Small-angle neutron-scattering studies of partially labelled crystalline polyethylene*

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Partially deuterated (DPE) and conventional (PE) polyethylene are used to study chain conformations in melt-crystallized blends. The deuterium fraction y ranged from 0.19 to 0.59, resulting in melting temperature differences $\Delta T_m = 1$–2°C between PE and DPE. Small-angle neutron scattering (SANS) from molten or quench-crystallized blends yields single-chain radii of gyration R_g which apparently depend on y and are as much as 15% larger than values reported from experiments with fully labelled ($y=1$) polyethylene. Quenched PE/DPE blends give Gaussian-like scattering patterns out to $q=0.1\,\text{Å}^{-1}$, the limit of these studies. This implies considerably more intramolecular correlations at distances of 10–50 Å than derived from a similar experiment employing fully deuterated chains. The present result is thought to be more representative of semicrystalline polyethylene since DPE and PE are nearly perfectly matched. Crystallization by slow cooling creates non-statistical concentration fluctuations which result in excess forward SANS, so a melting point difference of 1°C is still sufficient to trigger 'clustering' or 'segregation' of PE and DPE. Intensity decays at $q>0.05\,\text{Å}^{-1}$ to the same value as in quenched samples, regardless of crystallinity changing from 0.52 to 0.74. These results are shown to be consistent with dominant 'near-adjacent re-entry' during crystallization of polyethylene from the melt.

(Keywords: small-angle neutron scattering; deuterium labelling; polyethylene)

INTRODUCTION

While small-angle neutron scattering (SANS) has become an invaluable technique for the study of polymers in solutions and in condensed liquid and glassy states, the situation regarding crystalline polymers, particularly those crystallized from the melt, is much less clear[1,2]. We concentrate here on polyethylene, the most-studied crystallizable system by far. SANS relies on deuterium labelling of a fraction of the chains to achieve contrast, but deuteration is known to perturb thermodynamic interactions in solutions and amorphous blends[3,4] and in some crystalline polymers[5–7]. Crystallized mixtures of unlabelled polyethylene (h-PE) and perdeuteropolyethylene (d-PE) are particularly subject to non-random mixing ('clustering' or 'segregation') because the deuterated polymer has a melting temperature about 5°C below that of h-PE[5,6]. This difference is exacerbated in many instances by short-chain branching or other defects which cause the T_m of d-PE to be reduced by as much as 12°C[8].

Previous SANS studies of melt-crystallized polyethylene are reviewed; first we consider the 'low-angle' region of $qR_g \leqslant 1$, which measures the overall size of the chain trajectory. The momentum transfer vector has magnitude $q=4\pi\lambda^{-1}\sin(\theta/2)$, where λ is the neutron wavelength and θ is the scattering angle. The root-mean-square chain dimension R_g is reported to be the same in quench-crystallized polyethylene as in the melt[9,10], and the melt values are nearly identical to the unperturbed dimensions derived from dilute solution behaviour in theta solvents[9,11]. Something like Gaussian chain conformations of quench-crystallized polyethylene chains can be inferred from the experimental relation[9] $R_g = 0.46M_w^{1/2}$. Similar results have been reported by Sadler and Keller[12] and by Summerfield *et al.*[13]. However, deviations[14] from $M^{1/2}$ dependence are seen at low M, and the prefactor (0.46) is slightly larger than 0.44 for polyethylene in theta solvents near 140°C[15]. This Gaussian-like behaviour is restricted to rapidly crystallized blends in which the fraction of labelled component is less than 0.1. With larger amounts of the minority component or after slow cooling the SANS pattern exhibits strong forward scattering from concentration fluctuations formed during solidification. This effect has been analysed and reviewed in considerable detail[1,2]. When such 'segregation' or 'clustering' is present one cannot obtain R_g for the chain molecules without resorting to a model. Schelten *et al.*[10] were the first to consider the effects of non-random mixing on SANS. With their 'paracluster' analysis it was shown that R_g is the same after rapid or slow crystallization, i.e. with or without random mixing of isotopic species.

The second type of experiment employs intensity at larger angles ($qR_g > 1$; intermediate-angle neutron

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scattering or IANS). Coherent intensity scattered by the mixture here gives intramolecular monomer–monomer correlations at typical distances $1/q \approx 10$ Å. It can be shown by a number of theoretical approaches[1,2], and more convincingly by experiment, that excess forward scattering from non-random mixing decays to negligible levels at $q < 0.05$ Å^{-1}. A number of IANS studies of polyethylene have been reported[9,14,16], sometimes with h-PE in a d-PE matrix[8,12,17] to minimize the incoherent background. It should be appreciated that the coherent signal of interest decays approximately as q^{-2}, making background corrections relatively important in the IANS range.

IANS data are usually analysed in the format of a 'Kratky plot', $F(q) = q^2NP(q)$ against q. Here $P(q)$ is the normalized scattering factor ($P(0) = 1$) for a chain of N repeat units. It is assumed that the coherent cross-section per unit volume $I(q)$ of the blend reflects only intramolecular correlations

$$I(q) = \phi_d \phi_h KNP(q)$$
$$K = n_t(B_d - B_h)^2 \qquad (1)$$

The volume fractions of labelled and unlabelled polymer are ϕ_d and ϕ_h, and the contrast factor K is expressed in terms of the scattering lengths B_d and B_h of the repeat units and their number density n_t. If not all chains have the same degree of polymerization because of polydispersity or mismatch between labelled and unlabelled polymers, N and $P(q)$ are the appropriate averages[18,19]. Most IANS studies use low volume fractions of 'tagged' chains, meaning that N and $P(q)$ are dominated by that minority component. Coherent scattering is converted to $F(q)$ by one of the following

$$F(q) = \frac{q^2NI(q)}{I(0)} \qquad (2a)$$

$$F(q) = \frac{q^2I(q)}{\phi_d \phi_h K} \qquad (2b)$$

Equation (2a) does not require absolute intensity calibration, though $I(0)$ must be obtained by extrapolation to $q = 0$ and N must be measured separately. $F(q)$ as defined with equation (2b) dictates that the SANS instrument be calibrated, but absolute N is not needed; the normalization factors in the denominator are usually well known.

The scattering function $F(q)$ for polyethylene is based on CH_2 units. For reference[15], Gaussian chains with $C_\infty = 6.85$, appropriate for molten polyethylene at a crystallization temperature of 120°C, would display a 'Kratky plateau' at $F(q) = 0.74$ Å^{-2}. The experimental $F(q)$ for quench-crystallized polyethylene[20] increases from 0.45 to 0.60 Å^{-2} over the range 0.04 Å$^{-1} < q < 0.12$ Å^{-1}, indicating that the semicrystalline chain (crystallinity $\alpha \approx 0.6$) has appreciably fewer intramolecular correlations at distances of 8–20 Å than the random coil before crystallization! Such data have been the subject of a number of model calculations addressing the question of re-entry[1,2,20–22]. Needless to say, a case cannot be made for (complete) adjacent re-entry in the crystalline portions of quenched polyethylene.

Even more puzzling is the observation that the IANS intensity is independent of the melt crystallization conditions in mixtures of labelled and unlabelled polyethylene[9,12,16,17]. While it is true that slow crystallization causes 'segregation' as mentioned earlier, there is no measurable intensity change in the region where $q > 0.05$ Å^{-1}. It is possible that residual segregation effects might somehow compensate for changes in the 'true' $I(q)$ or $F(q)$, although such a coincidence seems unrealistic.

Thus one is left with the conclusion that chains in semicrystalline polyethylene have fewer intramolecular correlations at distances of ~10 Å than (molten) random coils, and that correlations at distances of less than ~20 Å are unaffected by crystallization rate. Regardless of details about chain folding, these neutron-scattering results are surprising. One potentially confounding aspect of such studies is the difference in melting temperature – as large as 12°C[8] – between the conventional and perdeuterated polyethylenes used in these experiments. Crist and Wignall[23] have investigated model ethylene–butene copolymers with partial deuterium labelling. The melting temperatures of labelled and unlabelled chains are within 2°C of each other, and segregation is absent at virtually all volume fractions and cooling rates. For these moderately crystalline copolymers IANS gives an $F(q)$ which is up to 40% larger than the value calculated for Gaussian coils of the same R_g; this is in distinct contrast to unbranched polyethylene, which has a lower $F(q)$ after crystallization.

It is plausible that some of the unexpected SANS and IANS results for polyethylene may be caused by what we term 'abnormal' crystallization. It is not obvious how d-PE chains will crystallize in a matrix of h-PE, or *vice versa*, when melting temperatures differ by ~10°C. Recall that a T_m disparity of this magnitude implies that d-PE is distinguished from h-PE by more than isotope content. Regardless of details, the crystallization of such 'labelled' molecules cannot be considered representative of chains in conventional polyethylene. Aside from quench crystallization, other strategies have been employed to minimize the consequences of melting temperature difference. Schelten *et al.*[9,10] have matched d-PE with branched h-PE of similar melting and crystallization behaviour. Sadler and coworkers[12,17] have crosslinked the blends, though this procedure has been shown to be ineffective in suppressing segregation[24]. Branching and crosslinking do, however, modify crystallization kinetics and morphology, and hence perturb the system under study.

We report here neutron-scattering experiments on partially deuterated polyethylene crystallized from the melt with unlabelled chains of the same polymer. Partial deuteration is shown to decrease the melting point difference, but 'segregation' or non-random mixing still occurs when crystallizing at slow rates. SANS with these quenched or molten polymers does provide results for both R_g and the shape of the scattering function $F(q)$ which differ from previous findings. Consideration is given to the insensitivity of IANS to well documented changes in morphology in differently crystallized polyethylenes.

EXPERIMENTAL

Polymers

The polyethylenes used here were based on standard reference materials from the National Institute of Science and Technology. The whole polymer SRM 1475 was referred to as WPE, and the high molecular weight

Table 1 Characterization of polymers

	y	M_w (kg mol^{-1})	M_w/M_n	T_{mf}^{a} (°C)	T_{cp}^{b} (°C)
PE		114	1.23	136.2	123.2
DPE.19	0.19	110	1.27	135.1	122.2
DPE.59	0.59	–	–	134.2	119.4
WPE		53	3.1	134.7	
DWPE.28	0.28	40	2.7	133.5	

[a] Heated at 5°C min^{-1} after cooling at 40°C min^{-1}
[b] Cooling at 0.62°C min^{-1}

fraction SRM 1484 was designated PE. Each was reported by the supplier to be free from measurable amounts of branching. The two polymers were used as received and after partial labelling by hydrogen–deuterium exchange over a rhodium catalyst. The reaction conditions and product characterization have been described previously[25]. The labelled whole polymer was called DWPE.28 and the labelled fractions were designated DPE.19 and DPE.59, where the numerical suffix is the fraction y of exchanged hydrogen sites; the labelled polymer had a repeat unit of average composition $CH_{2(1-y)}D_{2y}$. The final melting temperatures T_{mf} in *Table 1* are the return of the differential scanning calorimetry (d.s.c.) endotherms to the baseline on heating at 5°C min^{-1} after cooling at 40°C min^{-1}. Also reported are temperatures of maximum crystallization rate T_{cp} when cooling at 0.62°C min^{-1}.

Partial labelling by exchange is successful in that the melting temperature T_m is decreased by only 1–2°C in the 'tagged' polyethylenes. We note that the melting point difference increases with deuterium fraction y; the normalized shift $\Delta T_m/y = -4.5 \pm 1.1$°C, which is the size of the effect for perdeuterated polyethylene[5,6]. The peak crystallization temperature is lowered by 1°C when $y = 0.19$, and by nearly 4°C for the more-labelled DPE.59. The exchange reaction causes no significant change in molecular weight for the fractionated polyethylene. The modest decrease in M_w for the whole polymer DWPE.28 was attributed to selective adsorption of larger chains by the heterogeneous catalyst[25]. Molecular weight was not measured for the most-exchanged DPE.59, but SANS intensities (see below) indicate that M is unchanged.

SANS samples

Labelled and unlabelled polymers were blended in refluxing xylene, precipitated in cold methanol, dried and compression moulded in the usual fashion to form discs ~1 mm thick. The volume fraction ϕ_d of the labelled polymer was chosen to make the average scattering length density equal to zero, thereby minimizing any contribution of void scattering. This condition corresponds to an overall deuterium fraction of 0.04.

Three crystallization schedules were employed: quench crystallization by rapid immersion in iced water, slow cooling at -0.7°C min^{-1}, and very slow cooling at -0.06°C min^{-1}. Crystallization of the PE/DPE.19 blend occurs between 124 and 121.5°C (2.5 min; slow cool) and between 128 and 126°C (30 min; very slow cool). These intervals are respectively at the lower and upper limits of regime II for polyethylene crystallization[26]; quenching certainly results in regime III crystallization. The physical characteristics are presented in *Table 2*. The volume fraction crystallinity α_v was calculated from the density of the unlabelled polymer (not blends) crystallized in the same manner. The semicrystalline microstructure in the three differently crystallized PE/DPE.19 samples was further characterized by small-angle X-ray scattering (SAXS) with the 10 m instrument at Oak Ridge National Laboratory[28]. The long period L is from the Lorentz-corrected SAXS profiles, and the crystal thickness $l_c = \alpha_v L$.

SANS measurements and data handling

Experiments were done on the small-angle diffractometer at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory, with procedures described earlier[25]. The scattered neutron flux over the range 7×10^{-3} Å^{-1} $\leqslant q \leqslant 0.3$ Å^{-1} was converted to absolute cross-section per unit volume by comparison to a polystyrene–perdeuteropolystyrene standard. Subtraction of incoherent (hydrogen) background, which has a modest q dependence in a multiple-wavelength instrument[1,29], is very important in this work. The apparent cross-section of each sample at $q \approx 0.25$ Å^{-1}, where coherent intensity is negligible, was compared to scattering from unlabelled PE of similar thickness (and hydrogen density) at the same q value. This ratio of apparent cross-sections was used to scale the incoherent PE pattern used for background subtraction; the coherent cross-section per unit volume obtained in this manner is $I(q)$.

$I(q)$ was converted to the scattering function $F(q)$ by equation (2b), which requires neither the extrapolated intensity $I(0)$ nor absolute molecular weight or N. It should be emphasized that values of $F(q)$ reported here or elsewhere are subject to uncertainties from (hydrogen incoherent) background subtraction, particularly at large q where coherent intensity is small. Partial deuteration, used here to minimize changes in crystallization behaviour, also reduces the coherent intensity and thus makes the background relatively larger. The contrast factor K in equation (1) is proportional to y^2 ($K = 4n_t y^2 (b_d - b_h)^2$, where b_d and b_h are the scattering lengths of deuterium and hydrogen), meaning that the coherent cross-section is reduced to as little as 0.04 compared to a blend with perdeuterated ($y = 1$) polymer. While the coherent to incoherent (or signal to background) level is low, the background for each sample is observed directly (at $q \approx 0.25$ Å^{-1}). With this accurate definition of the background, reliable coherent cross-sections can be obtained even when they are small. For example, in the plot of $F(q)$ for PE/DPE.59 in *Figure 2* the ratio of

Table 2 Neutron-scattering samples

	ρ^{a} (g cm^{-3})	α_v	L (Å)	l_c (Å)
PE/DPE.19, $\phi_d = 0.20$				
Quenched	0.9311	0.52	297	154
SC	0.9568	0.70	360	252
VSC	0.9622	0.74	429	317
PE/DPE.59, $\phi_d = 0.068$				
Quenched	0.9311	0.52		
SC	0.9568	0.70		
WPE/DWPE.28, $\phi_d = 0.14$				
Melt	0.781^b	0.00		
Quenched	0.9480	0.65		

[a] Measured on unlabelled polymers
[b] From ref. 27

Table 3 SANS results from partially labelled blends

	$I(0)$ (cm^{-1})	$I(0)/I(0)^{\mathrm{calc}}$	R_g (Å)	a^2 ($\text{Å}^2\,\mathrm{mol\,g}^{-1}$)
WPE/DWPE.28, $\phi_d = 0.14$				
Melt	4.8	1.17	113	0.32
Quenched	8.3	1.69	106	0.27
PE/DPE.19, $\phi_d = 0.20$				
Quenched	12.6	1.52	159	0.23
PE/DPE.59, $\phi_d = 0.068$				
Quenched	31.2	1.00	183	0.29

coherent to incoherent intensities ranges from 1.3 at $q = 0.04\,\text{Å}^{-1}$ to 0.2 at $q = 0.10\,\text{Å}^{-1}$. The ratios are smaller for blends with less-labelled DPE. Despite the unfavourable signal to background ratio, the data presented here are reliable because of the refined background subtraction procedure made possible by the large q range of the time-of-flight diffractometer at IPNS.

RESULTS AND DISCUSSION

Preliminary SANS characterization

SANS of quench-crystallized blends was used to test the premise that random mixtures can be obtained for the three systems in *Table 2*. One aspect which had been overlooked in earlier work on polyethylene is that repulsive H–D interactions may cause excess concentration fluctuations, or even macroscopic phase separation, in the melt. SANS measurements by Londono *et al.*[30] of thermodynamic interactions between conventional and perdeuterated polyethylene have established that the Flory–Huggins interaction parameter $\chi_{\mathrm{hd}} = 2.5 \times 10^{-4}$ for $\mathrm{CH_2}$ and $\mathrm{CD_2}$ groups at 150°C. Partially labelled polyethylene is treated as a random copolymer with C–H and C–D bonds, leading to $\chi = y^2\chi_{\mathrm{hd}}$ for the interaction between $\mathrm{CH}_{2(1-y)}\mathrm{D}_{2y}$ on labelled polyethylene and $\mathrm{CH_2}$ on unlabelled polyethylene. Two sorts of isotope effects can be present in melt blends of deuterated and conventional polyethylene. The first bears on concentration fluctuations in the single-phase melt, which become appreciable as χ approaches the spinodal χ_s defined by

$$\chi_s = \frac{1}{2}\left(\frac{1}{N_{\mathrm{wh}}\phi_{\mathrm{h}}} + \frac{1}{N_{\mathrm{wd}}\phi_{\mathrm{d}}}\right) \tag{3}$$

The ratio $\chi/\chi_s < 0.08$ for the blends in *Table 2*, so melts of these samples can be considered 'ideal' in that they are far from the spinodal. The second condition pertains to phase separation by nucleation and growth; the single-phase melt may be metastable if $\chi N > 2$. Again $\chi N < 0.8$ for all blends considered here, so liquid–liquid phase separation in the melt is not possible. Earlier work on polyethylenes predated knowledge about isotope effects in the melt state. Some of the blends studied by Schelten *et al.*[9,10] and Sadler and Spells[17] had $\chi_{\mathrm{hd}}/\chi_s = 0.3$–$0.5$, meaning that measurable concentration fluctuations were present in the liquid before crystallization. Certain of those blends were potentially metastable as well, with $\chi_{\mathrm{hd}}N$ in the range from 4 to 9. We reiterate that H–D isotope effects are negligible in the melt for the work presented here; crystallization is from random mixtures of labelled and partially labelled polyethylene chains.

The SANS intensity over the range $7 \times 10^{-3}\,\text{Å}^{-1} < q < 30 \times 10^{-3}\,\text{Å}^{-1}$ was fitted to a generalized form of equation (1)[18]

$$I(q) = KS(q)$$

$$[S(q)]^{-1} = [\Sigma\phi_{\mathrm{di}}N_{\mathrm{di}}P(u_i)]^{-1} + [\Sigma\phi_{\mathrm{hi}}N_{\mathrm{hi}}P(u_i)]^{-1} \tag{4}$$

where the scattering factor is for Gaussian chains

$$P(u_i) = \frac{2}{u_i^2}[\exp(-u_i) + u_i - 1]$$

$$u_i = (qR_{\mathrm{gi}})^2$$

$$R_{\mathrm{gi}}^2 = CN_i \tag{5}$$

A two-parameter fitting procedure optimized the absolute intensity in terms of the contrast factor K and the q dependence in terms of the constant $C = R_g^2/N$. The individual volume fractions ϕ_{di} and ϕ_{hi} for appropriate N_{di} and N_{hi} were obtained from the overall blend compositions ϕ_{d} and ϕ_{h} and the experimental molecular weight distributions of each polymer. The results are summarized in *Table 3*. The first column gives $I(0)$, the experimental intensity extrapolated to $q = 0$ with the best-fit parameters K and C in equations (4) and (5). The second column is the ratio of $I(0)$ to $I(0)^{\mathrm{calc}}$, the intensity calculated for $q = 0$ with no adjustable parameters; this quotient will equal 1.0 if sample characterization and instrument calibration are correct and if the labelled and unlabelled chains form an 'ideal' solution. In the last two columns are the root-mean-square radius of gyration $R_g = \langle R_g^2\rangle_w^{1/2}$ and the coil dimension parameter $a^2 = C/14$. The coefficient a is that used by Wignall[1] to relate chain dimension and molecular weight: $R_g = aM_w^{1/2}$. The chain dimensions and the parameter a^2 determined in this manner are model dependent, in that the chains are assumed to have Gaussian conformations in equation (5). We cannot achieve the condition $qR_g < 1$ ($q < 0.01\,\text{Å}^{-1}$) over a sufficient range for a true 'low-angle' analysis.

First to be considered are the molten and quenched WPE/DWPE.28 blends, data for which are presented in *Figure 1*. $I(0)$ for the melt is within 17% of the calculated

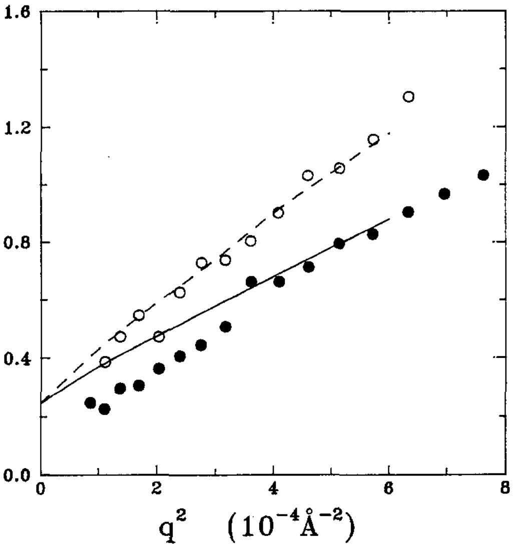

Figure 1 SANS data for WPE/DWPE.28 ($\phi_d = 0.14$) in the melt at 150°C (○) and at room temperature after quench crystallization (●). The solid line is calculated with experimental molecular weights and contrast factor K with a chain dimension parameter $a^2 = 0.22\,\text{Å}^2\,\mathrm{mol\,g}^{-1}$. The dashed line is based on $a^2 = 0.32\,\text{Å}^2\,\mathrm{mol\,g}^{-1}$

value, implying that the fractional labelling y and weight average molecular weights are correct. There is appreciably more intensity for the quench-crystallized blend than the 20% increment predicted from the higher density (n_t in equation (1)). This we attribute to non-random mixing in the quench-crystallized state, probably from the low molecular weight portion of the whole polymer; short chains are known to be more susceptible to 'segregation'[10]. The Zimm plot format of *Figure 1* can be used nevertheless to evaluate chain dimensions in the presence of excess concentration fluctuations (see Appendix). The slope for the crystallized sample is slightly smaller than that for the melt, implying a small decrease in R_g. Schelten *et al.* have reported similar plots for an h-PE/d-PE blend (Figure 4 of ref. 10) in which data for a molten and quench-crystallized sample are indistinguishable. It is not understood why the ~20% increase in $I(q)$, which is expected for the denser solid, was not seen.

The absolute R_g values in *Table 3* are generally different from those reported in other studies. The solid line in *Figure 1* is calculated for molten WPE/DWPE.28 with no adjustable parameters but with the chain dimension parameter $a^2 = 0.22$ Å^2 mol g^{-1} reported by Schelten *et al.*[9,10]; it clearly does not conform to our data. The dashed line utilizes $a^2 = 0.32$ Å^2 mol g^{-1}, implying that R_g^2 (or C_∞) is 50% larger than the mean-square dimensions in low molecular weight theta solvents[15]. It could be argued that this apparent difference is an artefact arising from some peculiarities of the exchange-labelled polymer and perhaps the smallness and uncertainty of the coherent cross-section $I(q) < 3$ cm^{-1}. But we point out that the intensity $I(0)$ for this molten blend is quite reasonable, and that similar 'expansions' have been seen in melts of model copolymers of ethylene and 1-butene[31,32]. We return to this issue later.

The two PE/DPE blends give somewhat contradictory results. The absolute intensity for quenched PE/DPE.19 is about 50% larger than that calculated for ideal mixing, though the chain dimension parameter $a^2 = 0.23$ Å^2 mol g^{-1} is in accord with the results of Schelten *et al.*[9,10]. Here the discrepancy in $I(0)$ is not attributed to 'segregation' since the molecular weight is large; this was confirmed by observing the same intensity ratio and R_g (or a^2) in a more dilute blend ($\phi_d = 0.1$). It is believed that exchange labelling to $y = 0.19$ results in a statistical non-uniformity (chain to chain) of deuterium concentration which would account for the enhanced intensity. This idea is supported by infra-red spectroscopy which reveals unexpectedly high absorption in the 720 cm^{-1} region characteristic of $(CH_2)_n$ groups[33]. The absolute SANS intensity of the quenched PE/DPE.59 blend, in which deuterium 'tagging' y is three times larger while ϕ_d is one third as great, is exactly that calculated for an ideal mixture with uniformly labelled chains. This agreement is consistent with the absence of $(CH_2)_n$ runs by infra-red spectroscopy[33]. The chain dimension R_g is some 15% larger than in PE/DPE.19 for reasons which are not understood. While molecular weight was not measured directly for the DPE.59 component, the SANS intensity indicates that M_w is the same as the gel permeation chromatography (g.p.c.) value for DPE.19. This should be the case, as the exchange reaction conditions were identical aside from the deuterium content of the cyclohexane solvent[33].

To summarize this subsection, molten or quenched blends based on exchange-labelled polyethylene have extrapolated SANS intensities $I(0)$ which are in reasonable accord with random mixtures of chains having degree of polymerization N and deuterium content y determined independently. There is evidence for heterogeneous labelling in DPE.19, and for some modest segregation of labelled and unlabelled chains in quench-crystallized whole polymer. Chain dimensions R_g are, with the exception of the PE/DPE.19 blend, about 13% larger than those found in earlier studies using perdeuterated polyethylene[9–11]. We see a small (~6%) decrease in R_g after quench crystallizing from the melt.

Different crystallization conditions

The two PE/DPE blends were also examined by SANS after the slow and very slow cooling described in Experimental. The whole polymer WPE/DWPE.28 was not used here because of evidence of some 'segregation' even when quenched. The experiments described below gave somewhat disappointing results: non-random mixing is observed when crystallization is conducted more slowly; and the observed intensity at $q > 0.05$ Å^{-1} is insensitive to the crystallization rates employed here. Both these findings are essentially the same as in earlier work with perdeuterated polyethylene.

The extent of non-random mixing is indicated by the enhanced values of $I(0)$ in *Table 4*. Slow cooling (SC, -0.7°C min^{-1}) causes $I(0)$ to increase seven-fold in PE/DPE.19 where ΔT_m has the smallest value of -1°C. The same crystallization rate increases $I(0)$ by less than half this amount in PE/DPE.59 where $\Delta T_m = -2$°C, leading us to conclude that a lower concentration ϕ_d is more effective than a smaller ΔT_m for suppressing 'segregation'. Very slow cooling (VSC, -0.06°C min^{-1}) increases $I(0)$ even more.

Also listed in *Table 4* are the scattering functions $F(q)$ evaluated at $q = 0.08$ Å^{-1}. These were chosen as a compromise between signal to background ratio and freedom from residual 'segregation' effects. The most reliable data are for PE/DPE.59, which has the largest coherent intensity. *Figure 2* shows that slow cooling (crystallinity $\alpha_v = 0.70$) causes increased intensity at low q, but the pattern decays to that for the quenched sample ($\alpha_v = 0.52$) for $q > 0.05$ Å^{-1}. Alternatively, plots of $[I(q)]^{-1}$ against q^2 (such as *Figure 1*, but not shown) are displaced vertically but are parallel to one another, as predicted for non-random mixing in the 'paracluster' model of Schelten *et al.*[10] and discussed in the Appendix.

The solid reference line in *Figure 2* is calculated for Gaussian polyethylene chains[9,10] having $a^2 = 0.22$ Å^2 mol g^{-1}, which gives a limiting $F(q) = 1/7a = 0.65$ Å^{-2}. Data for PE/DPE.59 fall below this line because the chains are more expanded; recall that for the

Table 4 SANS parameters for differently crystallized blends

	$I(0)$ (cm^{-1})	$F(0.08)$ (Å^{-2})
PE/DPE.19, $\phi_d = 0.20$		
Quenched	12.6	0.6 ± 0.1
SC	90	0.6 ± 0.1
VSC	400	0.65 ± 0.05 (0.69)[a]
PE/DPE.59, $\phi_d = 0.068$		
Quenched	31.2	0.50 ± 0.05
SC	111	0.50 ± 0.05

[a] After correction for segregation effects (see Appendix)

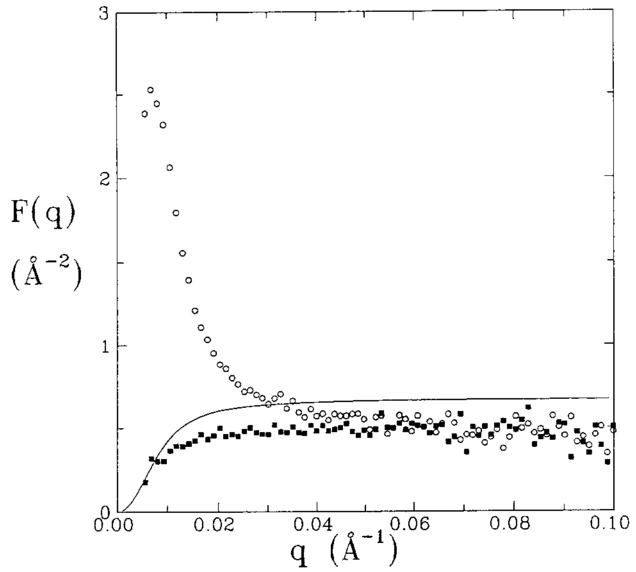

Figure 2 Kratky plots for PE/DPE.59 ($\phi_d = 0.068$) quench crystallized (■) and slowly cooled (○). The solid line is calculated for Gaussian chains with $a^2 = 0.22$ Å^2 mol g^{-1}

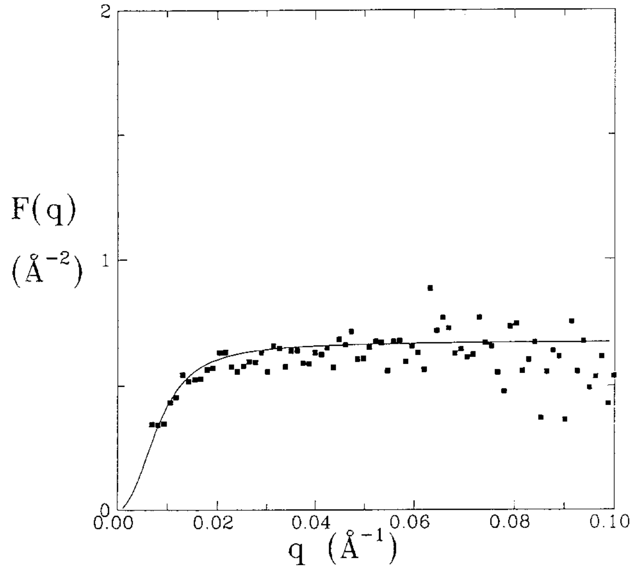

Figure 3 Kratky plot for PE/DPE.19 ($\phi_d = 0.20$) quench crystallized. The solid line is calculated for Gaussian chains with $a^2 = 0.22$ Å^2 mol g^{-1}

quenched sample we obtained $a^2 = 0.29$ Å^2 mol g^{-1} with a 'low-q' ($q < 0.03$ Å^{-1}) fitting to equations (4) and (5). One does not expect semicrystalline chains to have rigorously Gaussian conformations, but the solid points in *Figure 2* have a constant $F(q) \approx 0.5$ Å^{-2} which is consistent with Gaussian coils characterized by the same $a^2 = 1/7F(q) = 0.29$ Å^2 mol g^{-1}. Nowhere in the data handling for *Figure 2* is Gaussian behaviour assumed; inputs for $F(q)$ are absolute $I(q)$, for which background correction is not critical in this blend, experimental volume fractions and calculated contrast factor K. In short, the scattering from this quenched blend indicates that the polyethylene chains are Gaussian for distances q^{-1} between ~120 and 10 Å. It has been argued that such Gaussian-like scattering might be expected for a quenched polymer of low crystallinity ($\alpha_v = 0.52$)[22,34]. Where $F(q)$ is free of 'segregation' scattering, the pattern for the SC sample ($\alpha_v = 0.70$) is indistinguishable from that of the quenched blend. Intramolecular correlations are not changed by an observable amount in semicrystalline polyethylene formed by slow cooling.

The same result is obtained for quenched and slowly cooled PE/DPE.19 blends with volume fraction $\phi_d = 0.20$ or $\phi_d = 0.10$; scattering is enhanced at low q in the slowly cooled samples, but there is no measurable difference for $q > 0.5$ Å^{-1}. Data for the quenched sample are shown in *Figure 3*, where one sees that experimental intensity essentially matches the Gaussian reference line, again with $a^2 = 0.22$ Å^2 mol g^{-1}, out to $q = 0.1$ Å^{-1}. There is more scatter in $F(q)$ because of less coherent intensity with a smaller contrast factor. Note that the quenched blends in *Figures 2* and *3* each display 'Kratky plateaus', though with heights that reflect different coil dimension parameters. Both samples have $I(q) \propto q^{-2}$, a characteristic of chains with Gaussian conformations. This behaviour is quite different from the oft-quoted results of Schelten *et al.*[9] for quenched polyethylene. Their $F(q)$ increases by 30% over the q range from 0.04 to 0.1 Å^{-1}.

$F(q)$ for the very slowly cooled PE/DPE.19 blend is shown in *Figure 4*. Here again the solid line is for Gaussian chains with $a^2 = 0.22$ Å^2 mol g^{-1}. This pattern is dominated by intense forward scattering, though $F(q)$ decays to a value slightly above the Gaussian reference line. The dashed line is a fit to an extreme 'segregation' model described in the Appendix. An alternative analysis would use a Zimm plot like *Figure 1* in which the reciprocal intensity is shifted downwards but remains essentially parallel to that for the quenched sample. Either method indicates that intramolecular correlations in the quenched and very slowly cooled samples are similar at distances of $q^{-1} \approx 12$ Å. Even when the crystallization rate is slowed by an additional order of magnitude (compared to the SC blend), and the crystal thicknes l_c is twice that in the quenched sample, $F(q)$ is enhanced by ~15% at most.

CONCLUSIONS

These SANS studies were done with labelled polyethylene which is almost ideally matched to the unlabelled blend

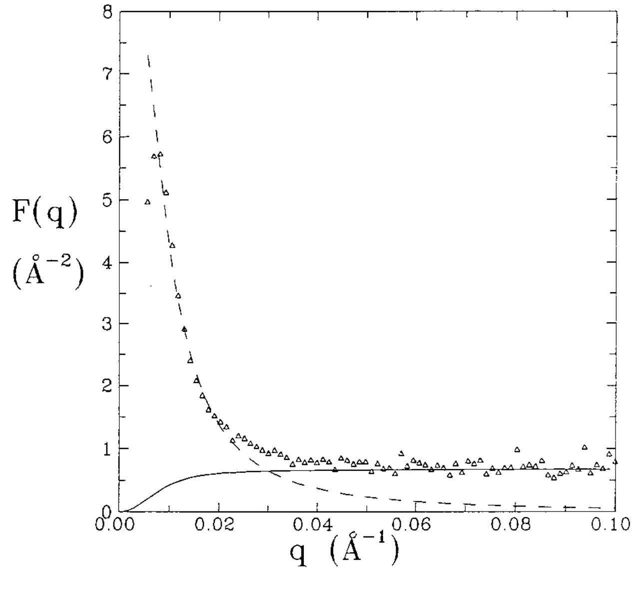

Figure 4 Kratky plot for PE/DPE.19 ($\phi_d = 0.20$) very slowly cooled. The solid line is calculated for Gaussian chains with $a^2 = 0.22$ Å mol g^{-1}. The dashed line describes the enhanced forward scattering in terms of 'segregation', as outlined in the Appendix

component. Partial deuteration reduces the difference in melting temperature ΔT_m to as little as 1°C. Furthermore, chains labelled by H–D exchange are otherwise the same as the starting polyethylene and are free of short-chain branching or other features which impede crystallization. Despite these refinements, 'clustering' or 'segregation' of isotopic species was observed by SANS after slow cooling.

Turning for the moment to molten or quenched blends which appear to be random mixtures, some of the present findings are different from previous reults. Quenched polyethylene here gives $I(q)$ or $F(q)$ which conforms to Gaussian chain conformations over the q range from $\sim 0.01\,\text{Å}^{-1}$ to $0.1\,\text{Å}^{-1}$. This observation depends only on the q dependence of the coherent intensity and is independent of the absolute contrast factor K, which a sceptic may question in these unconventionally labelled polymers. While Gaussian-like behaviour $R_g = aM^{1/2}$ has been deduced from 'low-q' analyses[14], the only comparable 'intermediate-q' study we know of shows $F(q)$ to be well below the Gaussian expectation[9,20]. As the labelled and unlabelled polymers are more closely matched in this work, we suppose that this continuation of Gaussian-like correlations to shorter distances is more representative of quench-crystallized polyethylene.

Another difference is related to the level of deuterium y in the labelled chains; recall that all previous experiments used perdeuterated polyethylene ($y=1$). We find a modest positive dependence of R_g (or a^2) on y (see *Table 3*). Even more unexpected are the absolute values of a^2, which depart from the 'conventional' SANS figure of $0.22\,\text{Å}^2\,\text{mol}\,\text{g}^{-1}$ (obtained[9,10] with $y=1$) as y increases from 0.19 to 0.28 to 0.59. The only melt sample studied here (WPE/DWPE.28) is free of known isotope effects. It gives $a^2 = 0.32\,\text{Å}^2\,\text{mol}\,\text{g}^{-1}$, which is the same as the melt dimensions of ethylene–1-butene copolymers extrapolated to pure polyethylene[31,32]. Those copolymers also employ partial deuteration ($y \approx 0.4$). The final observation is that the least-labelled DPE.19 gives results in close agreement with completely labelled polyethylene. Taken together, these facts point to anomalously large chain dimensions being associated with polymers having $y \approx 0.5$. When the deuterium labelling is substantially lower ($y=0.19$) or substantially higher ($y=1$) the 'conventional' result is seen. We have no explanation for this effect, and do not know if it is real (chain dimensions are indeed larger) or apparent (SANS with a $y \approx 0.5$ component has a q dependence which makes the chains seem larger than they are). Random-phase approximation (RPA) calculations for random AB copolymers[35], where A and B have different scattering lengths, predict an unmodified $I(q)$ aside from the expected change in contrast factor K. Gehlsen *et al.*[36] report no change in chain dimensions (expressed as segment length $l \propto a$) when y is varied from 0.3 to 1.0 in saturated polybutadiene. Resolution of what may be a technical synthesis/characterization issue or a fundamental SANS problem will have to await further developments.

The final item is the insensitivity of IANS at $q > 0.05\,\text{Å}^{-1}$ to changes in crystallization conditions. The labelled chains used here are virtually indistinguishable from the matrix polymer and should crystallize very similarly to conventional polyethylene. It is realized, of course, that segregation does occur on slow cooling, indicating that cocrystallization is not 'ideal'. This leads one to speculate on the significance of IANS – does it really reflect intramolecular correlations? This question is answered affirmatively by experiments[12,17] from the dependence of $I(q)$ on $\phi_d\phi_h$ and by analyses of 'paraclustering' or segregation (see Appendix). If such is the case, then why is IANS essentially independent of crystallinity? The following discussion is based on an idealized model of the semicrystalline microstructures in quenched and very slowly cooled samples given in *Figure 5*. Note that the sizes of the crystalline and amorphous regions are greater than 100 Å. On this basis the scattering function $F(q)$ at $q \approx 0.08\,\text{Å}^{-1}$ can be approximated by a two-phase model

$$F \approx \alpha_m F_c + (1 - \alpha_m) F_a \tag{6}$$

Here α_m is the mass fraction crystallinity and F_c and F_a represent the normalized intramolecular correlations within the crystalline and amorphous sections of a chain, respectively. Neglecting crystalline–amorphous correlations is reasonable at an averaging distance $1/q \approx 12$ Å, which is small compared to the length scale of either phase. To proceed we must assign values for F_c and F_a. The 'ideal' case uses $F_c = 1.1\,\text{Å}^{-2}$ (complete adjacent re-entry of polyethylene crystalline stems[2,20,21]) and $F_a = 0.66\,\text{Å}^{-2}$ (Gaussian segments with theta dimensions, $C_\infty = 7.6$ at 23°C[15]). The low value of F_c derives from the fact that monomer–monomer correlations exist only in the fold plane; the crystalline molecule is two-dimensional. With these 'ideal' values $F = 0.91\,\text{Å}^{-2}$ for the quenched sample ($\alpha_m = 0.56$) and $F = 1.00\,\text{Å}^{-2}$ for the very slowly cooled sample ($\alpha_m = 0.78$). Ignoring absolute values for the moment, the obvious conclusion is that changing the morphology as sketched in *Figure 5* leads to a 10% increase in $F(q)$. This is roughly what is observed (see *Figures 3* and *4* and *Table 4*).

The 'ideal' model, however, overestimates the size of $F(q)$ appreciably. This can be accommodated without much difficulty. Incorporation of a 'stem dilution factor'[2] of ~ 2 will decrease F_c to about $0.6\,\text{Å}^{-2}$. With this step $F(0.08)$ becomes effectively independent of crystallinity with a value of $\sim 0.63\,\text{Å}^{-2}$, which conforms to the present results for PE/DPE.19. ($F \approx 0.5\,\text{Å}^{-2}$ in PE/DPE.59, reflecting an anomalous a^2 as discussed above; the calculation here is based on 'conventional' Gaussian dimensions in amorphous polyethylene.) No claim is made that this argument is quantitatively rigorous. Other models[2] can give $F_c \approx 0.6\,\text{Å}^{-2}$, but the characteristic feature is a stem–stem correlation distance $r_s < 15$ Å, consistent with the 'near-adjacent re-entry' picture derived from gambler's ruin calculations for semicrystalline polyethylene[34,37].

When starting this project we thought the reports that

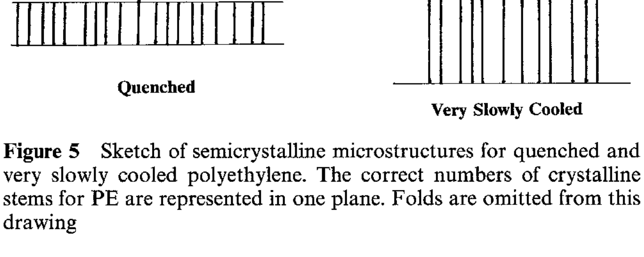

Figure 5 Sketch of semicrystalline microstructures for quenched and very slowly cooled polyethylene. The correct numbers of crystalline stems for PE are represented in one plane. Folds are omitted from this drawing

$I(q)$ and $F(q)$ at $q > 0.05\,\text{Å}^{-1}$ are independent of crystallization conditions[9,16,17] might be misleading because of appreciable differences in the melting temperatures of 'tagged' and matrix polyethylenes. The same behaviour is seen, however, in blends containing partially deuterated polyethylene which is almost perfectly matched to the unlabelled component. The most significant finding is that $F(q)$ in quench-crystallized samples is nearly constant for $0.02\,\text{Å}^{-1} < q < 0.1\,\text{Å}^{-1}$ at a level consistent with intramolecular correlations in Gaussian coils. While detailed modelling of semicrystalline chains has not been done, the present results indicate more correlations or folding in polyethylene crystals than inferred from calculations[20,21] on earlier experimental data[9]. We note in closing that the insensitivity of $F(q)$ to crystallinity implies that correlations in non-crystalline and crystalline regions are very similar. Because of this rather unhappy coincidence, neutron scattering is a 'very dull sword'[38] for attacking chain conformation problems in melt-crystallized polyethylene.

ACKNOWLEDGEMENTS

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REFERENCES

1 Wignall, G. D. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz), 2nd Edn, Vol. 10, John Wiley & Sons, New York, 1987, pp. 112–184
2 Sadler, D. S. in 'Structure of Semicrystalline Polymers' (Ed. I. H. Hall), Elsevier Applied Science, New York, 1984, pp. 125–180
3 Buckingham, A. D. and Hentschel, H. G. E. *J. Polym. Sci., Polym. Phys. Edn* 1980, **18**, 853
4 Wignall, G. D. and Bates, F. S. *Makromol. Chem., Macromol. Symp.* 1988, **15**, 105
5 Stehling, F. C., Ergos, E. and Mandelkern, L. *Macromolecules* 1971, **4**, 672
6 English, A. D., Smith, P. and Axelson, D. E. *Polymer* 1985, **26**, 1523
7 Bates, F. S., Keith, H. D. and McWhan, D. B. *Macromolecules* 1987, **20**, 3065
8 Stamm, M., Fischer, E. W. and Dettenmaier, M. *Faraday Discuss. Chem. Soc.* 1979, **68**, 263
9 Schelten, J., Ballard, D. G. H., Wignall, G. D., Longman, G. and Schmatz, W. *Polymer* 1976, **17**, 751
10 Schelten, J., Wignall, G. D., Ballard, D. G. H. and Longman, G. W. *Polymer* 1977, **18**, 1111
11 Lieser, L., Fischer, E. W. and Ibel, K. *J. Polym. Sci., Polym. Lett. Edn* 1975, **13**, 39
12 Sadler, D. M. and Keller, A. *Macromolecules* 1977, **10**, 1128
13 Summerfield, G. C., King, J. S. and Ullman, R. *J. Appl. Crystallogr.* 1978, **11**, 548
14 Ballard, D. G. H., Longman, G. W., Crowley, T. L. and Cunningham, A. *Polymer* 1979, **20**, 399
15 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley, New York, 1969, Ch. 2
16 Anderson, J. E. and Bai, S. J. *J. Appl. Phys.* 1978, **49**, 4973
17 Sadler, D. M. and Spells, S. J. *Polymer* 1984, **25**, 1219
18 Boué, F., Nierlich, M. and Leibler, L. *Polymer* 1982, **32**, 29
19 Crist, B., Tanzer, D. and Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 545
20 Flory, P. J. *Pure Appl. Chem.* 1984, **56**, 305
21 Guttman, C. M., Hoffman, J. D. and DiMarzio, E. A. *Faraday Discuss. Chem. Soc.* 1979, **68**, 297
22 Fischer, E. W. *Polym. J.* 1985, **17**, 307
23 Crist, B. and Wignall, G. D. *J. Appl. Crystallogr.* 1988, **21**, 701
24 Schelten, J., Zinken, A. and Ballard, D. G. H. *Colloid Polym. Sci.* 1981, **259**, 260
25 Nicholson, J. C. and Crist, B. *Macromolecules* 1989, **22**, 1704
26 Hoffman, J. D. *Polymer* 1983, **24**, 3
27 Hellwege, K.-H., Knappe, W. and Lehmann, P. *Kolloid Z. Z. Polym.* 1962, **183**, 110
28 Wignall, G. D., Lin, J. S. and Spooner, S. *J. Appl. Crystallogr.* 1990, **23**, 241
29 Nicholson, J. C., Finerman, T. M. and Crist, B. *Polymer* 1989, **31**, 2287
30 Alamo, R. G., Londono, J. D., Mandelkern, L., Stehling, F. C. and Wignall G. D. *Macromolecules* in press
31 Crist, B., Tanzer, J. D. and Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 545
32 Rhee, J. and Crist, B. *Polymer* submitted
33 Nicholson, J. C. PhD thesis, Northwestern University, 1989
34 Mansfield, M. L. *Macromolecules* 1986, **19**, 1421
35 Mori, K., Tanaka, H. and Hashimoto, T. *Macromolecules* 1987, **20**, 381
36 Gehlsen, M. D., Rosedale, J. H., Bates, F. S., Wignall, G. D., Hansen, L. and Almdal, K. *Phys. Rev. Lett.* 1992, **68**, 2452
37 Mansfield, M. L. *Macromolecules* 1991, **23**, 126
38 Hoffman, J. D. personal communication
39 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979, pp. 103–113
40 Wu, W. *Polymer* 1983, **24**, 43
41 Debye, P. and Bueche, A. M. *J. Appl. Phys.* 1949, **20**, 518

APPENDIX

SANS from non-randomly mixed systems

The first analysis of 'clustering' in crystallized mixtures of labelled and unlabelled polymers was presented by Schelten *et al.*[10]. With a statistical description of non-random mixing of the two components they arrived at an expression for the coherent cross-section per unit volume which can be written as

$$I(q) = \phi_d \phi_h K N \frac{P(q)}{1 - gNP(q)} \tag{A1a}$$

$$\frac{1}{I(q)} = \frac{1}{\phi_d \phi_h K}\left(\frac{1}{NP(q)} - g\right) \tag{A1b}$$

The tendency for chains to exhibit excess D–D or H–H associations is embodied in the parameter g. More 'paraclustering' (concentration fluctuations in excess of those in a random mixture) is reflected by a larger g, while for ideal mixtures $g = 0$ and equation (A1a) reverts to equation (1) in the text. Equations (A1a) and (A1b) have the same structure as those[18,39] for a polymer–polymer liquid subject to thermodynamic interactions expressed as the Flory–Huggins interaction parameter χ. Indeed g here is equivalent to 2χ, and the key assumption of the Gaussian chain conformation being unaffected by (local) concentration is common to both treatments. As in the random-phase analysis (RPA) of melts, scattering from excess concentration fluctuations decays rapidly with increasing q. The particular nature of the fluctuations leads to the simple 'offset' of $[(I(q)]^{-1}$ and permits one to extract $P(q)$ and R_g, even in the presence of such fluctuations, with equation (A1b). Notice that if $P(q)$ is unaffected by 'paraclustering' ($g > 0$), the shifted curve will be parallel to that for the unshifted or ideal ($g = 0$) case. Stated another way, the first intramolecular term in equation (A1b) dominates when $P(q)$ becomes small at large q, leading to $I(q) \propto P(q)$

and $F(q)$ approaching its value in the absence of 'paraclustering'. That is the behaviour seen in *Figures 2* and *4*.

Alternative models are based on more deterministic treatments of the 'segregation' of labelled and unlabelled chains during crystallization. Used here is the approach of Wu[40] without restrictions on the volume fraction ϕ_d of labelled chains. This analysis is based on the idea that unlabelled PE, having the higher T_m, will crystallize first during slow cooling to form regions which are free of labelled DPE. The volume fraction of unmixed PE is $1-\Omega$ (the local volume fraction of labelled chains in these regions is $\phi'_d=0$), while the remaining fraction Ω of the sample is enriched in DPE (local volume fraction $\phi'_d=\phi_d/\Omega$) which cocrystallizes with PE. Scattering thus consists of two components. One arises from contrast between multichain aggregates having different ϕ'_d, and the second is the usual molecular scattering from the 'ideal' mixture (local DPE volume fraction $\phi'_d=\phi_d/\Omega$) which occupies Ω of the overall sample. It is further assumed that the 'segregation' scattering is described by the Debye–Bueche expression for a random, two-phase system with well defined boundaries[41]. The resulting intensity, written as the coherent cross-section per unit volume of the entire sample, is

$$I(q)=\frac{K}{\Omega}\left[\frac{8\pi x^3(1-\Omega)\phi_d^2 n_t}{(1+x^2q^2)^2}+\phi_d(\Omega-\phi_d)NP(q)\right] \quad \text{(A2)}$$

The new variables are the volume fraction Ω wherein reside the mixed PE/DPE chains and the correlation length x for the segregated system. In the limit when $\Omega=1$ (no segregation), the first term vanishes and equation (1) of the text is recovered. As the extent of segregation increases, Ω decreases to the limiting value $\Omega=\phi_d$, at which point segregation is complete and the second term for molecular scattering becomes zero.

The intensity for the VSC PE/DPE.19 blend (*Figure 4*) is dominated by 'segregation' scattering for $q<0.02$ Å^{-1}. Data in this range were fitted to the first term in equation (A2) by the usual plot of $[I(q)]^{-1/2}$ against q^2 to establish $\Omega=0.55$ and $x=225$ Å. The 'segregation' scattering with these parameters, converted to $F(q)$ according to equation (2b), is given by the dashed line in *Figure 4*. This decays rapidly because of the q^{-4} dependence in the first term of equation (A2). The difference between the experimental and 'segregation' scattering functions is molecular scattering which derives from the second term of equation (A2). For VSC PE/DPE.19 we observe $F(0.08)=0.65$ Å^{-2}; when corrected for 'segregation' scattering, the molecular contribution is 0.55 Å^{-2}. This should, in principle, be considered in terms of the fraction Ω of mixed regions and the local volume fractions ϕ'_d and $\phi'_h=1-\phi'_d$. For the case in question the intensity from the mixed regions is 80% of that expected if no segregation had occurred; the second term of equation (A2) has 0.80 of the $\Omega=1$ value. Correcting the data in this fashion, $F(0.08)=0.69$ Å^{-2} for VSC PE/DPE.19 in the absence of segregation. It should be realized that this quantity is model dependent, but it gives the largest amount of intramolecular correlations which can be obtained from the data in *Figure 4*.