

Thermodynamics of polyolefin blends: small-angle neutron scattering studies with partially deuterated chains

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Small-angle neutron scattering is used to evaluate the binary interaction parameter χ in molten blends of polyethylenes having different levels of ethyl branching along the backbone. The labelled chains were partially deuterated to minimize the isotope effect on χ . The present results for equal-volume-fraction binary blends at 150°C can be summarized as $\chi = 0.4 \times 10^{-4} + 0.014 \Delta X_{br}^2$. The first term is from the hydrogen–deuterium isotope effect for chains labelled with about 33% deuterium. The second term is due to chemical composition differences, expressed here as the difference in X_{br} , the fraction of four-carbon repeat units having an ethyl branch. The observed contributions to χ are in reasonable accord with calculated estimates.

(Keywords: polyethylene; neutron scattering; interaction parameters)

INTRODUCTION

Polymer blends can be studied by a number of techniques—calorimetry, mechanical behaviour and scattering—which give either direct or indirect information on the state of mixing of the components. Scattering methods may be qualitative, e.g. cloud points indicating the onset of macroscopic phase separation, or quantitative, measuring non-statistical concentration fluctuations to establish the sign and magnitude of the segment–segment interaction parameter χ for binary systems. The study of non-ideal solution behaviour by small-angle neutron scattering (SANS) has been discussed by Higgins and Walsh¹ and reviewed by Wignall². For the present purposes, χ represents the excess free energy of mixing between repeat units of polymer A and repeat units of polymer B. Almost all studies of high polymer blends have dealt with attractive systems ($\chi < 0$) in which concentration fluctuations and hence scattered intensity are less than those for an ideal or statistically mixed solution.

Consideration of polymer blends with repulsive interactions ($\chi > 0$) is limited by phase separation, which occurs when $\chi N > 2$, where N is the number of repeat units per chain. Conventional (hydrogenous) and perdeuterated polymers differing only in isotopic composition have positive interaction parameters, which are small enough ($\chi = 10^{-4}$ – 10^{-3}) to permit solutions of high polymers. This has been demonstrated for blends of conventional and perdeuterated 1,4-polybutadiene³, atactic polystyrene⁴, 1,2-polybutadiene or poly(vinylethylene)^{5,6} and saturated 1,2-polybutadiene or poly(ethylene)⁵. When dealing with chemically different polymers having positive χ (one member of each pair being deuterated), immiscibility is generally observed because $\chi N > 2$; ex-

amples of this are polyethylene/polypropylene⁷ and polypropylene/ethylene–propylene copolymers⁸. If the degree of polymerization and hence N are made sufficiently small, solutions are obtained, as with oligomers of ethylene oxide and propylene oxide or styrene and butadiene⁹.

An interesting exception to the foregoing is mixtures of styrene/acrylonitrile copolymers of slightly different composition¹⁰. It was found that χ was small and positive, of the order of $(1-8) \times 10^{-3}$ based on repeat units of 90 cm³ partial molar volume. True solutions were formed, provided the concentration or molecular weights were small enough. Similar behaviour has been reported for poly(methyl methacrylate)/poly(ethylene oxide) (PMMA/PEO) blends¹¹. Those suitably rich in PMMA have a positive interaction parameter small enough ($\chi = 1 \times 10^{-3}$) to permit solutions of high polymers. It should be noted that the interaction parameter, particularly in the latter case, is close in magnitude to the isotope χ reported by Bates and others³⁻⁶. Wignall and Bates¹² have pointed out the need to consider the isotope contribution when dealing with small interaction parameters, either positive or negative.

With this caveat in mind, we have examined polyolefin blends in which the labelled polymer chains are incompletely but randomly deuterated. The chemical variable of interest is the frequency of short-chain (ethyl) branching along the backbone of polyethylene. All experiments were done in the melt state, avoiding more complicated questions of co-crystallization of dissimilar chains. It is shown that a small repulsive interaction ($\chi = 10^{-4}$ to 10^{-3} , based on C₄H₈ repeat units) results from differences in branch frequency up to $\Delta X_{br} = 0.27$, where X_{br} is the fraction of C₄H₈ repeats that are branched. These results would be very difficult to obtain with fully deuterated blend components in which the isotope effect causes

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$\chi_{hd} \approx 6 \times 10^{-4}$ for otherwise identical polymer pairs. Partial deuteration lowers χ_{hd} to acceptable levels above which the interactions due to chemical (as opposed to isotopic) differences are clearly observable. Partially deuterated chains have been used previously in some SANS experiments^{8,13-16}, though not for the express purpose of reducing thermodynamic interactions between labelled and unlabelled chains.

EXPERIMENTAL

Polymers and blends

The linear polyethylenes used in this work are the high-molecular-weight standard reference material from NIST (PE) and the same polymer that had been partially deuterated (DPE) by exchange in the presence of a rhodium catalyst. Details of the exchange reaction have been presented elsewhere¹⁷, though subsequent analysis has shown that the exchange product is not statistically uniform. The average fraction of sites replaced by deuterium is $\langle y \rangle = 0.19$, which is the product of 70% of the chains having $y = 0.27$ and the balance being essentially unreacted with $y = 0$. (This effective mixture composition was determined by SANS cross-sections of blends containing various amounts of PE and DPE¹⁸. Our earlier report¹⁷ was in error because of a still unexplained irregularity in the sensitivity or calibration factor of the SANS instrument.)

Model copolymers are based on saturated polybutadiene, either hydrogenated (HPB) or deuterated (DPB). Polybutadiene precursors were made by anionic polymerization so as to yield between 18 and 106 vinyl groups per 1000 backbone C atoms. After reaction with either H_2 or D_2 over a palladium catalyst, these polymers become models for random copolymers of ethylene and but-1-ene¹⁹. Analyses for molecular weight and short-chain branching were done on the polybutadiene precursors. Average deuterium concentration $\langle y \rangle$ for DPB was determined by density relative to that of HPB from the same precursor. Characterization of these polymers is summarized in Table 1 wherein suffixes indicate the number of ethyl branches per 1000 backbone C atoms. The quantity X_{br} is the fraction of C_4H_8 units containing a pendent ethyl branch. It is related to the number of branches per 1000 backbone C atoms, g , by:

$$X_{br} = \frac{4g}{2g + 1000}$$

Binary blends containing volume fraction $\phi_A = \phi_B = 0.5$ of each type of polymer were mixed in refluxing solvent (xylene or cyclohexane), then precipitated in an excess of cold methanol. After drying in vacuum, samples for

Table 1 Physical characteristics of polymers

Polymer	N_w^a	N_w/N_n	X_{br}	$\langle y \rangle$
PE	2110	1.23	0.0	0
DPE	2010	1.27	0.0	0.19
DPB18	1770	1.03	0.069	0.38
DPB22	390	<1.05	0.084	0.39
HPB39	3050	<1.05	0.145	0
HPB65	1910	<1.05	0.230	0
HPB88	1450	<1.05	0.299	0
HPB106	3390	<1.05	0.350	0

^a Based on C_4H_8 repeat units

SANS were compression moulded and quenched to form discs about 13 mm in diameter and 1 mm thick. In each A/B blend the B component is labelled with deuterium. Samples with DPB18 or DPB22 have volume fraction of deuterated repeats $\phi_{Bd} = \phi_B$ equal to 0.50. Blends based on DPE are actually ternary, containing $\phi_A = 0.50$ of one component, $\phi_{Bh} = 0.15$ of unlabelled PE and $\phi_{Bd} = 0.35$ of labelled PE.

SANS measurements

The Small-Angle Diffractometer at the Intense Pulsed Neutron Source, Argonne National Laboratories, was employed in these experiments. Scattered intensity was recorded over the range from $q = 0.005$ to $q = 0.25 \text{ \AA}^{-1}$, where $q = (4\pi/\lambda) \sin(\theta/2)$, λ is the neutron wavelength and θ is the scattering angle. Experiments were done at 135 or 160°C in a heated cell with fused silica windows. Sample thickness was not measured directly for the melts, but inferred from measured transmission of the melt and the linear absorption coefficient, which had been determined at room temperature. Data collection and analysis were straightforward, involving the usual corrections for parasitic scattering and detector noise. Incoherent backgrounds were subtracted; these were found to have a negative q dependence due to a combination of inelastic and multiple scattering effects²⁰.

ANALYSIS AND RESULTS

For generality, we start with the treatment of Warner, Higgins and Carter¹⁶ for scattering from a ternary system of polymers A and B in which a fraction f_B of the B chains is deuterated. One makes the usual assumptions that unperturbed chain dimensions are maintained, that the solution is incompressible and that the thermodynamic interaction between hydrogenated and deuterated segments is negligible ($\chi_{hd} \approx 0$). Two additional simplifications are permitted in the present consideration of polyethylene and copolymers of ethylene and but-1-ene. The molar volume of a C_4H_8 repeat is the same (to within 0.5%) for the homopolymer and all copolymers considered here^{19,21}. Similarly, the coherent scattering lengths of C_4H_8 repeats in A chains and in hydrogenous B chains are the same, i.e. $B_A = B_{Bh}$. The scattering length of the labelled B chains, B_{Bd} , is calculated for a representative repeat of composition $C_4H_{8(1-y)}D_{8y}$. Under these conditions one can write¹⁶:

$$I(q) = K f_B^2 \{ [\phi_A N_A P(u_A)]^{-1} + [\phi_B N_B P(u_B)]^{-1} - 2\chi \}^{-1} + K \phi_B f_B (1 - f_B) N_B P(u_B) \quad (1)$$

with

$$K = (B_A - B_{Bd})^2 n_t = (B_{Bh} - B_{Bd})^2 n_t \quad (2a)$$

$$(B_A - B_{Bd}) = 8y(b_h - b_d) \quad (2b)$$

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

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

Here $I(q)$ is the coherent cross-section per unit volume. The contrast factor K in (2a) is the product of the number density of repeat units of all types, n_t , and the squared difference in scattering lengths between unlabelled and labelled repeats, B_i . This in turn is a function of the fractional extent of deuteration of the labelled B chains, y , and the difference in scattering lengths for 1H and 2H ,

$b_h - b_a$ (equation (2b)). The remaining symbols have their usual meanings: $P(u_i)$ in (2c) is the normalized scattering factor for a single Gaussian chain with radius of gyration R_{gi} ; N_i is the (weight-average) degree of polymerization, and χ is the interaction parameter for repeat units on A and B chains (this χ is assumed to be unaffected by isotopic substitution). Equation (1) has been written for monodisperse chains; the product $\phi_i N_i P(u_i)$ is replaced by an appropriately weighted sum over a distribution of chain sizes N_i if necessary²². The molecular-weight distributions of labelled and unlabelled chains of polymer B are of course assumed to be identical.

It is worth emphasizing that equation (1) contains two terms. The second describes monomer-monomer correlations of labelled B chains and unlabelled B chains; this 'self-term' is proportional to $f_B(1 - f_B)$. The first term derives from interactions between labelled B chains and unlabelled A chains, and scales with f_B^2 . These different dependences on f_B permit separation of the two terms and hence evaluation of the interaction parameter χ ^{1,16,23}. If, however, the system is well defined, i.e. N_i , R_{gi} and f_B are known, then a fit of equation (1) to the experimental cross-section can be done in terms of χ alone. Note that a plot of I^{-1} versus q^2 with $\chi \neq 0$ will not give a curve that is strictly parallel to the $\chi = 0$ case, because of the influence of the second 'self-term' in the overall intensity.

Intensity data for the HPB39/DPE and HPB65/DPE blends were analysed with equation (1), letting R_{gA} and R_{gB} be fitting parameters as well as χ . An example of the fit to experimental data is shown in Figure 1. The full curve in Figure 1 is the reciprocal of the cross-section for an ideal solution, $I^i(q)$, calculated for $\chi = 0$ with no adjustable parameters: N_A and N_B are from Table 1, and $R_{gi} \propto N^{1/2}$ are those from Θ -solvents at about 150°C for PE²⁴ and HPB of appropriate branch concentration²⁵. As implied in Figure 1, the chain dimensions R_g obtained by fitting to equation (1) agree with those predicted from solution properties, typically to within $\pm 5\%$. Although χ can be evaluated from the (extrapolated) cross-section at $q = 0$, and hence is independent of real or assumed chain dimensions, it is reassuring to know that solution behaviour conforms to equation (1) with unperturbed chains.

The second series of blends, having DPB as the labelled

component, was treated in a similar manner. Here all the B chains are (partially) deuterated to the same extent and $f_B = 1$. Equation (1) thus reduces to:

$$I(q) = K \{ [\phi_A N_A P(u_A)]^{-1} + [\phi_B N_B P(u_B)]^{-1} - 2\chi \}^{-1} \quad (3)$$

Evaluation of χ from equation (3) is essentially the same as with equation (1); again, a best fit to experimental intensities was obtained by varying R_{gi} and χ . The derived R_{gi} were virtually those from solution measurements under Θ -conditions²⁵, and the χ values are summarized in Table 2. The error limits on χ were estimated with $\pm 10\%$ uncertainties in both extrapolated $I(0)$ and calculated $I^i(0)$ for $\chi = 0$. Uncertainties in the experimental $I(0)$ derive from machine calibration and data manipulation, including extrapolation to $q = 0$. Error in $I^i(0)$ comes from imprecision in degree of polymerization N_i and extent of deuteration y .

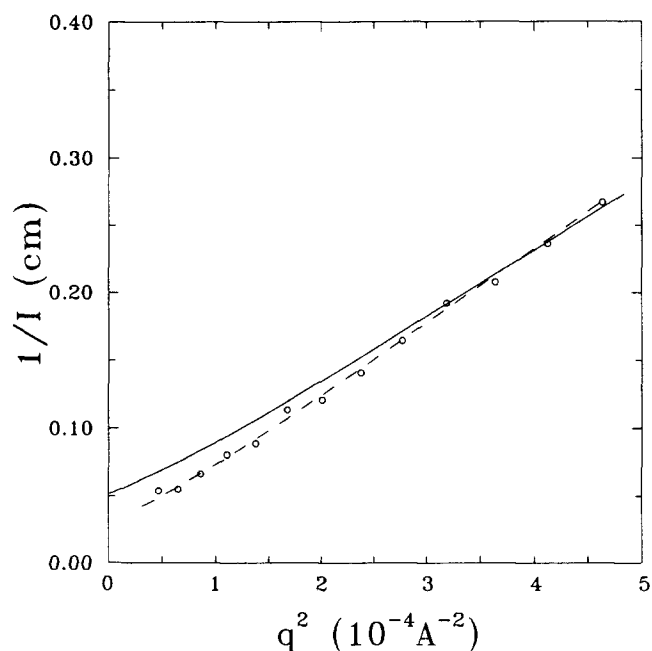


Figure 1 Reciprocal intensity vs. q^2 for HPB65/DPE blend at 160°C. Full curve is $1/I^i(q)$ (equation (1) with $\chi = 0$) with no adjustable parameters. Broken curve is fit to data with $\chi = 6.0 \times 10^{-4}$

Table 2 Interaction parameter from SANS

Blend	ΔX_{br}	Temp. (°C)	$I^i(0)$ (cm ⁻¹)	$I(0)$ (cm ⁻¹)	$10^4 \chi$
HPB39/DPE	0.0145	135	21.6	25.9	2.0 ± 1.7
		160	21.6	25.9	2.0 ± 1.7
HPB65/DPE	0.230	160	19.3	33.8	6.0 ± 1.6
HPB106/DPE	0.350	160	22.3	(160)	^a
PE/DPB18	0.069	135	38.6	49.1	2.3 ± 1.2
		160	38.6	45.3	1.6 ± 1.2
HPB39/DPB18	0.076	160	47.6	60.8	2.0 ± 1.1
HPB65/DPB18	0.160	160	39.2	71.4	5.2 ± 1.3
HPB88/DPB18	0.246	160	34.1	75.2	7.0 ± 1.4
HPB106/DPB18	0.281	160	49.3	(525)	^a
HPB106/DPB22	0.266	160	14.1	28.3	14.2 ± 3.2

^a No χ is reported because blends are phase-separated

DISCUSSION

Inspection of Table 2 reveals that χ is small, positive and increasing with the difference in chemical composition ΔX_{br} of the blend components. Where temperature dependence was investigated, no real effect was observed. The available temperature range was limited by crystallization at the low end and by heater capacity at the high end. Assuming $\chi \propto T^{-1}$, the anticipated 6% change of χ cannot be observed in experiments of this sort.

It should be mentioned that χ results are not reported for two blends, HPB106/DPE and HPB106/DPB18 in Table 2. For those systems equation (1) (or equation (3)) could not be employed to fit the experimental patterns. Most obvious in Figure 2 is that $I(q)$ falls below the $I^1(q)$ limit established by $\chi = 0$; this scattering behaviour is consistent with phase separation of the components^{3,26}. Attempts to fit intensity profiles for these two systems resulted in very large R_g , indicative of an excessive q dependence, which also reflects incompatible components. For example, the broken curve in Figure 2 corresponds to $R_g = 210 \text{ \AA}$, whereas coil dimensions of the components are $146 \pm 2 \text{ \AA}$. It will be shown below that χ inferred from compatible systems predicts that those two blends should indeed be phase separated. Decreasing the molecular weight of B chains in the HPB106/DP22 blend resulted in a homogeneous system with subcritical fluctuations of the two components.

We analyse the dependence of χ on chemical composition difference of the two blend components ΔX_{br} . On the basis of pairwise interactions between repeat units, it is well established^{10,27,28} that χ is predicted to be proportional to $\Delta X_{br}^2 = (X_{brA} - X_{brB})^2$. Recall that X_{br} is the fraction of four-carbon repeat units in the polymer A or B having a short-chain (ethyl) branch. Designating the enthalpic interaction due to chemical composition differences as χ_{cc} , we write:

$$\chi_{cc} = \xi \Delta X_{br}^2 \quad (4)$$

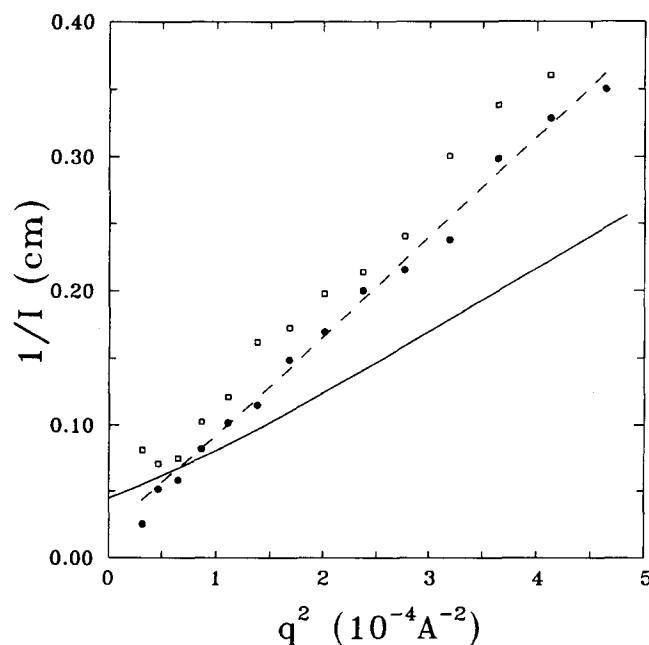


Figure 2 Reciprocal intensity vs. q^2 for HPB106/DPE blend at 135°C (\square) and 160°C (\bullet). Full curve is $1/I^1(q)$ (equation (1) with $\chi = 0$) with no adjustable parameters. Broken line is a fit to $T = 160^\circ\text{C}$ data (see text)

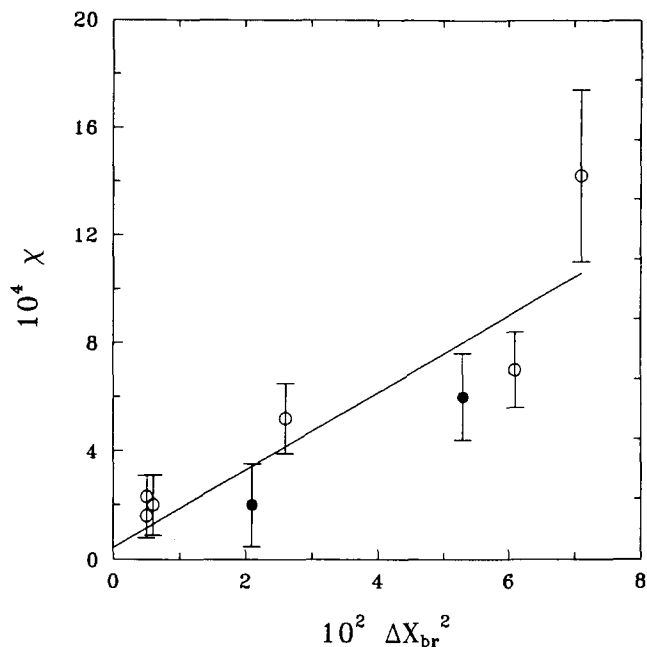


Figure 3 Measured χ values vs. ΔX_{br}^2 . Full line is least-squares fit with correlation coefficient of 0.89. Open circles are for blends based on labelled DPB; full circles are for blends using DPE

The parameter ξ will depend on the nature of the comonomer (e.g. size of the short-chain branch), but is supposed to be insensitive to molecular weight (N_i) or volume fraction (ϕ_i) of the blend components.

The SANS experiment of course requires isotopic labelling to achieve contrast—see equation (2a). For the binary system (equation (3)), χ may in principle be due to both chemical composition differences and isotope effects. If the latter are present, one expects χ to depend on y for a constant ΔX_{br} . We make the reasonable assumption that the experimental χ is the sum of the isotopic and chemical composition effects:

$$\chi = \chi_{hd} + \chi_{cc} \quad (5a)$$

$$\chi = \beta y^2 + \xi \Delta X_{br}^2 \quad (5b)$$

Equation (5b) can be derived by treating the blend as a mixture of two different random copolymers of ethylene and but-1-ene, one having hydrogenous repeats and the other partially deuterated repeats. This analysis is presented in Appendix A. The dependence of χ_{hd} on y^2 results from particular models discussed in Appendix B.

The situation with ternary systems is not so straightforward. Equation (1) is written with the underlying assumption that $\chi_{hd} = 0$ for interactions between labelled B units and unlabelled A units or unlabelled B units. One supposes nevertheless that equation (5) would apply for a 'composite' interaction parameter ($\chi_{hd} \neq 0$), at least in the limit of $\chi_{hd} \ll \chi_{cc}$.

In this spirit we proceed and plot χ versus ΔX_{br}^2 in Figure 3. Provided that χ_{hd} is small compared to χ_{cc} , the variation in χ_{hd} caused by different values of y^2 will be moderate, and we are able to approximate the data for both DPE and DPB blends by:

$$\chi \approx D + \xi \Delta X_{br}^2 \quad (6)$$

Inspection of Figure 3 is revealing on a number of points. One sees the rather systematic increase of χ with ΔX_{br}^2

and strong indication that the $\Delta X_{br}=0$ intercept (or D) is positive. Finally, the two full circles for blends with $y^2=0.07$ are generally consistent with the open circles ($y^2=0.14$), indicating that χ_{hd} is a small contributor to the overall χ .

One can use the intercept $D=0.43 \times 10^{-4}$ to evaluate $\beta=(4.4 \pm 1.4) \times 10^{-4}$ for the isotopic interaction in equation (5b). The variation comes from using two values of y and a single D , but this uncertainty is consistent with the overall precision of the measurement. The quantity β equals χ_{hd} for the perdeuterated case ($y=1$), and corresponds reasonably to various theoretical estimates of χ_{hd} as described in the Appendix. More convincing, however, is near-agreement with the experimental value $\chi_{hd}=6.6 \times 10^{-4}$ derived from the data of Bates *et al.*⁵ for poly(ethylene) at about 150°C. The reasonable intercept in Figure 3 thus lends credence to the format used to analyse the composition dependence of χ .

Some comments are in order regarding χ_{hd} and earlier SANS experiments with polyethylene and related systems. The experimental interaction factor $\beta \approx 6 \times 10^{-4}$ can be used to estimate isotope effects. Schelten *et al.*²⁹ observed no apparent increase in $I(0)$ over $I^i(0)$ for a molten blend of polyethylene and perdeuteropolyethylene, $\phi_d=0.1$, whereas equation (3) with $\chi_{hd}=6 \times 10^{-4}$ predicts a 40% increase. Somewhat more understandable is the result of Tanzer *et al.*³⁰ for a $\phi_d=0.5$ blend of HPB and DPB, $y=0.39$. Despite high concentration and molecular weights ($N=3810$), partial deuteration keeps χ_{hd} small enough so that $I(0)/I^i(0)=1.2$. A ratio of 1.09 was observed in quench-crystallized samples, indicating clearly that χ_{hd} is reduced for $y < 1$. Other experiments of which we are aware used small enough molecular weights or volume fractions to preclude observable $\chi_{hd}N$ effects.

Turning now to the slope of the line in Figure 3, ξ equals 0.014 in the expression for χ_{cc} (equation (4)). In the limit of $\Delta X_{br}=1.0$, this implies that $\chi_{PE/PEE}=1.4 \times 10^{-2}$ for a blend of linear polyethylene ($X_{br}=0$) and poly(ethylene) ($X_{br}=1.0$) in the melt near 150°C. From the Appendix C we obtain χ estimated from solubility parameters ($\chi_{PE/PEE}=1.2 \times 10^{-2}$) and heat of mixing of oligomers ($\chi_{PE/PEE}=4.1 \times 10^{-2}$). As with the isotope effect, such independent evaluations of a small interaction parameter serve to establish its approximate magnitude. The present experimental value lies within the range established by these two estimates, and agreement should be considered reasonable. One other unpublished measurement of χ in a polyethylene-poly(ethylene-co-but-1-ene) system has been made with SANS by Ree *et al.*³¹. In terms used in this study, $\chi=6 \times 10^{-4}$ for $\Delta X_{br}=0.077$, which is about three times larger than the interaction parameter seen here with comparable conditions. There are differences in sample uniformity, etc., which may be responsible for the discrepancy, but one notes that $\chi \approx 6 \times 10^{-4}$ is what is expected for the isotope effect χ_{hd} with blends of normal and perdeuterated polyethylenes.

Mention was made earlier that phase separation had taken place in two blends, HPB106/DPE and HPB106/DPB18. Equation (6) with $D=0.4 \times 10^{-4}$ and $\xi=0.014$ can be used to calculate the interaction parameter in these two systems, $\chi=1.8 \times 10^{-3}$ and $\chi=1.1 \times 10^{-3}$, respectively. The second derivative of the ideal entropy of mixing for systems with $\phi_A=\phi_B=0.5$ gives:

$$2\chi_s = 2(N_A + N_B)/N_A N_B \quad (7)$$

Phase separation is predicted for $\chi \geq \chi_s$. Evaluating the

ratio χ/χ_s , one gets 2.3 and 1.3 for HPB106/DPE and HPB106/DPB18, respectively. This calculation with experimentally derived χ predicts two-phase behaviour where it is seen by SANS, confirming the dependence of χ on ΔX_{br} summarized in equations (5) and (6).

CONCLUSIONS

The small binary interaction parameter based on compositional differences in polyolefin copolymers has been measured for the first time. SANS from blends incorporating *partially* deuterated labelled chains permit evaluation of interaction effects due to both isotope and chemical composition differences. The present findings are for polyethylenes with varying amounts of ethyl branches. At $150 \pm 15^\circ\text{C}$, equal-volume-fraction melt blends give:

$$\chi = 0.4 \times 10^{-4} + 0.014 \Delta X_{br}^2 \quad (8)$$

for blends with one component having partial deuteration level $y=0.33 \pm 0.05$. This relation was established for composition difference ΔX_{br} from 0 to 0.27.

This and related systems provide the opportunity to study polymer thermodynamics and critical phenomena in blends dominated by chemical composition as opposed to isotopic substitution. Experiments are under way to examine the effects of temperature and volume fraction, with emphasis on the second χ_{cc} term in equation (8). Beyond supplying insights into solution properties, this type of information is essential for understanding the phase behaviour in complex copolymer systems such as linear low-density polyethylene (LLDPE). Mirabella *et al.*³² have proposed that the extreme compositional heterogeneity in LLDPE (ethylene-but-1-ene copolymer) causes phase separation, which is responsible for the enhanced fracture toughness of such materials. Further work on model and commercial copolymers is required to explore this and related mechanisms for property modification by copolymerization.

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APPENDIX A

χ in a copolymer blend

Consider a blend of two copolymers that differ in both chemical composition and isotopic content. Let the unlabelled copolymer be composed of linear C_4H_8 units (R) and a mole fraction g_h of branched C_4H_8 or but-1-ene units (S). This copolymer is designated $R_{(1-g_h)}S_{g_h}$. The labelled copolymer is composed of linear and branched $C_4H_{8(1-y)}D_{8y}$ units; fractional deuteration is assumed to be the same for each of the comonomers. This labelled copolymer is represented by $T_{(1-g_d)}U_{g_d}$ where g_d is the fraction of (labelled) but-1-ene monomer incorporated in the chain.

For a blend of these two copolymers $R_{(1-g_h)}S_{g_h}/$

$T_{(1-g_d)}U_{g_d}$ one can write for the interaction parameter:

$$\chi = (1-g_h)(1-g_d)\chi_{RT} + (1-g_h)g_d\chi_{RU} + g_h(1-g_d)\chi_{ST} + g_hg_d\chi_{SU} - (1-g_h)g_h\chi_{RS} - (1-g_d)g_d\chi_{TU} \quad (A1)$$

Here χ_{ij} is the interaction parameter between repeat units i and j ; the two negative terms correct for interactions present in the unmixed component copolymers. We now make the isotope interaction terms the same for linear-linear and branched-branched contacts, i.e. $\chi_{RT} = \chi_{SU} = \chi_{hd}$. Likewise, linear-branched interactions between hydrogenous or partially deuterated repeats within the same chain are the same, i.e. $\chi_{RS} = \chi_{TU} = \chi_{lb}$, where subscript lb refers to 'linear-branched'. The remaining contacts are between linear hydrogenous units and branched deuterated units (χ_{RU}) and between branched hydrogenous and linear deuterated units (χ_{ST}); assume that these are given by the additive relation:

$$\chi_{RU} = \chi_{ST} = \chi_{hd} + \chi_{lb} \quad (A2)$$

Combining these with equation (A1), one obtains:

$$\chi = \chi_{hd} + \chi_{lb}(g_h - g_d)^2 \quad (A3)$$

This is the same as equation (5) in the text if one converts to χ_{lb} to ξ and g_i to X_{bri} .

APPENDIX B

Estimates of χ_{hd}

The substitution of deuterium for hydrogen in hydrocarbons is known to cause a decrease in the molar volume³, which leads to an interaction parameter χ_{hd} of the form:

$$\chi_{hd} = \frac{1}{RT} \frac{(V_h - V_d)^2}{2\kappa V} \quad (A4)$$

V_h and V_d are molar volumes of unlabelled and labelled repeats, respectively, V is the molar volume and κ is the isothermal compressibility of the mixture. Equation (A1) was first applied to polymers by Buckingham and Hentschel³³, who also concluded that the change in dispersive energy (beyond that required by the volume change of mixing given in equation (A4)) is negligible.

If the labelled polymer is partially deuterated in a statistical manner, we make the logical assumption that molar volume is a linear function of extent of deuteration y : $V_d = V_h(1 - ay)$. Substituting this relation into equation (A4), one obtains:

$$\chi_{hd} = \frac{Va^2}{2RT\kappa} y^2 \quad (A5)$$

where $V_h/V = 1$, justified by the small value of a , has been employed. Using quantities appropriate for polyethylene at 150°C ($V = 7.16 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ (ref. 21), $a = 4.6 \times 10^{-3}$ (ref. 5, 34) and $\kappa = 11 \times 10^{-10} \text{ Pa}^{-1}$ (ref. 21)) equation (A5) yields $\chi_{hd} = 1.9 \times 10^{-4} y^2$. Recall that this is based on C_4H_8 repeat units.

Singh and Van Hook³⁵ have proposed a different treatment, which considers both intermolecular and intramolecular responses to volume changes that occur during mixing isotopically distinct polymers. Their result can be written as:

$$\chi_{hd} = \frac{hy_h n y (V_h - V_d)}{2kT} \frac{1}{V} [1 - (\mu_h/\mu_d)^{1/2}] \quad (A6)$$

The stretching frequency of a C–H bond is ν_h , h is Planck's constant, each repeat unit contains n C–H (or C–D) bonds, γ is the Gruneisen parameter for the C–H stretching frequency, and μ_i is the reduced mass of a C–H or C–D oscillator. For the partially deuterated case, clearly $(V_h - V_d)/V = ay$. The quantity n , which gives the number of unlike oscillator interactions per repeat, can be replaced by ny , leading to:

$$\chi_{hd} = \frac{h\nu_h n \gamma a}{2kT} [1 - (\mu_h/\mu_d)^{1/2}] y^2 \quad (\text{A7})$$

Using the values suggested by Singh and Van Hook³⁵ ($\nu_h = 3000 \text{ cm}^{-1}$, $\gamma = 0.035$) one obtains $\chi_{hd} = 23.8 \times 10^{-4} y^2$. This order of magnitude difference between the Buckingham–Hentschel and Singh–Van Hook treatments has been noted earlier⁵.

One additional scheme for calculating χ_{hd} has been proposed by Bates *et al.*⁵. This treatment is cast in terms of the change in dispersion interactions on mixing hydrogenous and deuterous repeats, and is written in terms of the polarizability per unit volume, α/v , of each of the components:

$$\chi_{hd} = \frac{2\pi^2 I'}{3kT} [(\alpha/v)_h - (\alpha/v)_d]^2 \quad (\text{A8})$$

Here α and v are the polarizability and volume of a repeat unit, respectively, and I' is the ionization potential of the appropriate hydrocarbon. One unusual feature of this expression is that χ_{hd} appears to be independent of the size of the repeat unit; α/v is of course the same for $-\text{CH}_2-$, $-\text{C}_2\text{H}_4-$, $-\text{C}_4\text{H}_8-$, etc. This is an approximation resulting from the choice of a size-dependent 'cut-off' or hard-sphere radius in the derivation of equation (A8). We use equation (A8) for C_4H_8 repeats, equivalent to that chosen by Bates *et al.*⁵. Before evaluating equation (A8) we rewrite it in differential form:

$$\chi_{hd} = \frac{2\pi^2 I'}{3kTv^2} (\Delta\alpha - \alpha\Delta v/v)^2 \quad (\text{A9})$$

Here $\Delta v/v = a$ as in equations (A5) and (A7), and $\Delta\alpha = 8(\alpha_{\text{CH}} - \alpha_{\text{CD}})$, where α_{CH} and α_{CD} are polarizabilities of CH and CD bonds. The CD bond polarizability is smaller; expressing the ratio as $\alpha_{\text{CD}}/\alpha_{\text{CH}} = (1 - b)$, then $\Delta\alpha = 8b\alpha_{\text{CH}}$.

For the partially deuterated case we assume that $\Delta v/v = ay$ and $\Delta\alpha = 8by\alpha_{\text{CH}}$, leading to:

$$\chi_{hd} = \frac{2\pi^2 I'}{3kTv^2} (8b\alpha_{\text{CH}} - a\alpha)^2 y^2 \quad (\text{A10})$$

Once again χ_{hd} depends quadratically on y . To evaluate this for polyethylene at 150°C , we use $I' = 1.58 \times 10^{-18} \text{ J}$

(ref. 36), $v = 1.19 \times 10^{-28} \text{ m}^3$ (ref. 22), $a = 4.6 \times 10^{-3}$ (refs. 5, 35) and $b = 0.0165$ (ref. 5). The bond polarizabilities of Denbigh³⁷ are used to calculate $\alpha_{\text{CH}} = 6.5 \times 10^{-31} \text{ m}^3$ and $\alpha = 7.76 \times 10^{-30} \text{ m}^3$. Combining these in equation (A10), one obtains $\chi_{hd} = 3.0 \times 10^{-4} y^2$. The similarity of this to the result from equation (A5) is probably fortuitous.

Thus three rather different calculations give β of equation (5b) in the text in the range of $(2-24) \times 10^{-4}$, based on C_4H_8 repeats in polyethylene at 150°C . It is noted that each of these models is approximate and depends on sometimes uncertain parameters for evaluation. Given the complexity of the problem, these estimates best serve to establish the order of magnitude expected for χ_{hd} . It is gratifying that the experimental results of Bates *et al.*⁵ for poly(ethylene) extrapolated to 150°C and $y = 1$ ($\beta = 6.6 \times 10^{-4}$) and the present work ($\beta \approx 4.4 \times 10^{-4}$) are within the bounds of the calculated estimates.

APPENDIX C

Estimates of χ_{cc}

Accepting the quadratic dependence of χ_{cc} on ΔX_{br}^2 (see equation (4) in the text), we consider the limiting case of a mixture of linear polyethylene, $X_{\text{br}} = 0$, and poly(ethylene), $X_{\text{br}} = 1.0$. This limiting value of $\chi_{cc} = \xi$ will be termed $\chi_{\text{PE/PEE}}$.

Cohesive energy densities based on the solubility parameter scheme may be used to evaluate $\chi_{\text{PE/PEE}}$. We use³⁸:

$$\chi_{\text{PE/PEE}} = \frac{V}{RT} (\delta_{\text{PE}} - \delta_{\text{PEE}})^2 \quad (\text{A11})$$

where δ_i is the solubility parameter component i , which can be calculated from group molar attraction constants. Using the two sets of constants in ref. 39, we calculate $\chi_{\text{PE/PEE}} = (1.2 \pm 0.3) \times 10^{-2}$ at 150°C (423 K).

Another measure of χ_{cc} can be made from enthalpies of mixing of oligomers:

$$\Delta H_m = \phi_1 \phi_2 \chi RT \quad (\text{A12})$$

Data are available for equimolar n-octane and 4-ethylheptane at 298 K ⁴⁰. The quantity $\Delta H_m = 14 \text{ J mol}^{-1}$, when converted to a C_4H_8 basis with $\Delta X_{\text{br}} = 1.0$ at 423 K , gives $\chi_{\text{PE/PEE}} = 4.1 \times 10^{-2}$. The experimental value $\xi = 1.4 \times 10^{-2}$ derived from this work lies between the estimates from equations (A11) and (A12). It is very close to the solubility parameter prediction (equation (A11)), though the nearly quantitative agreement may be fortuitous.