scale geometry can be explored. The polymers also contain some ethyl groups distributed along the chain backbone ($\sim$18 ethyl groups per 1000 main chain carbon atoms). The presence of these groups reduces both crystallinity and melting temperature compared to linear polyethylene. This and the fact that only a fraction of the hydrogen is replaced by deuterium are likely to reduce the clustering problem that has complicated SANS studies of polyethylene in the solid state. The interesting possibility of obtaining single chain conformations on crystallized polymers even at high concentrations of labelled molecules is offered by such a system.

EXPERIMENTAL METHODS

Samples

Two linear polymers, HPB-L and DPB-L, and two three-arm star polymers, HPB-S3 and DPB-S3, were used in these experiments. The hydrogenated (HPB) and deuterated (DPB) polymers were not in this case obtained from common polybutadiene precursors; there is a modest difference in chain length for the labelled and unlabelled three-arm stars, the effects of which are considered below. All the parent polybutadienes were prepared anionically, then hydrogenated or deuterated over $Pd/CaCO_3$ by a procedure which has been shown to leave the large scale molecular structure intact[1,2]. The residual unsaturation is less than 0.3%. Molecular weights of the HPB were determined from the limiting viscosity number $[\eta]$ measured in trichlorobenzene at 135°C. The values for deuterated samples were not measured directly; viscosity average molecular weights of hydrogenated polymers from the same parent polybutadienes, M_H, were first evaluated by[2]

$$[\eta] = 4.86 \times 10^{-4} g^{\frac{1}{2}} M_H{}^{0.706}$$

where $g = 1$ for linear polymers and $g = 7/9$ for three-arm stars. The molecular weights for DPB-L and DPB-S3 were then calculated according to

$$M = M_H m_D / m_H$$

where m_D and m_H are the formula weights of a repeat unit in the deuterated and hydrogenated polymers, respectively. The molecular weights determined in this manner agree to within 5% with those measured by g.p.c.[3]; no correction for polydispersity is used since $M_w/M_n < 1.05$ for these polymers.

The value of m_D depends on the fractional deuteration y, which was measured by i.r. spectroscopy[3]. This fraction (see *Table 1*) is higher than $y = 0.25$ expected for simple addition of D_2 to polybutadiene, and undoubtedly reflects some H–D exchange occurring during the reaction. Had y

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Table 1 Physical characteristics of HPB and DPB

Sample	y	$[\eta]$ (dl/g)	M	R_g (Å)	ρ (g cm^{-3})	T_m (K)
HPB-L	0	1.14	60 300	111	0.906	375.7
DPB-L	0.33	1.13*	62 400	110	–	375.5
HPB-S3	0	1.76	133 000	145	0.907	376.4
DPB-S3	0.43	1.42*	104 400	124	–	375.9

* Measured on hydrogenated polymers from the same parent polybutadiene

equalled 0.25 as expected for quantitative deuteration of polybutadiene, the resultant DPB would be uniformly deuterated with the repeat unit –CH$_2$CHD–. We assume that the H–D exchange is statistically uniform along the labelled chains, and use $C_2H_{4(1-y)}D_{4y}$ as the formula for a repeat unit. Also included in *Table 1* is the root mean square radius of gyration R_g for polyethylene in a θ solvent, calculated according to

$$R_g(\text{Å}) \simeq 0.45 g^{\frac{1}{2}} M_{\mathrm{H}}^{\frac{1}{2}}$$

Densities were measured at 23°C in a gradient column of isopropanol and water. Melting behaviour was determined in a Perkin-Elmer DSC-II at a heating rate of 10°/min after first cooling from the melt at 20°C/min. Melting temperatures (*Table 1*) were defined by the peak of the d.s.c. trace. Unlike protonated and fully deuterated linear polyethylene, the hydrogenated and deuterated components here have essentially the same melting temperature.

Blends containing 10% to 30% DPB in HPB were prepared by dissolving the polymers in refluxing cyclohexane and precipitating in an excess of cold methanol containing 0.1% of an anti-oxidant, Irganox 1010. After drying, the polymers were compression moulded to form bubble-free discs of 16 mm diameter and 0.75 mm thickness. Normally the samples were quenched in ice water from the moulding temperature of 150°C. However, additional samples containing 10% DPB were slowly cooled (~1°C/min) to room temperature. All blends are designated by molecular structure and composition, e.g., L-10 is a blend of 10% DPB-L in 90% HPB-L. Only linear–linear and star–star blends were used.

SANS measurements

Experiments were performed on the 30 meter SANS facility at the National Center for Small Angle Scattering Research at Oak Ridge National Laboratory[4]. Neutrons with wavelength $\lambda = 4.75$ Å were used. Scattering patterns were recorded with a 64×64 element two-dimensional detector. In the room temperature experiments the beam was defined by a primary collimator (1.9 cm × 1.9 cm) and the sample collimator (1.4 cm diameter); the sample to detector distance was 10.8 m. In the high temperature experiments the samples were supported between quartz plates in a cell thermostatically controlled at 150°C. The sample holder and sample collimator in this case were 1.0 cm in diameter, and the sample to detector distance was 10.5 m. In both configurations the detector resolution was $10^3 \Delta q \sim 1.2$ Å^{-1} where $q = 4\pi\lambda^{-1}\sin(\theta/2)$ is the magnitude of the scattering vector, and θ is the scattering angle. A few measurements were also made in the intermediate q range (0.04 Å$^{-1} < q < 0.15$ Å^{-1}); in this case the sample-detector distance was reduced to 2.7 m.

The recorded patterns were corrected for instrumental background, parasitic scattering and non-uniform detector sensitivity. The patterns were symmetric around the incident beam, so radial averaging was performed to improve the counting statistics. With typical acquisition times of 2–4 h the precision of the intensities was about 2% over the range 0.008 Å$^{-1} < q < 0.04$ Å^{-1}. Incoherent scattering, determined from experiments on the unlabelled samples HPB-L and HPB-S3, was subtracted. These hydrogenated blanks had very little coherent intensity (~0.75 cm^{-1}), even at the smallest measured q; subtracting this component had no significant effect on the derived values for the radius of gyration or molecular weight reported below. The corrected coherent scattering intensity was converted to absolute units by comparison to the scattering of vanadium, water, and mixtures of protonated and deuterated polystyrenes[5].

RESULTS AND DISCUSSION

For a blend of otherwise identical labelled and unlabelled chains which mix ideally, the coherent cross section per unit volume can be expressed as[6–8]:

$$\frac{d\Sigma}{d\Omega}(q) = \frac{M_w}{m_D} K_\phi P(q) \tag{1}$$

Here M_w (weight average molecular weight) and m_D (repeat formula weight) refer to the deuterated polymer, and $P(q)$ is the normalized scattering function ($P(0) = 1$) which depends on the conformation of the polymer molecules and on the molecular size distribution. The factor K_ϕ contains both the number density and the contrast of the repeat units along the chain:

$$K_\phi = (B_D - B_H)^2 n_t \varphi (1 - \varphi) \tag{2}$$

where φ is the volume fraction of labelled polymer, n_t is the number of repeat units (labelled and unlabelled) per unit volume of sample, and (B_D–B_H) is the difference between coherent scattering lengths of repeat units of deuterated and hydrogenated polymers. For partially deuterated polyethylene, this may be written as:

$$(B_D - B_H) = 4y(b_D - b_H)$$

where $(b_D - b_H) = 1.041 \times 10^{-12}$ cm is the difference in coherent scattering lengths of deuterium and hydrogen[9].

Equation (1) is applicable to ideal mixtures of any composition φ for polymers of arbitrary molecular weight distribution, provided the molecular size distributions of the labelled and unlabelled polymers are identical. If the size distributions differ the SANS intensity contains information on both species. The general scattering law for such systems is rather complicated, but Boué, *et al.*[8]

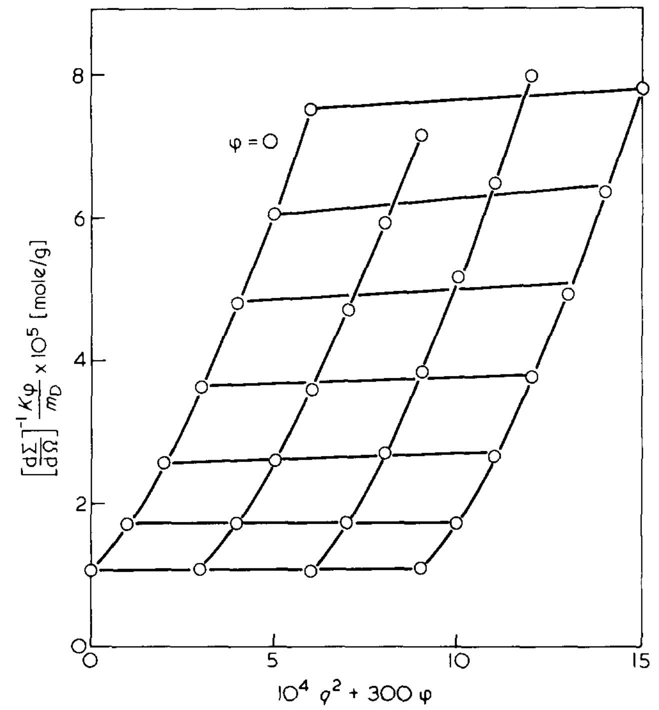

Figure 1 Modified Zimm plot of SANS data for the 3-arm star polymer in the rapidly crystallized solid state. Volume fractions of labelled species are $\phi = 0.09, 0.19$ and 0.29

have shown that behaviour in the Guinier range ($q R_g < 1$) for ideal mixtures of Gaussian chains is given by

$$\left(\frac{d\Sigma}{d\Omega}(q)\right)^{-1} = \frac{m_D}{M_w K_\phi}\left\{\left[1 - \frac{\varphi\Delta_w}{1+\Delta_w}\right] + \frac{q^2 R_g^2}{3}\left[1 + \frac{\varphi(\Delta_z - \Delta_w)}{1+\Delta_w}\right]\right\} \tag{3}$$

The correction terms in square brackets depend on the mismatch in average degrees of polymerization:

$$N_{n\mathrm{H}} = N_{n\mathrm{D}}(1+\Delta_n) \tag{4a}$$

$$N_{w\mathrm{H}} = N_{w\mathrm{D}}(1+\Delta_w) \tag{4b}$$

$$N_{z\mathrm{H}} = N_{z\mathrm{D}}(1+\Delta_z) \tag{4c}$$

Where $N_{n\mathrm{H}}$ is the number average degree of polymerization of the hydrogenated polymer, etc. A discussion of equation (3) and other expressions for the coherent intensity of polymer mixtures is presented in the Appendix.

From equation (3) one sees that the molecular weight of the deuterated polymer at any φ is given by the intercept of a plot of $[d\Sigma/d\Omega]^{-1}$ *versus* q^2:

$$M_w = \left[\frac{d\Sigma}{d\Omega}(0)\right] m_D K_\phi^{-1}\left[1 - \frac{\varphi\Delta_w}{1+\Delta_w}\right] \tag{5}$$

The radius of gyration of the deuterated polymer is obtained from the ratio of limiting slope $S(0)$ to intercept:

$$R_g = \left[\frac{3S(0)}{\frac{d\Sigma}{d\Omega}(0)}\right]^{1/2}\left[1 + \frac{\varphi\Delta_z}{1+\Delta_w(1-\varphi)}\right]^{-1/2} \tag{6}$$

For either very dilute blends ($\varphi \rightarrow 0$) or for blends of equal molecular size distribution polymers (Δ_w, $\Delta_z \rightarrow 0$), the correction terms arising from scattering by the hydrogenated polymers vanish.

Regardless of effects attributable to molecular size differences, the unambiguous analysis of SANS patterns at large φ requires sensibly ideal mixing of the labelled and unlabelled polymers. Because the melting temperatures of HPB and DPB are identical, it was hoped that the thermodynamic driving forces for segregation or clustering of isotopic species in the solid would be minimal in these systems. Scattering data for the star polymer in the quenched solid at different φ are presented in *Figure 1* in the form of a modified Zimm plot, $\frac{K_\phi}{m_D}\left[\frac{d\Sigma}{d\Omega}(q)\right]^{-1}$ vs. $q^2 + K_\phi$. The result clearly demonstrates the absence of any strong concentration effect over the range $0.1 \leqslant \varphi \leqslant 0.3$. In the low q region, where the intensities are most reliable, the constant q lines are horizontal. We believe that the apparent slightly positive slope for $q > 0.01$ Å results primarily from uncertainties in the subtraction of background rather than interference from the larger HPB-S3 molecules. Equation (3) predicts a 5% increase in $K_\phi\left[\frac{d\Sigma}{d\Omega}(0)\right]^{-1}$ over this range due to molecular size mismatch ($\Delta_w = \Delta_z \sim 0.25$), an effect which would probably be unobservable in practice.

From these results we conclude that DPB/HPB blends conform to ideal mixture scattering behaviour in the quenched solid state. The ability to measure single chain size properties by SANS at high concentrations has been demonstrated with amorphous polymers by several groups[6-8]. This study, however, is the first to demonstrate the principle in a semicrystalline polymer. Although Stamm *et al.* observed the $\varphi(1-\varphi)$ dependence of SANS intensity at $q \approx 0.25$ Å^{-1} with high concentrations of labelled polyethylene[10] and polypropylene[11], the intermediate q region is not as sensitive as the Guinier region to non-ideality (segregation) or size mismatch.

The scattering curves were used to determine M_w and R_g for the deuterated polymers according to equations (5) and (6); the corrections due to molecular size differences are negligible for the linear samples and less than 8% (corresponding to $\varphi = 0.3$) for the star samples. The results are summarized in *Table 2*. The SANS derived molecular weights from the quenched samples are systematically displaced from the expected results, however. For the linear polymer, SANS gives $M_w = 79\,700 \pm 7000$, greater than the known value of 62 400, while that for the star polymer is lower than anticipated (82 800 ± 4000 *versus*

Table 2 Single chain parameters of SANS samples

Sample	ϕ	$(d\Sigma(0)/d\Omega)^{-1}$ (cm)	M_W	R_g (Å)
L-10	0.097	0.105	86 500	111
L-10,SC*	0.097	0.096	94 000	110
L20	0.193	0.070	72 800	102
S3-10	0.093	0.064	86 200	121
S3-10,SC*	0.093	0.053	103 300	124
S3-10,M**	0.093	0.071	88 500	126
S3-20	0.185	0.035	85 800	128
S3-30	0.288	0.028	76 500	118

* Slowly cooled from the melt
** Measured at 150°C

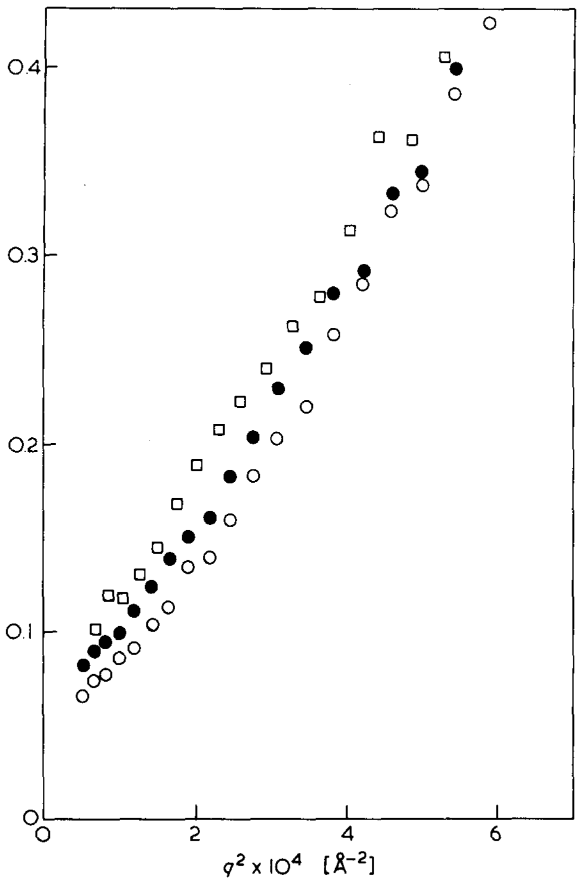

Figure 2 SANS data for the 3-arm star polymer S3-10 in the melt, slowly crystallized solid and rapidly crystallized solid. The points represent melt state data (□), rapidly crystallized solid (●) and slowly crystallized solid (○)

104 000). Because the errors for the two systems are in opposite directions, and because the R_g values are those expected from the known molecular weights, we eliminate systematic miscalibration of absolute intensities, etc. as sources of these errors. They may result from imprecision in determining the fractional deuteration, y. This factor enters quadratically in the contrast factor K_ϕ, thus strongly influencing the calculated M_w. For instance, if y were 0.38 and 0.40 for DPB-L and DPB-S3, respectively, the SANS molecular weights would agree with the known values.

Slow cooling for both polymers causes an increase of about 15% in the apparent molecular weight (*Table 2*). *Figure 2* compares the scattering curves for S3–10 samples which are molten, quenched or slowly cooled. The upward displacement of the data for the molten sample is expected owing to the decrease in n_t from the lower density (see equation (A-5) in the Appendix). Beyond this, the scattering curves for the molten and quenched samples are identical and yield the same M_w and R_g (*Table 2*). Some evidence of modest clustering or segregation is seen in the slowly cooled S3–10 from the enhanced intensity at $q < 0.02$ Å^{-1}; the curves for slowly cooled and quenched samples merge at higher q. This enhancement in intensity is trivial, however, compared to that seen in slowly cooled mixtures of hydrogenated and deuterated high density polyethylene[12]. A similar effect of cooling rate is seen in L-10. The apparent similarity of segregation effects in linear and star polymers is somewhat surprising. Theoretically, the diffusion coefficient of branched polymers is very small[13], so less clustering was expected in the DPB-53/HPB-S3 blend.

Positive curvature of the reciprocal intensity plots (*Figures 1* and *2*) is characteristic of scattering by random coil (Gaussian) chains with very narrow molecular weight distributions. Equations (1) and (A-9) were used to calculate the scattering of ideally mixed, monodisperse blends of linear (L-10) and three-arm star (S3-10) Gaussian chains. *Figure 3* shows the excellent agreement between experiment and theory over the observable range of q. Even the more pronounced curvature for the three-arm star, reflecting a more compact segment density distribution in a branched polymer, is reproduced by the data.

The Gaussian nature of the DPB chains is more directly shown by scattering at intermediate q presented for S3-30 in *Figure 4*. The plot of $[\mathrm{d}\Sigma/\mathrm{d}\Omega]^{-1}$ *versus* q^2 is rigorously linear with an extrapolated intercept of zero (see equation (A-10)), indicating Gaussian behaviour for distances as small as $(2\pi/q_{\max}) \sim 50$ Å. This scattering law at intermediate q is independent of any mismatch or distribution in molecular sizes as discussed in the Appendix. Since decidedly non-Gaussian effects arising from morphology in melt crystallized polyethylenes normally occur at $q > 0.2$ Å^{-1}, the present finding of Gaussian behaviour up to $q_{\max} = 0.15$ Å^{-1} is not unexpected. Furthermore, the reduced crystallinity of HPB due to the ethyl branches means that an appreciable fraction of the labelled polymer segments are in the noncrystalline phase. Perhaps this, coupled with the small thickness of the lamellar crystals ($l_c \approx 50$ Å)[14], accentuates the random coil character of these chains in the semicrystalline state.

The plot of reciprocal absolute intensity in *Figure 4* can be used to determine directly the molecular weight dependence of the radius of gyration of the Gaussian

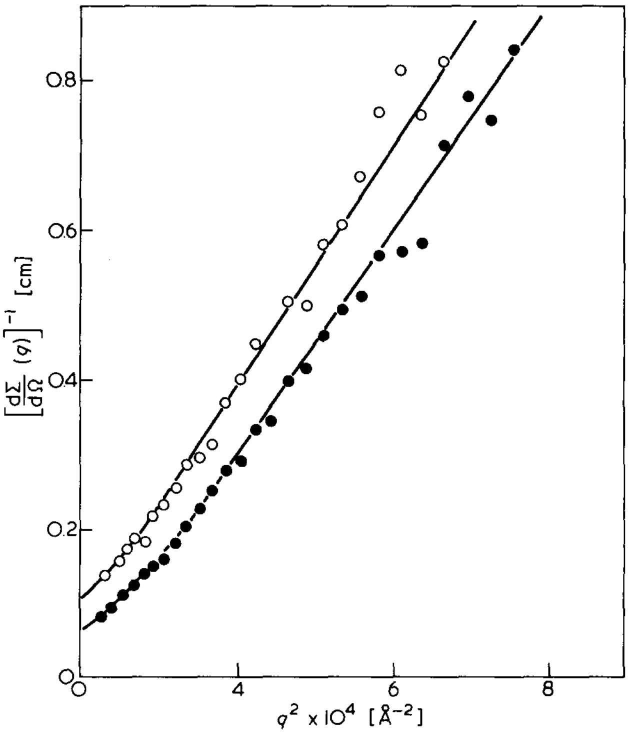

Figure 3 SANS data for the linear and 3-arm star polymers in the rapidly crystallized solid state. The points represent data on L-10 (○) S3-10 (●); the solid lines were calculated from equation (1) and equation (A-9) with R_g = 111 Å for L-10 and R_g = 123 Å for S3-10

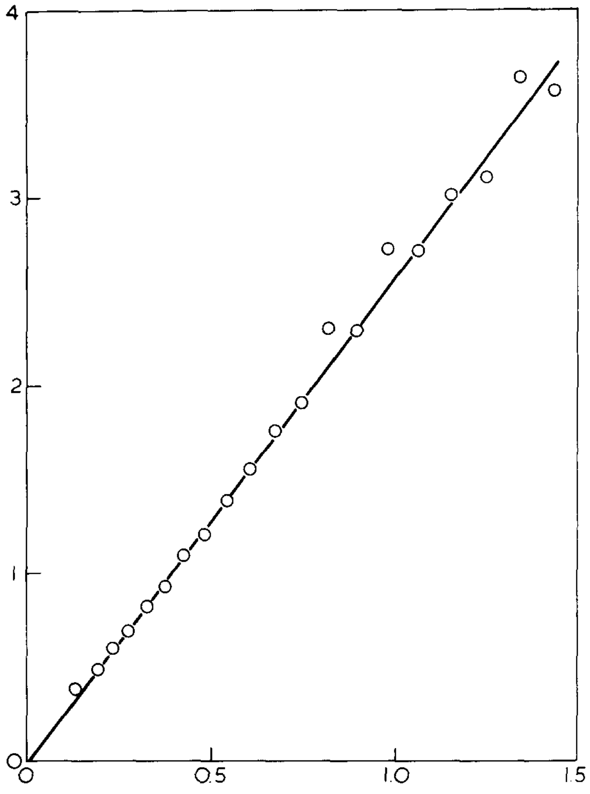

Figure 4 Intermediate *q* SANS data for the 3-arm star polymer S3-30. The solid line represents equation (8)

chains. Rearrangement of equation (A-10) gives for three-arm stars in the intermediate *q* region:

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(q)\right]^{-1}=\frac{m_{\mathrm{D}}}{M_w K_\phi}\,\frac{q^2 R_g{}^2}{2g} \qquad (8)$$

where $g=(3f-2)/f^2=7/9$ for $f=3$. Thus the slope of *Figure 4* can be used to evaluate the ratio R_g^2/gM_w, leading in this case to

$$R_g(\text{Å})=0.47g^{\frac{1}{2}}M_w{}^{\frac{1}{2}} \qquad (9)$$

This is remarkably close to the expression derived from coil dimensions of polyethylene in a theta solvent:

$$R_g(\text{Å})=0.45g^{\frac{1}{2}}M_{\mathrm{H}}{}^{\frac{1}{2}} \qquad (10)$$

The agreement between equation (9) and equation (10) can in fact be made perfect if we adjust the fractional deuteration to $y=0.40$, the same value required to obtain the correct molecular weight from the $q=0$ intensity (see earlier discussion). Thus we have a completely self-consistent argument for Gaussian behaviour of the labelled DPB-S3 chains from both the *q* dependence in the Guinier region and the absolute value of scattering at intermediate *q*.

We have shown that SANS at intermediate *q* can be used to evaluate the characteristic ratio or $R_g{}^2/gM_w$ for Gaussian polymer chains with a single sample. This technique is applicable to labelled polymers having any molecular size distribution with respect to the matrix, and furthermore does not require knowledge of molecular weight of either polymer. We demonstrate the method for a three-arm star polymer, but an identical procedure can be used for linear ($f=2$) or more branched stars ($f>3$). It is possible to invert the procedure and establish either the absolute cross-sections or the value of the factor K_ϕ, provided the numerical constant in equation (10) is known. Some caution should be exercised of course to insure that Gaussian behaviour is indeed obtained. For instance, Guenet[15] has found that isotactic polystyrene will give linear plots of $[\mathrm{d}\Sigma/\mathrm{d}\Omega]^{-1}$ vs. q^2, though the slope depends on crystallization conditions. In such cases the extrapolated intercept is indicative of non-Gaussian behaviour, though a complete interpretation would generally require knowledge of the number average molecular weight (see Appendix, in sections dealing with the intermediate *q* range ($qR_g>1$) and star-shaped molecules).

CONCLUSIONS

HPB/DPB blends are shown to be very useful systems for SANS studies of semicrystalline polymers. Segregation effects are minimal, and the molecular uniformity of these polymers makes interpretation of the SANS patterns straightforward. The labelled DPB molecules exhibit strictly Gaussian behaviour over the range investigated, $0.8<qR_g<15$, and the chain dimensions are the same in the molten and semicrystalline states. In this sense, DPB more closely resembles isotactic polypropylene[16] than isotactic polystyrene[15], since chain conformation and dimensions of the latter polymer are altered by crystallization.

The conformation of a long-chain branched polymer in the condensed phase has been measured for the first time. Scattering from the three-arm star DPB-S3 follows the single chain scattering factor $P(q)$ for a random coil star[17], and it yields a radius of gyration in good agreement with random flight statistics.

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APPENDIX

A growing number of SANS experiments with high concentrations of labelled polymers are being reported; these studies use variable and sometimes imprecise nomenclature. In this appendix we will review the most general treatment of Boué *et al.*[8] and demonstrate how their results reduce to more familiar expressions in simpler cases. In addition, some comments will be made on the applicability to scattering from star-shaped polymers.

Guinier region ($qR_g \leqslant 1$)

Boue *et al.*[8] derived an expression which can be written as

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right]^{-1}=\frac{1}{K'_\phi}\left\{\frac{1-\varphi}{N'_{w\mathrm{D}}}+\frac{\varphi}{N'_{w\mathrm{H}}}+\frac{q^2l'^2}{18}\left[\frac{N'_{z\mathrm{D}}(1-\varphi)}{N'_{w\mathrm{D}}}+\frac{N'_{z\mathrm{H}}\varphi}{N'_{w\mathrm{H}}}\right]\right\} \tag{A-1}$$

where $K'_\phi=[(B'_\mathrm{D}-B'_\mathrm{H})^2n'_t\varphi(1-\varphi)]$

This equation was obtained by evaluating the single chain (intramolecular) correlation functions for the labelled and unlabelled chains, each of which is assumed to be linear and possess Gaussian segment density functions. Each real polymer molecule is represented by an equivalent freely jointed chain of N'_D (or N'_H) statistical segments of length l' (deuteration is assumed not to affect l'); the subscripts w and z indicate the appropriate average number of statistical segments in the polydisperse polymers, e.g. $N'_{w\mathrm{D}}$ is the weight average number of statistical segments of the deuterated chains. As these statistical segments are taken as the basic scattering centres, n'_t is the total number of statistical segments/cm^3 and B'_D and B'_H are the coherent scattering lengths of these segments. Note that those quantities based on statistical segments of the equivalent chains are primed to distinguish them from similar quantities based on the repeat unit of the actual polymer molecules (see equations (1) to (4) in the text). Modification of equation (A-1) into a form based on these actual repeat units ($C_2H_{4(1-y)}D_{4y}$ for polyethylenes) is accomplished with the identity

$$(B'_\mathrm{D}-B'_\mathrm{H})^2n'_tN'_{w\mathrm{D}}=(B_\mathrm{D}-B_\mathrm{H})^2n_tN_{w\mathrm{D}}. \tag{A-2}$$

For instance, if the size of the arbitrary repeat unit chosen to be the scattering centre is doubled, $(B_\mathrm{D}-B_\mathrm{H})^2$ increases by a factor of 4, while the number of such centres per cm^3 (n_t) and the number per chain (N_w) each decreases by a factor of 2. In addition, we use the fact that the mean square radius of gyration of the ensemble of polymer molecules is identical to that of the corresponding set of equivalent chains, i.e.

$$R_g^2=\frac{N'_{z\mathrm{D}}l'^2}{6}$$

Further substituting for N'_H in terms of N'_D and Δ (equation (4) in text) and converting to molecular weight according to $M_w=m_\mathrm{D}N_{w\mathrm{D}}$ equation (A-1) now reads

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right]^{-1}=\frac{m_\mathrm{D}}{M_wK_\phi}\left\{\left[1-\frac{\varphi\Delta_w}{1+\Delta_w}\right]+\frac{q^2R_g^2}{3}\left[1+\frac{\varphi(\Delta_z-\Delta_w)}{1+\Delta_w}\right]\right\} \tag{A-3}$$

where $K_\phi=[(B_\mathrm{D}-B_\mathrm{H})^2n_t\varphi(1-\varphi)]$

This is identical to equation (3) in the text. Note that the weight average molecular weight M_w and the formula weight of the repeat m_D refer to the deuterated polymer.

In the simplified case where the molecular sizes (not the molecular weights) of the labelled and unlabelled polymers are equal, $\Delta_w=\Delta_z=0$ and equation (A-3) reduces to

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right]^{-1}=\frac{m_\mathrm{D}}{M_wK_\phi}\left\{1+\frac{q^2R_g^2}{3}\right\} \tag{A-4}$$

One occasionally sees variations of the form of equation (A-4), though those which utilize 'concentration' in place of volume fraction φ are incorrect. Wignall *et al.*[7] replace φ by the mole fraction of labelled or deuterated polymer. Because it is assumed that deuteration does not affect molar volume and the molecular sizes of the polymers are equal, the mole fraction equals the volume fraction. In the more general case of unequal molecular weights (equation (A-3)), volume fractions must be used.

Incorrect evaluation of n_t will lead to an erroneous value of molecular weight as inferred from the limiting intensity at $q=0$. Since most blends are prepared according to weight fractions (with X_D the weight fraction of deuterated polymer), the total number of repeats is conveniently expressed as

$$n_t=\left[\frac{X_\mathrm{D}}{m_\mathrm{D}}+\frac{1-X_\mathrm{D}}{m_\mathrm{H}}\right]\rho N_\mathrm{A} \tag{A-5}$$

where m_H is the formula weight of an unlabelled repeat unit, ρ is the density of the sample and N_A is Avogadro's number. In some cases the approximation

$$n_t\approx\rho N_\mathrm{A}/m_\mathrm{D}$$

is used in place of equation (A-5). For blends having low concentrations of a fully deuterated, saturated hydrocarbon polymer, this approximation leads to a positive error of 14% in M_w. A proper analysis results in the following expression for the inverse of equation (A-4):

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}=\frac{M_w}{m_\mathrm{D}^2}(B_\mathrm{D}-B_\mathrm{H})^2X_\mathrm{D}\rho N_\mathrm{A}\left\{1-\frac{q^2R_g^2}{3}\right\} \tag{A-6}$$

Note that in this formula the coherent intensity is proportional to the weight fraction of deuterated polymer in dilute blends. It should be realized that equation (A-6) also pertains to dilute blends of polymers having different molecular sizes; in such systems the correction terms involving Δ vanish, as they are proportional to φ. In obtaining equation (A-6), the identities

$$\varphi=X_\mathrm{D}\rho/\rho_\mathrm{D}$$

and

$$m_{\mathrm{H}}/m_{\mathrm{D}} = \rho_{\mathrm{H}}/\rho_{\mathrm{D}}$$

were used. The subscripted densities refer to the hydrogenated and deuterated polymers; these are assumed to be proportional to the formula weights of the repeat units, as molar volume is constant.

If desired, the weight fraction X_{D} can be converted to a concentration (g cm^{-3}) of labelled polymer according to

$$C = X_{\mathrm{D}}\rho.$$

This results in

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega} = \frac{M_w}{m_{\mathrm{D}}^2}(B_{\mathrm{D}} - B_{\mathrm{H}})^2 C N_{\mathrm{A}}\left\{1 - \frac{q^2 R_g^2}{3}\right\} \qquad \text{(A-7)}$$

This is analogous to the expression used for dilute solutions of labelled polymer in low molecular weight solvents.

Intermediate q *range* (q$R_g > 1$)

Still addressing the case of linear polymer chains, Boué *et al.* show that the cross section at intermediate q can be written as

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right]^{-1} = \frac{m_{\mathrm{D}}}{K_\phi}\left\{\frac{1}{2M_n}\left[(1-\varphi) + \frac{\varphi}{1+\Delta_n}\right] + \frac{q^2 l'^2}{12 m_{\mathrm{D}}}\right\} \text{(A-8)}$$

In this region, all intramolecular interference effects have vanished and a plot of reciprocal intensity *versus* q^2 is linear with a slope depending only on the volume fractions of the labelled and unlabelled polymers. As the scattering function in this range is independent of the manner in which the scattering centres are connected to one another, its slope is not affected by molecular weight or molecular weight distribution. The $q = 0$ intercept of this asymptotic region gives the number average molecular weight of the deuterated polymer. These characteristics of the slope and intercept of intermediate q behaviour are consistent with earlier analyses of light scattering intensities from dilute polymer solutions[17].

Star-shaped molecules

Extension of the preceding equations for blends of linear polymers to those of star-shaped macromolecules involves evaluation of the intramolecular correlation function for the molecules in question. This step has been done by Casassa and Berry, so we use their results to modify the finding of Boué *et al.* For this purpose we utilize the normalized scattering function for an isolated star-shaped polymer[17]

$$P(u) = \frac{2}{u^2}\left\{u - f[1 - \exp(-u/f)] + \frac{f(f-1)}{2}[1 - \exp(-u/f)]^2\right\} \qquad \text{(A-9)}$$

where $$u = q^2 R_g^2\left[\frac{f^2}{3f-2}\right]$$

and f is the number of equal length branches on the molecule. For $f = 2$, equation (A-9) reverts to the familiar expression for a linear polymer.

The form of the scattering equation in the Guinier region does not depend on the detailed shape of the polymer molecule, so equation (A-3) applies without modification to star-shaped macromolecules as well as linear ones. But the asymptotic behaviour at intermediate q does depend on molecular shape, as can be seen by evaluating $P(u)^{-1}$ at large u to obtain

$$\lim_{u\to\infty} P(u)^{-1} = \frac{-f(f-3)}{4} + \frac{u}{2}$$

While the slope of this function (which is proportional to $[\mathrm{d}\Sigma/\mathrm{d}\Omega]^{-1}$) is independent of molecular shape, the extrapolated intercept is sensitive to the number of long chain branches per molecule. Of interest in this work are the cases of linear chains ($f = 2$, intercept $= \frac{1}{2}$) and the three-arm stars ($f = 3$, intercept $= 0$). From this we conclude that the inverse scattering function for three-arm stars at intermediate q should read

$$\left[\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right]^{-1} = K_\phi^{-1}\frac{q^2 l'^2}{12} \qquad \text{(A-10)}$$

The extrapolated intercept should be zero for blends of three-arm star polymers having any concentration or combination of molecular weights.