and κ is the temperature coefficient of chain dimensions:

$$\kappa = \mathrm{d} \ln \langle r^2 \rangle / \mathrm{d}T \qquad \text{(A6)}$$

Aside from numerical factors, the viscosity for entangled linear chain liquids can be written as[27]

$$\eta_0 = \zeta \langle r^2 \rangle \nu N^b \qquad \text{(A7)}$$

where $b \sim 2.4$. Equations A2, A3, and A7 combine to give

$$\frac{\mathrm{d} \ln \eta_0}{\mathrm{d}T} = \frac{\mathrm{d} \ln \zeta}{\mathrm{d}T} - (1 + ab - b)\alpha + (1 + 2ab - 3b)\kappa \qquad \text{(A8)}$$

When temperature dependence is expressed as an activation energy, $E_{D/T} \equiv -R \, \mathrm{d} \ln (D/T)/\mathrm{d}T^{-1}$ and $E_\zeta \equiv +R \, \mathrm{d} \ln \zeta/\mathrm{d}T^{-1}$, eq A4 becomes (for $a = 2.3$ and $b = 2.4$)

$$E_{D/T} = E_\zeta + RT_{\mathrm{av}}^2(1.3\alpha - 1.6\kappa) \qquad \text{(A9)}$$

and eq A8, with $E_{\mathrm{v}} \equiv +R \, \mathrm{d} \ln \eta_0/\mathrm{d}T^{-1}$, becomes

$$E_{\mathrm{v}} = E_\zeta + RT_{\mathrm{av}}^2(4.12\alpha - 4.84\kappa) \qquad \text{(A10)}$$

where T_{av} is some midrange (average) value of the experimental temperatures. For polyethylene melts[28,29]

$$\alpha = 0.68 \times 10^{-3} \ \mathrm{K}^{-1} \qquad \text{(A11)}$$

$$\kappa = -1.15 \times 10^{-3} \ \mathrm{K}^{-1} \qquad \text{(A12)}$$

which gives, for $T_{\mathrm{av}} = 418$ K (145 °C)

$$E_{\mathrm{v}} - E_{D/T} = +8.2 \ \mathrm{kJ/mol} \qquad \text{(A13)}$$

and, with $E_{D/T} = 22.8$ kJ/mol

$$E_\zeta = 18.0 \ \mathrm{kJ/mol} \qquad \text{(A14)}$$

References and Notes

(1) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(2) Klein, J. *Macromolecules* **1978**, *11*, 852.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802.
(4) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
(5) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(6) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, Ser. A* **1979**, *365*, 53.
(7) Klein, J. *Philos. Mag. A* **1981**, *43*, 771.
(8) Klein, J.; Fletcher, D.; Fetters, L. J. *Nature (London)* **1983**, *304*, 526.
(9) Bachus, R.; Kimmich, R. *Polymer* **1983**, *24*, 964.
(10) Fleischer, G. *Polym. Bull.* **1983**, *9*, 152.
(11) Leger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.
(12) Bartels, C.; Graessley, W. W.; Crist, B. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 495.
(13) Crist, B.; Graessley, W. W.; Wignall, G. D. *Polymer* **1982**, *23*, 1561.
(14) Boué, F.; Nierlich, M.; Leibler, L. *Polymer* **1982**, *23*, 29.
(15) Tanzer, J. D.; Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2708.
(16) Rachapady, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.
(17) Stamm, M.; Fischer, E. W.; Dettenmaier, M.; Convert, P. *Discuss. Faraday Soc.* **1979**, *68*, 263.
(18) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(19) Raju, V. R.; Rachapady, H.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1223.
(20) Klein, J.; Fletcher, D.; Fetters, L. J. *Faraday Symp. Chem. Soc.* **1983**, *No. 18*, 159.
(21) Mendelson, R. A.; Bowles, W. A.; Finger, F. L. *J. Polym. Sci., Part A-2* **1970**, *8*, 105.
(22) McCall, D. W.; Douglass, D. C.; Anderson, E. W. *J. Chem. Phys.* **1959**, *30*, 771.
(23) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.
(24) de Gennes, P.-G. *J. Phys. (Paris)* **1975**, *36*, 1199.
(25) Graessley, W. W.; Raju, V. R. *J. Polym. Sci., Polym. Symp.* **1984**, *No. 71*, 77.
(26) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.
(27) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(28) Richardson, M. J.; Flory, P. J.; Jackson, J. B. *Polymer* **1963**, *4*, 221.
(29) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.

Dimensions of Polymer Chains in the Semicrystalline Solid State

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ABSTRACT: Chain dimensions in the semicrystalline solid state have been investigated by small-angle neutron scattering (SANS) for a series of well-characterized hydrogenated polybutadienes. Labeled and unlabeled samples with matched chemical structures and narrow molecular weight distributions were used. The coherent SANS patterns for matched mixtures were found to fit the predicted shapes for monodisperse random coils. The data yielded values of radius of gyration R_g which also obeyed the random coil model: $R_g \propto M^{1/2}$ for the linear chains and $(R_g^2)_B/(R_g^2)_L = 0.80$ for a three-arm star, in good agreement with the theoretical value of $^7/_9 = 0.78$. Chain dimensions in the semicrystalline solid state were slightly larger (~13%) than those for linear polyethylene at the Θ condition.

Introduction

Small-angle neutron scattering (SANS) is now widely applied to obtain information on the conformation of chains in bulk polymers. In particular, the SANS technique has been used to investigate chain dimensions in the semicrystalline solid state for polyethylene,[1–3] isotactic polypropylene,[4] isotactic polystyrene,[5] and hydrogenated polybutadiene.[6] In this paper more extensive data are reported for hydrogenated polybutadiene, a model material that is equivalent in composition to an ethylene–1-butene copolymer (~4 mol % 1-butene or ~18 ethyl branches/1000 skeletal carbon atoms) with a uniform chemical microstructure and narrow molecular weight distribution. The polymers were prepared by anionic polymerization of butadiene, followed by saturation of the double bonds, either with H_2 to give hydrogenated polybutadiene (HPB)

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or with D_2 to give a partially deuterated version of the same polymer (DPB). Since HPB and DPB samples prepared from the same polybutadiene precursor have the same chemical structure, precisely matched pairs of labeled and unlabeled samples are available for blending and SANS analysis.

The interpretation of SANS patterns for semicrystalline polymers has been hampered in some cases by void scattering and by segregation of labeled and unlabeled chains during crystallization. Schelten et al.[7] minimized the effect of voids in polyethylene by using hydrogenous polyethylene (HPE) as the major component, the coherent cross section for protons being relatively small. Segregation problems vary with polymer species and have received considerable attention. Summerfield et al.[8] have derived scattering equations for nonideal mixtures of labeled and unlabeled components by assuming that progressive crystallization leads to decreasing amounts of the rapidly crystallizing component in each successive crystal. They suggest that R_g, the root-mean-square radius of gyration of the chains, can be determined from a three-parameter fit of their model to the observed scattering. Schelten et al.[1] were able to eliminate segregation in DPE/HPE mixtures by using small concentrations of the labeled polymer (<6% DPE), solution blending at temperatures well above the melting point of the bulk polymers, and quenching very rapidly after compression molding of the melted mixture. Segregation is more easily avoided in DPB/HPB mixtures. This is due, at least in part, to the smaller difference in component melting temperatures, typically 2 °C for HPB/DPB as opposed to 6 °C for HPE/DPE. We were able to prepare nonsegregated DPB/HPB mixtures over the full range of compositions by a relatively simple quenching procedure.

It is now well established that chain dimensions in the undiluted liquid or glassy polymer are unperturbed: R_g^2 is proportional to the molecular weight M, and within experimental error R_g is the same as that deduced from dilute solution measurements at the Θ condition.[9] Previous SANS studies have shown that the chain dimensions are essentially unchanged when either polyethylene[1] or hydrogenated polybutadiene[6] is quenched rapidly from the melt to the solid state. Similar results are reported for isothermally crystallized isotactic polypropylene[10] and slowly cooled poly(ethylene oxide).[11] Thus, whatever the adjustments in local conformation that may be required to allow incorporation of chain segments into crystallites, the spatial distribution at large distances is practically unaffected. In the present study we examine this remarkable result in more detail. Scattering patterns and the relationship between R_g and M are determined for linear and star hydrogenated polybutadiene in the semicrystalline solid state. The nearly monodisperse nature of the components and absence of segregation enable a relatively unambiguous interpretation of the SANS results.

Experimental Procedures

A. Sample Preparation and Characterization. Butadiene was polymerized anionically to form linear polybutadiene (PB) containing an average of 18 vinyl groups per 1000 skeletal carbon atoms.[12] Termination was accomplished by deactivating the polybutadienyl anions by the addition of dry 2-propanol. The vinyl groups are produced by 1,2 addition of butadiene monomers during polymerization. The microstructure of each PB sample was determined by infrared spectroscopy (Table I). Sample designations indicate the PB molecular weight in 1000's; e.g., PB-19 has a light scattering molecular weight of 19300. A three-arm star polybutadiene (designated by S in the sample code) was synthesized in a similar way except for the termination step. Methyltrichlorosilane was used to link three polybutadienyl anions at a common junction. All PB's were stabilized by 0.1% Santonox (Monsanto) and stored in a refrigerator.

Table I
Molecular Characterization of Polybutadienes

sample	% vinyl	$[\eta]_{THF}$, dL/g	$M_{PB} \times 10^{-3}$ $([\eta])^a$	$M_{PB} \times 10^{-3}$ (LS)
PB-19	8.7	0.39	21	19.3
PB-46	8.0	0.74	48	46.3
PB-70	8.1	1.05	77	70.2
PB-91	7.1	1.25	97	90.6
PB-101	8.2	1.33	106	101
PB-153	6.8	1.76	154	153
PB-206	7.8	2.13	198	206
PB-71S	8.2	0.95	80	71.0

[a] Calculated from eq 1 for the linear samples; for PB-72S, $[\eta] = (7/9)^{0.5}(2.27 \times 10^{-4} M_{PB}^{0.75})$ was used.

Molecular weights were determined for the PB samples by light scattering measurements in cylcohexane and intrinsic viscosity measurements in tetrahydrofuran at 25 °C. Molecular weights were evaluated from the latter by[12,13]

$$[\eta] = 2.27 \times 10^{-4} M_{PB}^{0.75} \tag{1}$$

Molecular weight distribution breadths were estimated by gel permeation chromatography (Waters GPC, Model 200). For the linear samples, $\bar{M}_w/\bar{M}_n$ is less than 1.05; for the star sample, $\bar{M}_w/\bar{M}_n$ is approximately 1.1.

Hydrogenation to HPB was accomplished in cyclohexane solution at 70 °C and $P_{H_2} = 500$ psi in the presence of a heterogeneous catalyst, palladium metal on calcium carbonate.[14,15] Samples of DPB were prepared similarly with D_2 in place of H_2. After filtration to remove the catalyst, the polymer was precipitated by addition of methanol. No antioxidants were added to the saturated polymers. It was determined that such additives can increase the SANS scattering in both HPB and DPB blanks, presumably caused by particles of undissolved antioxidant.

The fraction of deuterium in the DPB was calculated from density measurements on DPB and HPB pairs from the same polybutadiene precursor. The samples were conditioned for density measurements in an identical manner, compression molding at 150 °C followed by an ice water quench. The densities, ρ_D for DPB and ρ_H for HPB, were measured at 23 °C with a density gradient column. On the basis of the reasonable assumption that matched HPB and DPB pairs have the same crystallinity and unit cell dimensions, the fractional substitution of deuterium for hydrogen in the DPB sample is given by

$$y = \frac{m_H}{8}\left(\frac{\rho_D - \rho_H}{\rho_H}\right) \tag{2}$$

where $m_H = 56.10$ is the molecular weight of the HPB mer (C_4H_8). The average DPB mer then has the structure $C_4H_{8(1-y)}D_{8y}$. The values of y exceed the ideal value of 0.25, presumably because of H–D exchange during the deuteration step. Densities and fractional deuteration from eq 2 are included in Table II. Replicate tests showed density was reproducible to $\pm 6 \times 10^{-4}$ g/cm^3, corresponding to ± 0.01 in y.

Melting behavior was measured by differential scanning calorimetry (Perkin-Elmer DSC-2). Compression-molded samples were conditioned for 2 min at 140 °C in the DSC and cooled at 80 °C/min. Heating curves were then recorded at a heating rate of 5 °C/min. The peak melting temperature T_p and the final melting temperature T_f are given in Table II. Values of T_p and T_f for duplicate samples differed by less than 0.3 °C. The values of T_f are practically the same from sample to sample in the HPB series, indicating a nearly constant frequency of ethyl branches (from vinyl groups in the PB precursors). Although lower by approximately 2 °C, the values of T_f for the DPB series are also nearly the same, reflecting the nearly constant fraction of deuterium substition ($y \sim 0.40$). The melting range is broad for both HPB and DPB, so the enthalpies of melting obtained by DSC are rather imprecise. Allowing for this, the enthalpy of melting per mer obtained for each component of a matched pair appeared to be the same ($\pm\sim 5\%$).

Table II

(a) Properties of Hydrogenated Polybutadienes

sample	ρ(23 °C), g/cm^3	T_p, °C	T_f, °C	$[\eta]_{TCB}$, dL/g	N[a]
HPB-19	0.915_8	104.3, 107.4[b]	109.6	0.48	357
HPB-46	0.909_0	103.9	108.1	0.88	856 807[c]
HPB-70	0.906_4	105.6	108.7	1.23	1300
HPB-91	0.905_7	106.8	109.9	1.40	1680
HPB-101	0.904_5	105.2	108.6	1.57	1870
HPB-153	0.902_6	104.0	107.8	1.97	2830 2620[c] 2640[d]
HPB-206	0.903_5	104.0	106.8	2.56	3810
HPB-71S	0.909_6	105.6	108.5	10.6	1310

(b) Properties of Labeled (Partially Deuterated) Hydrogenated Polybutadienes

sample	ρ(23 °C), g/cm^3	T_p, °C	T_f, °C	$[\eta]_{TCB}$, dL/g	y
DPB-19	0.967_5	102.0, 105.5[f]	107.4	0.44	0.39
DPB-46(1)[e]	0.962_5	102.4	106.1	0.83	0.41
DPB-46(2)[e]	0.957_2	102.5	106.2	0.84	0.37
DPB-70	0.959_0	103.5	106.5	1.22	0.40
DPB-91	0.956_5	105.4	108.5	1.35	0.39
DPB-101	0.957_3	103.3	106.7	1.53	0.40
DPB-153	0.951_3	103.3	106.9	1.81	0.37
DPB-206	0.953_8	101.7	106.8	2.42	0.39
DPB-71S	0.964_1	103.6	105.8	0.99	0.41

[a] From light scattering on the PB (Table I), except as noted. [b] Double melting peak. [c] Measured on the HPB by light scattering in TCB at 135 °C. [d] Measured on the DPB by light scattering in TCB at 135 °C. [e] (1) and (2) refer to separate deuterations of the same PB-46. [f] Double melting peak.

Molecular weights of the saturated polymers were checked by intrinsic viscosity in trichlorobenzene (TCB) at 135 °C (Table II). In addition, values of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ were determined by a combination of light scattering and GPC in TCB at 135 °C on selected samples through the courtesy of Dr. Gary VerStrate, Exxon Chemical Co. (Table II). The distributions remain narrow ($\bar{M}_w/\bar{M}_n < 1.1$), and $\bar{M}_w$ values agreed with data on the precursor polybutadienes. The large-scale chain structure remains intact during the hydrogenation process, supporting the conclusions of earlier work.[14,15] The values of $[\eta]$ for DPB in trichlorobenzene are consistently smaller than those for the corresponding HPB. This is to be expected, since

$$[\eta]_{DPB}/[\eta]_{HPB} = m_H/m_D \tag{3}$$

if the matched pairs have the same chain length, partial molar volume, and coil dimensions. Here, m_H and m_D are the formula weights of the repeat units in HPB and DPB, respectively. Allowing for experimental errors, the observed ratios of intrinsic viscosity are consistent with eq 3, m_H/m_D being 0.94–0.95 for all pairs. Table IIa gives the degree of polymerization $N = M/m_{PB}$, where M is the light scattering molecular weight of the parent polybutadiene (Table I) and $m_{PB} = 54.09$.

B. SANS Measurements. Blends were prepared by mixing DPB and HPB in trichlorobenzene solution at 140 °C, precipitating with an excess of methanol, and drying under vacuum at 60 °C. The blends were compression molded at 150 °C to a known film thickness of about 1.5 mm, and then quenched in ice water. Blends were made with 50% and sometimes 10% DPB in HPB from the same parent polybutadiene (matched samples). Three blends of 10% DPB in HPB of different molecular weights (mismatched samples) were made as well. The volume fraction ϕ of DPB in the blends is given in Table III.

Scattering measurements were made at the 30-m SANS facility at the National Center for Small Angle Scattering Research, Oak Ridge National Laboratory.[16] The wavelength of the incident neutrons was 4.75 Å, the sample-to-detector distance was 11 m, and the beam collimator diameters were 3.0 and 1.3 cm. Scattering patterns were recorded at room temperature with a 64 × 64 element, two-dimensional detector. Corrections for detector sensitivity and instrument background were made in the usual manner. The scattering pattern was circularly symmetric in all cases, so azimuthal averaging was used to enhance the counting statistics. The scattering data were converted to absolute units, $d\Sigma/d\Omega$, the scattering cross section per unit volume, by calibrations with an aluminum standard. The magnitude of the scattering vector, $q = 4\pi\lambda^{-1} \sin (\theta/2)$, ranged from 0.0070 to 0.040 Å^{-1}.

Table III
Neutron Scattering Results on HPB/DPB Mixtures

sample	ϕ	R_g, Å	$R_g/M^{1/2}$
Mixtures with Matched Components			
DPB-19/HPB-19	0.099	82	0.579
DPB-46(2)/HPB-46	0.50_0	112	0.511
DPB-70/HPB-70	0.50_0	142	0.526
DPB-91/HPB-91	0.096	151	0.492
DPB-101/HPB-101	0.50_0	168	0.519
DPB-153/HPB-153	0.50_0	209	0.525
DPB-19/HPB-19	0.50_0	243	0.526
DPB-71S/HPB-71S	0.50_0	125	0.461
Mixtures with Mismatched Components			
DPB-46(1)/HPB-91	0.095	109	0.497
DPB-101/HPB-91	0.095	158	0.488
DPB-153/HPB-91	0.096	213	0.535

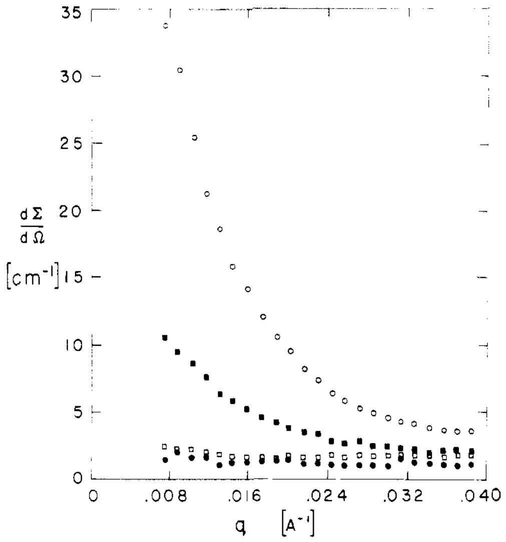

Figure 1. Scattering curves for matched blends of DPB-101/HPB-101, ϕ = 0.5 (○), and DPB-91/HPB-91, ϕ = 0.1 (■). The lower curves are for blanks of pure HPB (●) and DPB (□).

Coherent scattering profiles were obtained by subtracting the scattered intensity of a pure HPB blank at each q from the measured intensity of the blend. This background from pure HPB is dominated by hydrogen incoherent scattering and should be independent of angle. Our experiments showed, however, a modest but reproducible increase in intensity at small angles in the HPB blanks. Patterns of similar shape and intensity were observed for pure DPB. We have no explanation for this unexpected behavior. It cannot have been caused by scattering from voids, since in that case, the scattering at low q would be much greater for pure DPB because of its larger coherent cross section. The scattering curves for two blends of DPB in HPB and for the pure HPB and DPB blanks are shown in Figure 1. It is apparent that the low-q intensities for the blends are much larger than either background and thus the corrected coherent intensities are insensitive to the pecularities of the blanks.

Radius of Gyration

In a thermodynamically ideal mixture of matched monodisperse pairs of protonated and deuterated chains, the coherent scattering cross section per unit volume can be expressed as[17]

$$d\Sigma_c(q)/d\Omega = KNP(q) \tag{4}$$

Here, N is the degree of polymerization ($N = N_H =$

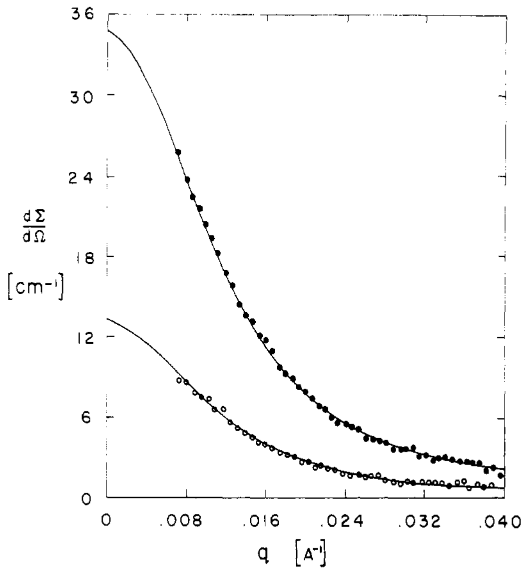

Figure 2. Background-corrected scattering curves for matched blends of DPB-70/HPB-70, $\phi = 0.5$ (●), and DPB-91/HPB-91, $\phi = 0.1$ (○). The solid curves are calculated with eq 4 and 7.

$M_H/m_H = N_D = M_D/m_D$, where M_H and M_D are the molecular weights of the hydrogenated and deuterated polymers, respectively), $P(q)$ is the normalized single-chain scattering function ($P(0) = 1$), and K is the contrast factor. The contrast factor depends on blend composition:

$$K = (B_D - B_H)^2 n\phi(1 - \phi) \tag{5}$$

where ϕ is the volume function of one component, n is the number of mers per unit volume, and $B_D - B_H$ is the difference in coherent scattering lengths of the DPB and HPB mers:

$$B_D - B_H = 8y(b_D - b_H) \tag{6}$$

in which $b_D - b_H = 1.041 \times 10^{-12}$ cm^{-1} is the difference in coherent scattering lengths of deuterium and hydrogen.[18] For linear chains, the single-chain scattering function for unperturbed random coils is given by the Debye formula:[19]

$$P(q) = 2u^{-2}[\exp(-u) - 1 + u] \tag{7}$$

where $u = q^2R_g^2$. For regular star polymers[20]

$$P(q) = \frac{2}{u^2}\left\{u - f[1 - \exp(-u/f)] + \frac{f(f-1)}{2}[1 - \exp(-u/f)]^2\right\} \tag{8}$$

where $u = q^2R_g^2f^2/(3f - 2)$ and f is the number of arms. Equation 8 reduces to eq 7 for $f = 1$ or 2.

In view of the nearly monodisperse character of the polymers used in this study, we chose to establish R_g for the matched pairs by direct fitting to eq 7 or, for the three-arm star, to eq 8 with $f = 3$. The adequacy of the random coil model was judged by the agreement between experimental and theoretical q dependence over the observable q range. This method is preferred to the more common Zimm analysis[21] because of distinct positive curvature in Zimm plots of SANS intensities for the HPB/DPB blends.[6,22] Curvature is expected for nearly monodisperse samples, and our analysis would be restricted to chains with $R_g \lesssim 130$ Å to obtain linear Zimm plots in the available q range. Such a restriction can be relaxed somewhat if $P(q)$ is well represented by eq 7 or eq 8.

Only relative intensities were used in the fitting procedure (absolute intensities are treated in the next section), and R_g was adjusted to give the best visual fit of the random coil model to the angle dependence of the observed intensities. The agreement is good, as can be seen from examples of linear polymers (Figure 2) and the three-arm star polymer (Figure 3). A worst case is shown in Figure 4, where minor discrepancies are present at the highest q. In this region of low coherent intensity the background correction becomes quite significant; no attempt was made to adjust background to improve the overall fit. Also shown in Figure 4 is the effect of altering R_g by ±5%, from which we conclude that the fitting procedure establishes R_g with a precision of ~5%. The R_g values obtained are presented in Table III, together with the ratio $R_g/M^{1/2}$, where M is based on light scattering molecular weight of the precursor polybutadienes.

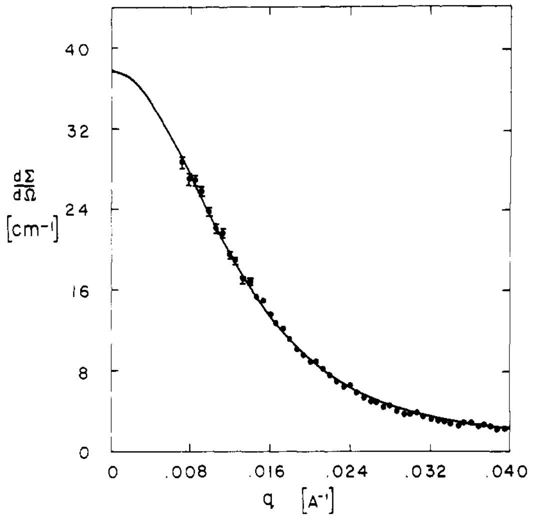

Figure 3. Background-corrected intensity for the system DPB-71S/HPB-71S, $\phi = 0.5$. The solid line is calculated from eq 4 and 8.

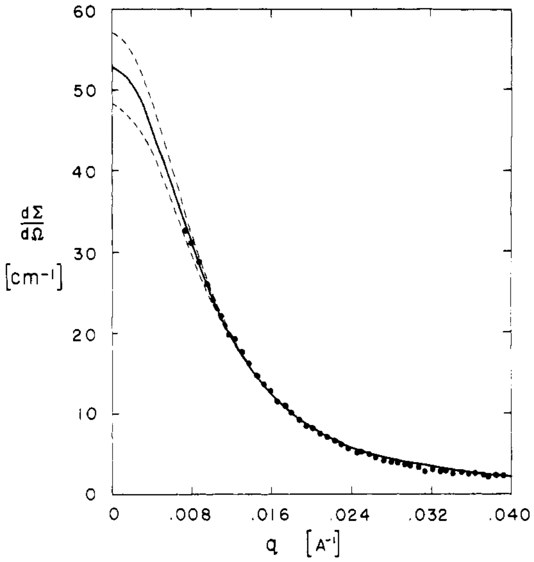

Figure 4. Background-corrected intensity for the system DPB-101/HPB-101, $\phi = 0.5$. The broken lines show the effect of changing R_g by ±5% from the value used in calculating the solid line.

Analysis of the scattering curves from mismatched systems was modified to account for the effects of the matrix. The procedure is based on the treatment of Boué et al.,[17] who showed that for ideal mixtures the component scattering intensities add reciprocally, i.e.

$$\frac{d\Sigma_c}{d\Omega} = (B_D - B_H)^2 n\left[\frac{1}{N_H\phi_H P_H(q)} + \frac{1}{N_D\phi_D P_D(q)}\right]^{-1} \tag{9}$$

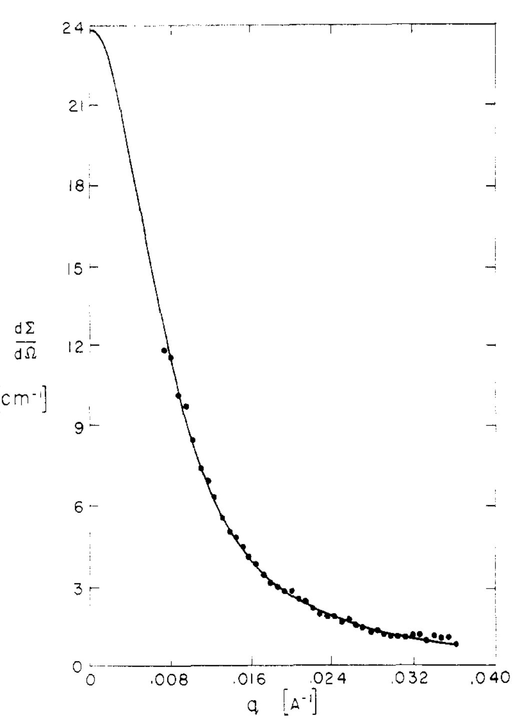

Figure 5. Background-corrected intensity for the mismatched system DPB-153/HPB-91, $\phi = 0.1$. The solid line is calculated by using eq 9 as described in the text.

The subscripts D and H refer to the labeled and unlabeled chains, respectively. Boué et al. have proposed an analysis of the intensity in the "Guinier range" (more properly in the linear range of Zimm plots) which corrects the apparent R_g (and $q = 0$ intercept) to give the component R_g's (and N's), provided the ratio of molecular sizes N_H/N_D is known. We have not used that method because of the curvature of Zimm plots mentioned above. Instead, the relatively small matrix contribution (the first term in brackets in eq 9) was calculated at each q for known values of $\phi_H = 1 - \phi_D$, the ratio N_H/N_D from light scattering, $(R_g)_H$ from Table III, and eq 7 for $P_H(q)$. The unknown $(R_g)_D$ was adjusted to give the best fit of eq 10 to the observed intensity, as shown in Figure 5. The values of $(R_g)_D = R_g$ so obtained are presented in Table III. It can be seen that the agreement with chain dimensions measured with matched systems is excellent.

There is, of course, no way to evaluate either $(R_g)_D$ or $(R_g)_H$ from the intensity profile of a mismatched system without independent knowledge of the ratio N_H/N_D. In these studies, however, the concentration of the DPB was moderate and the molecular sizes were not too disparate. The matrix contribution to eq 9 was ~10% of the total intensity, and its q dependence was not very different from that of the DPB component. For these reasons the result of this procedure is insensitive to the particular choice of N_H/N_D, provided it is reasonable. Thus the agreement of R_g measured with matched and mismatched systems is expected and cannot be construed as a rigorous test of eq 9. A more complete discussion of the scattering from mismatched systems of monodisperse polymers is given in the Appendix.

The samples in this study are not truly monodisperse, of course, so the values obtained for R_g are averages. They would be z-averages if evaluated from scattering in the Guinier range. As it is, R_g is weighted less heavily by the largest chains because it represents a best fit over a wide range of $P(q)$. Fortunately, the effects of polydispersity are always small in our case, so the relationship between coil dimensions and chain length should be essentially the same as that for monodisperse samples.

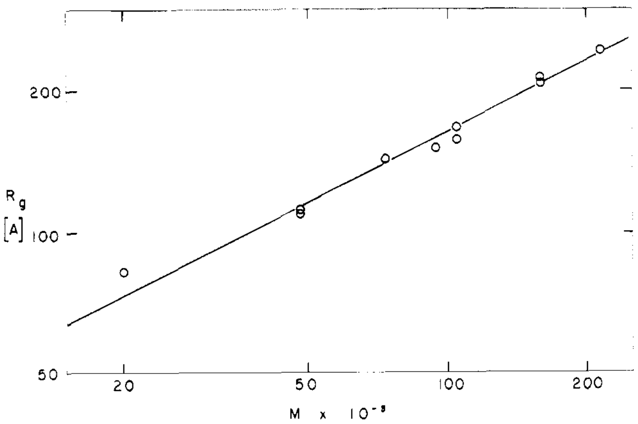

Figure 6. Radius of gyration vs. molecular weight in semicrystalline HPB at 25 °C. R_g was determined by SANS and M was derived from light scattering on the parent polybutadienes.

Figure 6 shows R_g vs. M for the linear HPB's. As expected for random coils, $R_g \propto M^{1/2}$, with the result

$$R_g\ [\text{Å}] = (0.52 \pm 0.03)M^{1/2} \tag{10}$$

This relation can be compared to that from other SANS studies. Schelten et al.[1] obtained $R_g = (0.48 \pm 0.07)M^{1/2}$ for quench-crystallized linear polyethylene. Here both R_g and M are weight averages, the former having been corrected for polydispersity. Summerfield et al.[2] performed similar experiments; considering only the two highest molecular weight polymers and conditions which minimize clustering, their data yield $R_g = (0.49 \pm 0.05)M^{1/2}$. Values of R_g were established by a fitting procedure similar to that used here, but no correction was made for polydispersity.

A further comparison can be made to unperturbed dimensions inferred from solution properties. The value $R_g^2/M = 0.194$ is obtained for linear polyethylene at 140 °C from dilute solution measurements of viscosity at the Θ condition.[23] Applying the reported temperature coefficient of chain dimensions for polyethylene,[23] $\mathrm{d}\ln\langle r^2\rangle/\mathrm{d}T = -1.15 \times 10^{-3}/°\mathrm{C}$, we obtain $R_g^2/M = 0.21$ at 80 °C, the approximate temperature of HPB crystallization for the quench conditions used. This gives $R_g = 0.46M^{1/2}$, indicating slightly smaller chain dimensions than found in the solid state.

Our studies show a modest expansion of HPB coil dimensions over those expected for linear polyethylene in a Θ solvent. Nevertheless, the shape of the scattering patterns and the fact that $R_g \propto M^{1/2}$ indicate that the chain conformation is Gaussian. It may be that the presence of ~18 ethyl branches/1000 skeletal carbons is responsible for part of this discrepancy.

The three-arm star polymer has a smaller size than a linear polymer of the same total molecular weight. For random coil stars, the relation between the radius of gyration $(R_g)_B$ and $(R_g)_L$ of a linear polymer of the same degree of polymerization is[20]

$$\frac{(R_g^2)_B}{(R_g^2)_L} = \frac{3f - 2}{f^2} \tag{11}$$

where f is the number of arms. For the case of the three-arm star HPB-71S, $R_g = (R_g)_B = 125$ Å (Table III). Using $(R_g)_L = 140$ Å from eq 10, one obtains

$$(R_g^2)_B/(R_g^2)_L = (125/140)^2 = 0.80$$

which agrees well with the value from eq 11 for three-arm stars, 7/9 = 0.778.

Table IV
Degree of Polymerization of HPB from SANS and Light Scattering

polymer system	ϕ	$\frac{d\Sigma}{d\Omega}(0)$, cm^{-1}	N(SANS)	N(LS)
DPB-19/HPB-19	0.10	3.95	416	357
DPB-46(2)/HPB-46	0.50	20.7	889	856
DPB-70/HPB-70	0.50	34.6	1250	1300
DPB-91/HPB-91	0.10	13.1	1450	1680
DPB-101/HPB-101	0.50	52.6	1860	1870
DPB-153/HPB-153	0.50	71.8	2970	2830
DPB-206/HPB-206	0.50	106	4140	3810
DPB-71S/HPB-71S	0.50	37.6	1270	1310

Absolute Intensities

The preceding considerations of R_g were based entirely on the q dependence of intensity profiles, with no regard for the absolute cross section. The degree of polymerization N was subsequently adjusted in eq 4 (with the proper value for K for each system) to establish a match of calculated coherent cross sections (eq 4) with the observed values. The values of N so determined, using the fractional deuteration y from density measurements (Table IIb), are presented in Table IV. The SANS values correspond very well with light scattering molecular weights of the parent polybutadienes, suggesting a gratifying internal consistency of all results. However, studies to confirm the values of y used in the analysis have led to a very puzzling discrepancy.

Fractional deuteration was measured for sample DPB-46(2) by ^{2}H NMR spectroscopy (courtesy of Dr. K. Rose of Exxon) and gave $y = 0.29 \pm 0.02$. That figure was confirmed by an elemental analysis (Gollob Analytical Service) which gave $y = 0.30 \pm 0.02$. The value from density for the same polymer, however, is 0.37 (Table IIb). Since the absolute intensity is proportional to y^2N, a modest change in y has a pronounced effect on the value of N obtained from eq 4. With $y = 0.3$ as indicated by chemical analysis, the N(SANS) values in Table IV would be increased by ~50%; i.e., N(SANS) for DPB-46(2) would increase from 890 to 1350, with corresponding increases for the other polymers. These higher N's are quite inconsistent with any of the other molecular weight measurements and cannot be accepted. The cause of this peculiar situation is not known at present; our results are entirely self-consistent on the basis of independent molecular weights, y from density, and absolute SANS intensities based on standard calibration procedures. If the two separate determinations of y by spectroscopy and chemical analysis are correct, one is forced to conclude that molar volume is not conserved (or that morphology is radically changed) on deuteration and also that the calibration of the SANS instrument is seriously in error. It is hoped that this discrepancy will be resolved, but we state once again that it has no effect on the evaluation of R_g or the relation in eq 10.

Summary and Conclusions

We have used small-angle neutron scattering to examine chain dimensions in the solid state for a semicrystalline polymer. The SANS patterns for the mixtures of hydrogenated polybutadiene and its partially deuterated analogue clearly indicate random coil conformations over the q range studied ($0.007 < q < 0.040$ Å^{-1}), i.e., down to distances of the order of ~50 Å. The experimental relationship between radius of gyration and molecular weight ($R_g \propto M^{1/2}$) provides additional evidence for the random coil shape. The dimensions are slightly larger (~13%) than those obtained for linear polyethylene in a Θ solvent. The scattering pattern and the dimensions obtained for a three-arm star are also consistent with random coil conformations. There is clearly no evidence of component segregation for the quenching conditions used in the study.

Table V
$P(u_e)$ for Matched and Mismatched Systems ($\phi = 0.5$)

u_e	$P(u_e)$ ($N_H/N_D = 1$)	$P(u_e)$ ($N_H/N_D = 10$)
0	1.0	1.0
0.1	0.967	0.967
0.2	0.937	0.935
0.3	0.907	0.904
0.5	0.852	0.845
1.0	0.736	0.720
2.0	0.568	0.549
3.0	0.456	0.441
5.0	0.321	0.313
10.0	0.180	0.179
15.0	0.124	0.124

The relative values of molecular weight determined by SANS are in excellent agreement with values obtained from dilute solution light scattering measurements on the polybutadiene precursors. However, depending on the means used to establish the fractional substitution of deuterium, there is an unresolved discrepancy of ~50% in the absolute values.

The remarkable similarity between random coil dimensions in the semicrystalline state and the liquid state, noted by others and extensively documented here, seems difficult to reconcile with a regular lamellar morphology in the semicrystalline state and remains to be explained.

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Appendix. Scattering Profiles for Mismatched Systems

The coherent cross section for an ideal mixture of polymer chains can be written in the general form[17]

$$d\Sigma_c/d\Omega = (B_D - B_H)^2 n\{[\phi_H\langle N_H P_H(q)\rangle]^{-1} + [\phi_D\langle N_D P_D(q)\rangle]^{-1}\}^{-1} \quad \text{(A1)}$$

where all quantities are the same as in eq 9, with the exception that the angular brackets indicate averages over the molecular size distribution of each component. Letting $g(N)\,dN$ represent the weight fraction of N-mer of a particular type of chain, these averages look like

$$\langle N_H P_H(q)\rangle = \int_0^\infty N_H P_H g(N_H)\,dN_H \quad \text{(A2)}$$

It is assumed in eq A1 that the fractional deuteration y is the same for all N_D. For the case of monodisperse polymers, eq A1 reduces to eq 9 in the text.

While Boue et al.[17] have pointed out that eq A1 is not generally useful because the weighting of the component intensities is not expressed in terms of the usual averages of molecular size, we are interested in the case of mismatched monodisperse polymers, i.e., eq 9. What is the effect of mismatching and volume fraction ϕ_D on the shape of the scattering profile?

Equation 9 is rewritten as an expression equivalent to that for a matched system:

$$d\Sigma_c/d\Omega = (B_D - B_H)^2 n\{[\phi_H N_H P_H(q)]^{-1} + [\phi_D N_D P_D(q)]^{-1}\}_{-1} = K N_e P_e(q) \quad \text{(A3)}$$

where K is defined by eq 5 and N_e is the effective or apparent length of the labeled chain, given by[17]

$$N_e = N_D(1 + \Delta)/(1 + \phi_H \Delta) \quad \text{(A4)}$$

in which Δ is defined by

$$N_H = N_D(1 + \Delta) \quad \text{(A5)}$$

The correction term $w = (1 + \Delta)/(1 + \phi_H\Delta)$ can be used to relate the apparent molecular weight of the mismatched system to that of either of the components N_D or N_H. The effective scattering function of the chains in the mismatched system, $P_e(q)$, is the quantity of interest here. From eq A3 one can write

$$P_e(q) = (1 + \phi_H\Delta)\left\{\frac{\phi_H(1 + \Delta)}{P_D(q)} + \frac{\phi_D}{P_H(q)}\right\}^{-1} \quad \text{(A6)}$$

This may be evaluated for any choice of ϕ_H and Δ, with $P_D(q)$ and $P_H(q)$ given by the Debye function, eq 7. The different scattering functions are most easily compared in terms of $u = q^2R_g^2$, so we write

$$P_e(q) = P_e(u_e) \quad \text{(A7a)}$$

$$P_D(q) = P(u_D) = P(u_e/w) \quad \text{(A7b)}$$

$$P_H(q) = P(u_H) = P(u_e(1 + \Delta)/w) \quad \text{(A7c)}$$

where $u_e = q^2(R_g^2)_e$ and

$$(R_g^2)_e = \left(\frac{1 + \Delta}{1 + \phi_H\Delta}\right)(R_g^2)_D = w(R_g^2)_D \quad \text{(A8)}$$

The rather surprising result is that $P(u_e)$ is extremely insensitive to the extent of mismatching. This is illustrated by Table V, which presents the scattering function of a matched system and one with $\phi_H = 0.5$ (the volume fraction at which mismatching effects are maximized) and $N_H/N_D = 10$. Equation A6 is symmetric in response to mismatching, so the result applies to $N_H/N_D = 0.1$. The largest difference in $P(u_e)$ is about 3% of $P(u)$ for a single coil; this difference is of course smaller for other choices of ϕ_H and smaller quotients N_H/N_D. Changes of this magnitude are virtually unobservable in any experiment, so one is entitled to use single-chain scattering functions to fit intensity profiles with mismatched blends of monodisperse polymers. Although the results, N_e and $(R_g)_e$, must be corrected for mismatching effects according to eq A4 and A8, the shape of the curve should fit $P(u)$ for a simple, matched monodisperse system, provided of course that the solution is ideal.

A similar conclusion can be reached for mismatched systems in which each component has the most probable distribution of molecular weights (with different averages for each component). Here one can see by inspection of eq A1 that the reduced shape of the intensity profile $P(u_e)$ is independent of either Δ or ϕ, since, for example[19]

$$\frac{1}{\langle N_H P_H(q)\rangle} = \frac{1}{N_{wH}}\left[\frac{1}{2} + \frac{q^2(R_g^2)_{zH}}{3}\right] \quad \text{(A9)}$$

where subscripts w and z refer to the appropriate averages of the molecular weight distribution. Linear Zimm plots will be observed for all concentrations and degrees of mismatch, provided both the labeled and unlabeled chains have most probable distributions of molecular weight.

It has been shown for two particular choices of molecular weight distribution, monodisperse and most probable, that $P(u_e)$ is independent of relative chain lengths at all volume fractions of ideal solutions. It may be that this holds for other choices of molecular weight distribution, but that generalization has not been considered here. However, with two distributions most commonly approximated in experiments one can expect $P(u_e)$ to be constant. This makes studies of mismatched systems more attractive.

References and Notes

(1) Schelten, J.; Ballard, D.; Wignall, G.; Longman, G.; Schmatz, W. *Polymer* **1976**, *17*, 751.
(2) Summerfield, G. C.; King, J. S.; Ullman, R. *J. Appl. Crystallogr.* **1978**, *11*, 548.
(3) Sadler, D.; Keller, A. *Science (Washington, D.C.)* **1979**, *203*, 263.
(4) Ballard, D.; Cheshire, P.; Janke, E.; Nevin, A.; Schelten, J. *Polymer* **1982**, *23*, 1875.
(5) Guenet, J. M.; Picot, C.; Benoit, H. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 251.
(6) Crist, B.; Graessley, W. W.; Wignall, G. D. *Polymer* **1982**, *23*, 1561.
(7) Schelten, J.; Wignall, G.; Ballard, D. *Polymer* **1974**, *15*, 682.
(8) Summerfield, G.; King, J.; Ullman, R. *Macromolecules* **1978**, *11*, 218.
(9) Flory, P. J. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 14.
(10) Ballard, D.; Cheshire, P.; Longman, G.; Schelten, J. *Polymer* **1978**, *19*, 379.
(11) Fischer, E. W. *Pure Appl. Chem.* **1978**, *50*, 1319.
(12) Rochefort, W.; Smith, G.; Rachapudy, H.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1197.
(13) Xu, Z.; Song, M.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1981**, *14*, 1591.
(14) Rachapudy, H.; Smith, G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.
(15) Raju, V. R.; Rachapudy, H.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1223.
(16) Koehler, W., et al. In "Scattering Techniques Applied to Supramolecular and Nonequilibrium Systems"; Plenum Press: New York, 1981; pp 75ff.
(17) Boué, F.; Nierlich, M.; Leibler, L. *Polymer* **1982**, *23*, 29.
(18) Kostorz, G.; Lovesey, S. In "Treatise on Materials Science and Technology: Neutron Scattering"; Academic Press: New York, 1979; Vol. 15, pp 5–8.
(19) Debye, P. *J. Phys. Colloid Chem.* **1947**, *51*, 18.
(20) Casassa, E. F.; Berry, G. C. *J. Polym. Sci., Part A-2* **1966**, *4*, 881.
(21) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(22) Crist, B.; Graessley, W. W.; Wignall, G. P. *Polym. Commun.* **1984**, *25*, 136.
(23) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley: New York, 1969.