the polysilynes provide the first examples of soluble σ-delocalized materials with a composition intermediate between that of linear polysilanes and elemental silicon. Investigations into the properties and potential applications of these and related new materials are in progress.

Acknowledgment. We thank M. E. Galvin, S. Glarum, M. Y. Hellman, N. Hobbins, A. M. Mujsce, and L. S. Stillwagon for experimental advice and assistance.

Registry No. 1 (SRU), 94904-85-5; 1 (homopolymer), 97036-67-4; 2 (homopolymer), 118018-35-2; 3 (homopolymer), 118018-36-3; 4 (homopolymer), 118018-37-4; NaK, 11135-81-2; poly(phenylmethylsilane) (SRU), 76188-55-1; poly(phenylmethylsilane) (homopolymer), 31324-77-3.

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(12) If the pH of the hydrolyzed reaction mixture was not exactly neutral, a buffer solution such as 1.0 M $NaHCO_3$ was used instead of water.

(13) If the polymer remained in solution in the organic phase, the layers were quickly separated and methanol was added to the organic layer. The precipitated polymer was collected by filtration and purified as stated.

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Hydrogen–Deuterium Exchange for Labeling Polyethylene

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Received August 1, 1988; Revised Manuscript Received September 12, 1988

ABSTRACT: Hydrogen–deuterium exchange on linear polyethylene is achieved with a heterogeneous rhodium catalyst. Results are presented for nearly monodisperse and whole polymers with fractional deuteration $y \approx 0.2$–0.3, although $y = 0.6$ can be obtained. The exchange reaction appears statistically uniform and causes little or no change in the degree of polymerization. Small-angle neutron-scattering intensities indicate ideal mixtures of exchanged and unexchanged molecules, with some excess concentration fluctuations being seen in the semicrystalline whole polymer. The isotopic interaction parameter, χ_{hd}, is evaluated as a function of average deuterium fraction, y.

Introduction

Small-angle neutron scattering (SANS) has evolved as a powerful method for studying such features as chain dimensions and thermodynamic interactions of polymers, particularly in condensed or highly concentrated systems. Virtually all experiments employ deuteration of one component to achieve contrast for sufficient scattered intensity. Preparation of "labeled" chains can be accomplished by

0024-9297/89/2222-1704$01.50/0

polymerization of deuterated monomers or by reacting already formed polymers in such a way as to incorporate deuterium. Deuterated polybutadiene (DPB) in an example of the latter scheme; D_2 is added to the double bonds of the parent polybutadiene, forming a saturated analogue of polyethylene containing about 40% deuterium.[1]

Hydrogen–deuterium exchange reactions, particularly those involving nonlabile C–H bonds, provide an alternative route which seems to have attracted little attention. Case and Atlas[2] managed to exchange about 3% of the hydrogens for deuterium in polypropylene. Aromatic hydrogens in polystyrene are effectively exchanged in the presence of a homogeneous catalyst, though rather large changes in polymer molecular weight can occur.[3] Tanzer and Crist[4] exchanged about 6% of the hydrogens in a model ethylene–1-butene copolymer; the product was nonuniform in the sense that 10% of the chains had a fairly large deuterium fraction, $y = 0.6$, while the remainder was essentially unmodified.

The advantages of a successful H–D exchange scheme are obvious. Such a method automatically provides "matched" pairs of labeled and unlabeled chains, provided molecular architecture is unaffected by the exchange reaction. Perhaps more important is the ability to control the amount of deuterium labeling; this may be significant if chain–chain interactions based on isotopic composition ($\chi_{hd} \neq 0$) are present.[5,6]

We report here the procedure and results for an H–D exchange reaction performed on linear polyethylene over a heterogeneous rhodium catalyst. Fractional deuteration (y) as high as 0.6 can be obtained, though the present study is for polymers with $y \leq 0.3$, a value chosen to minimize unwanted thermodynamic effects from isotropic composition. The partially deuterated polymer appears to be labeled in a statistically uniform manner, and molecular weight is modified little or not at all.

Experimental Section

Materials and Reactions. The linear polyethylenes used in this study are the NBS fractions PE14, PE32, and PE114 and whole polymer PE53. The numerical suffix indicates weight-average molecular weight in the 1000s. Partially deuterated, exchanged polymers are designated DPE14, DPE32, etc.

The exchange reaction was conducted in a stirred, high-pressure batch reactor of 1-L volume. It was found that using partially deuterated cyclohexane solvent for the deuterium source was more effective than the previous method[4] which employed only gaseous D_2. Benzene was readily reacted with D_2 (15 bar, $T \approx 100$ °C) over the heterogeneous exchange catalyst (5% Rh on carbon, Strem chemicals) to yield a product with average composition $C_6H_6D_6$. Since polar impurities (e.g., water) poison the catalyst, it and the polymer to be exchanged were dried overnight under vacuum ($\sim 10^{-2}$ Torr) at room temperature. All solvents were dried over molecular sieves.

For making partially deuterated polyethylene, the reactor was charged with 300 mL of a $C_6H_{12}/C_6H_6D_6$ mixture of the desired deuterium fraction (typically ~ 0.25), 1 g of PE, and 0.5 g of catalyst. The system was pressurized to 35 bar with a H_2/D_2 gas mixture having the target deuterium fraction. The reaction was run at 135 °C for 24 h, after which the product was redissolved in xylene and filtered to remove the catalyst. DPE was reprecipitated in cold methanol, further washed, and dried in a vacuum oven at 60 °C.

SANS samples were prepared by solution blending DPE and its parent PE in refluxing xylene and then precipitating in methanol. After washing and drying, the blend was compression molded and quench crystallized to form a disk about 1 mm thick. The volume fraction of DPE was chosen to make the average coherent scattering length of the blend equal to zero. This minimizes any scattering due to voids, semicrystalline microstructure, etc.

Table I
Physical Properties of PE and DPE

sample	ρ, g/cm^3	$\langle y \rangle$	T_m, °C
PE14	0.9600		131.4
DPE14	1.0037	0.30	130.6
PE32	0.9460		132.9
DPE32	0.9861	0.31	132.1
PE53	0.9480		134.7
DPE53	0.9875	0.28	133.5
PE114	0.9311		136.2
DPE114	0.9580	0.19	135.1

Characterization. Physical characterization included the density of quenched, compression-molded films (gradient column) and melting temperatures by DSC (heating rate of 5 °C/min after cooling at 40 °C/min). FT-IR was performed on thin films, and GPC-LALLS (135 °C in trichlorobenzene)[7] was used to evaluate molecular weights of reactants and products.

SANS was done on the small-angle diffractometer[8] at the Intense Pulsed Neutron Source at Argonne National Laboratory. The useful range of q was 0.007 Å$^{-1} \leq q \leq$ 0.35 Å^{-1}, where $q = 4\pi\lambda^{-1} \sin(\theta/2)$, λ is the neutron wavelength, and θ is the scattering angle. Measurements were done at room temperature and at 150 °C in a heated cell having silica windows. Data analysis was standard, involving azimuthal averaging, parasitic scattering corrections, etc. Intensities were put on an absolute basis (coherent cross section per unit volume, inverse centimeters) by comparison to a polystyrene/perdeuteriopolystyrene sample of known scattering power.[9] A q-independent incoherent signal (ca. 0.9 cm^{-1}) was subtracted from the total pattern. This correction is not negligible, as the coherent cross section of interest is less than 10 cm^{-1}. The incoherent level is quite well defined, however, by the constant intensity at $q > 0.15$ Å^{-1}.

Results and Discussion

There are a number of important characteristics of the product of this H–D exchange reaction: the overall amount of deuterium incorporated in the polymer; the distribution of deuterium within one chain and from chain to chain; and the presence of undesired side reactions which modify the length or shape of the chain. These are evaluated for the DPE made here, after which the SANS characteristics are discussed.

Extent of H–D Exchange and Melting Temperature. The most convenient parameter for estimating the average deuterium fraction, $\langle y \rangle$, is the mass density of DPE, ρ_d, relative to that of the parent PE, ρ_h. This was employed with matched pairs having identical thermal history. Assuming that the small change in molar volume is a linear function of $\langle y \rangle$, one obtains

$$\langle y \rangle = \frac{(\rho_d/\rho_h) - 1}{0.1436 + 0.0052(\rho_d/\rho_h)} \qquad (1)$$

The first term in the denominator derives from atomic weights of C, H, and D, while the second is based on the measured contraction of molar volume of crystalline perdeuterioalkanes.[10] Infrared spectroscopy is not useful for $\langle y \rangle$ because partial exchange leads to various CHD and CD_2 moieties for which absorption coefficients are not known. NMR is difficult to perform with the required accuracy, but quantitative proton resonance experiments are consistent with $\langle y \rangle$ derived from density.

Results for the exchange reaction run on the series of PE samples with different molecular weights are shown in Table I. Conditions for the reactions of PE14, PE32, and PE53 were identical, with a D/H ratio of solvent and gas chosen to achieve $\langle y \rangle \approx 0.3$. Note that the amount of H–D exchange observed is independent of molecular weight and molecular weight distributions. The DPE114 sample was made under conditions to achieve a smaller $\langle y \rangle$.

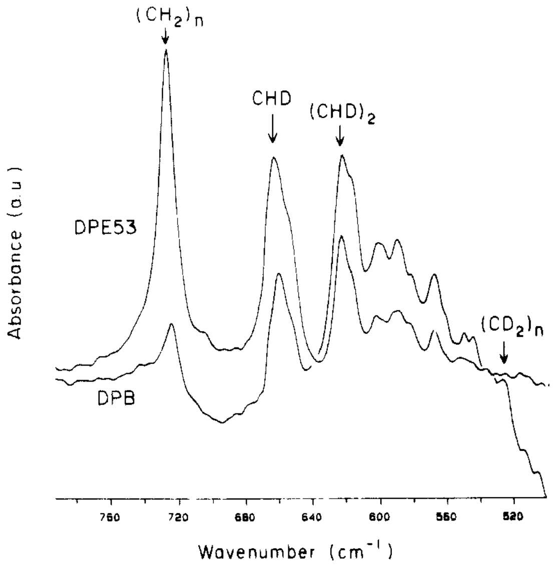

Figure 1. Infrared absorption spectra of DPE 53, $\langle y \rangle = 0.28$, and DPB, $y = 0.40$. Various methylene moieties responsible for absorption peaks are indicated.

Final melting temperatures corresponding to the most stable crystals are reported in Table I. The melting temperature of DPE is about 1 °C less than that of parent PE, a difference which is considerably smaller than the −5 °C change seen with perdeuteriopolyethylene ($y = 1$). Bates et al.[10] have calculated relative melting temperatures of nonpolar molecules when fully deuterated. Making the reasonable assumption that both molar volume and net bond polarizability of the monomer vary linearly with y (see below), one obtains for polyethylene

$$T_{mh}/T_{md} \approx (1 + 5.83 \times 10^{-3}y)^2 \qquad (2)$$

Here T_{mh} refers to the normal, hydrogenous polymer, and T_{md} is for the partially deuterated material. Equation 2 predicts $\Delta T_m = -1.5$ °C for $y = 0.3$ and $\Delta T_m = -0.9$ °C for $y = 0.2$, in general agreement with the data in Table I. Here we have further assumed that the average $\langle y \rangle$ for the DPE sample is equal to y for each chain, an assertion which is justified below.

Uniformity of Exchange. The question of uniformity of exchange sites arises when dealing with less than complete labeling. As an extreme example, $\langle y \rangle = 0.3$ could correspond to 30% of the chains being fully exchanged (local $y = 1$) and the balance being unmodified (local $y = 0$). It is desired to have each chain statistically exchanged so the local deuterium fraction equals the average, i.e., $y = \langle y \rangle$. Furthermore, the local deuterium content should be essentially constant along each chain.

Some information on the distribution of exchange sites can be had from infrared spectroscopy in the methylene rocking region at wavenumbers from 500 to 800 cm^{-1}. Figure 1 presents spectra for DPE53 with $\langle y \rangle = 0.28$ and deuterated polybutadiene (DPB) with $y = 0.40$. DPB is formed by the addition of D_2 to polybutadiene to form a partially deuterated chain which is statistically uniform. The occurrence of some H–D exchange as well as addition causes y to exceed 0.25 in this reaction, resulting in some isolated CHD groups (660 cm^{-1}) and $(CH_2)_n$ blocks (720 cm^{-1}) as well as the expected $(CHD)_2$ groups (620 cm^{-1}). Note the absence of a peak at 520 cm^{-1} corresponding to "blocks" of $(CD_2)_n$, $n > 4$.[11] The spectrum for the exchange product DPE is generally similar. In particular, there is no absorption indicating blocks of CD_2 units. Peaks corresponding to isolated CHD units and $(CH_2)_n$ blocks are larger than for DPB, as expected from deuteration by statistical mechanism. The absolute absorbance of the 720-cm^{-1} peak in DPE is predicted reasonably by a ideal random exchange model. Attempts to analyze relative intensities of other DPE peaks were not successful, in part because of very approximate absorption coefficients. The spectrum in Figure 1, which is typical of all the DPE samples prepared in this manner, is qualitatively consistent with expectations from a statistically uniform exchange product.

Table II
Molecular Weights of PE and DPE

polymer	M_w, g/mol	M_w/M_n
PE53	53 000	3.1
DPE53	40 000	2.7
PE114	114 000	1.23
DPE114	110 000	1.27

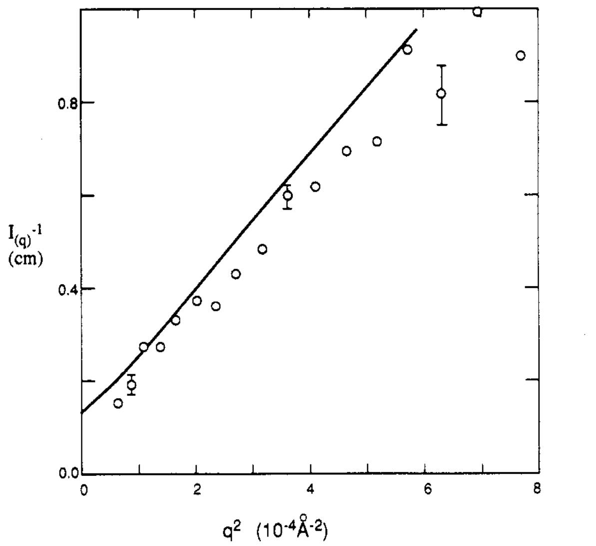

Figure 2. $I(q)^{-1}$ versus q^2 for quench crystallized PE114/DPE114. The line is calculated with no adjustable parameters.

Molecular Weight. Molecular weights and molecular weight distributions on the two highest molecular weight polymers were generously determined by Dr. G. VerStrate of Exxon Chemical Company.[7] The results are shown in Table II; values for DPE are for equivalent hydrogen-containing macromolecules. The high molecular weight fraction PE114/DPE114 is not affected significantly by the exchange reaction. The whole polymer shows some modification, noticeable in Table II as a drop in M_w and M_w/M_n. The reason for this is not understood, though scission of longer chains in the distribution appears unlikely in light of the unchanged M_w of DPE114. One possible cause is preferential adsorption onto heterogeneous catalyst particles of long chains, thus removing them from the system.

Hence, the exchange reaction appears to be "ideal" or nearly so in that the chain backbone is modified by a small amount at most. When altered to yield higher deuteration levels, the exchange reaction formed a product with $\langle y \rangle = 0.60$ and a limiting viscosity number which was 93% that of the polydisperse parent polymer.[12]

Small-Angle Neutron Scattering. SANS was done on blends of PE53/DPE53, $\phi_d = 0.14$, and PE114/DPE114, $\phi_d = 0.20$, where ϕ_d is the volume fraction of labeled polymer. These volume fractions were chosen to minimize scattering from density fluctuations, as mentioned in the Experimental Section. Results are presented in Figures 2 and 3 as reciprocal intensity versus q^2. The solid lines are calculated with the following assumptions: (1) exchange labeling is statistically uniform, i.e., $y = \langle y \rangle$;

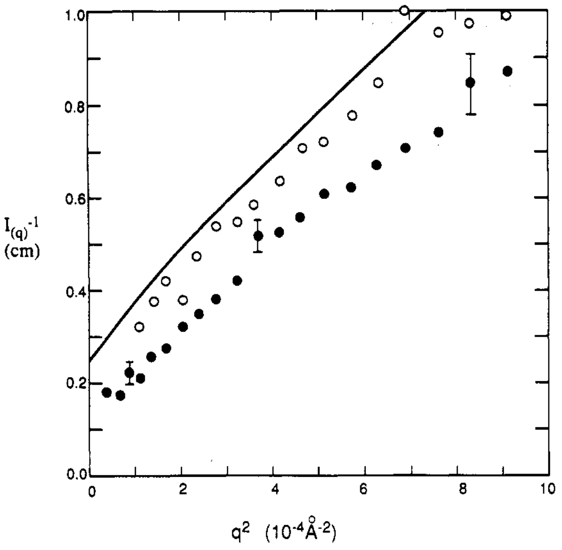

Figure 3. $I(q)^{-1}$ versus q^2 for molten (○) and quench-crystallized (●) PE53/DPE53. The line is calculated at 150 °C with no adjustable parameters.

and (2) the mixture is ideal, with interaction parameter $\chi_{hd} = 0$. The relevant equations are[1,13]

$$I = KS(q) \tag{3}$$

$$K = n_t[8y(b_D - b_H)]^2 \tag{4}$$

$$S(q)^{-1} = [\sum \phi_{di} N_{di} P(u_{di})]^{-1} + [\sum \phi_{hi} N_{hi} P(u_{hi})]^{-1} \tag{5}$$

$$P(u_i) = 2u_i^{-2}[\exp(-u_i) + u_i - 1] \tag{6}$$

$$u_i = (qR_{gi})^2 \tag{7}$$

$$R_{gi}^2 = CN_i \tag{8}$$

Here each chain is treated as a Gaussian coil composed of N C_4H_8 (or $C_4H_{8(1-y)}D_{8y}$) scattering centers. This choice of the "monomer" is arbitrary, but it emphasizes that very local structures cannot be probed with a randomly labeled polymer. The other symbols have their usual meanings: n_t is the number density of scattering centers, $b_{H,D}$ are atomic scattering lengths, and $\phi_{h,d}$ are volume fractions of normal and labeled chains. C is taken to be 10.6 Å^2 for the melt (corresponding to $C_\infty = 6.7$[14] or $R_g = 0.43M^{1/2}$) and 11.9 Å^2 for the quench crystallized solid (corresponding to $R_g = 0.46M^{1/2}$[15]). PE density in Table I and $\rho = 0.781$ g/cm^3[16] were used to determine n_t at room temperature and 150 °C, respectively. No attempt has been made to optimize the agreement between theory and experiment; the calculated curves are determined by experimental values of $\langle y \rangle$ and molecular weight distributions from GPC-LALLS on these polymers.

Calculated and observed intensities for the quench crystallized PE114/DPE114 are compared in Figure 2. Agreement is by and large excellent. What might be a ~10% increase in experimental intensity at small q ($q^2 < 2 \times 10^{-4}$ Å^{-2}) is within the uncertainty of absolute molecular weight (±5%) or degree of deuteration, $\langle y \rangle$. A 5% relative change in the latter, e.g., incrementing $\langle y \rangle$ from 0.19 to 0.20, will cause $I(0)$ to increase by 10%. The fact that the scattering curve for this semicrystalline polymer implies nearly Gaussian configurations of the chains is consistent with Mansfield's analysis.[17] For a sample having crystallinity $\alpha = 0.53$ ($\rho = 0.93$ g/cm^3), the Gambler's Ruin treatment predicts that R_g^2 is expanded by 2% over the unperturbed melt value. The same model predicts that the intensity at $qR_g > 1$ is increased by ~10% relative to that for Debye coils, which may explain the modest departure of the points below the calculated line in Figure 2. The experimental SANS pattern for this blend with exchanged high molecular weight linear polyethylene is exactly what is expected for chains which are statistically labeled with $\langle y \rangle = y = 0.19$.

The situation with the exchanged whole polymer, PE53/DPE53, is similar but not quite so straightforward. The open points in Figure 3 for the molten sample are systematically within 15% but below the line calculated for PE at 150 °C. Recall that no attempt has been made to adjust the theoretical curve to comply with experimental results. It is obvious that this discrepancy could be accounted for by a small change in either weight-average molecular weight or $\langle y \rangle$. More problematic is the relative intensity (coherent cross section per unit volume) of the molten and quench crystallized samples. One expects the intensity of the solid blend to be 20% greater than that of the melt on the basis of macroscopic density (n_t in eq 4). But at small q this ratio is about 1.5, clearly greater than expected. It appears that the whole polymer may be more susceptible than the high molecular weight fraction to "segregation" or "clustering" which gives rise to excess concentration fluctuations in the semicrystalline state.[18] The exact reason for this is not known, but it is noted that rapid crystallization is more efficient in quenching high molecular weight PE114 than the whole polymer PE53 (see densities in Table I).

Interaction Parameter, χ_{hd}. Partial deuteration has two obvious effects on SANS experiments: the intensity, $I(q)$, is lowered by a factor y^2 (eq 3 and 4); the interaction parameter, χ_{hd}, for isotopically distinct chains is decreased. Dependence of χ_{hd} on y can be estimated following the scheme of Bates and Wignall:[6]

$$\chi_{hd} = \frac{(\bar{V}_h - \bar{V}_d)^2}{2RT\kappa\bar{V}} + \frac{2\pi^2 I'(\alpha_h - \alpha_d)^2}{3RT\bar{V}^2} \tag{9}$$

The first term is based on the volume change of mixing, involving molar volumes, $\bar{V}_h$ and $\bar{V}_d$, for hydrogenous and deuterated polymer; isothermal compressibility, κ; and thermal energy, RT. The second term is for modification of intermolecular bonding at constant volume, $\bar{V}$, written in terms of ionization potential, I', and polarizabilities, α_h and α_d, of the segments.

We proceed by letting molar volume and polarizability be linear functions of fractional deuteration, y:

$$\bar{V}_d = \bar{V}_h(1 - ay) \tag{10a}$$

$$\bar{V}_h - \bar{V}_d = \bar{V}_h ay \tag{10b}$$

$$\alpha_d = 8\alpha_{CH}(1 - by) + 4\alpha_{cc} \tag{11a}$$

$$\alpha_h - \alpha_d = 8\alpha_{CH}by \tag{11b}$$

The parameters $a = 0.0052$[10] and $b = 0.0165$[10] are both small, justifying the linear form of eq 10 and 11. For the polarizability, we explicitly consider a group of eight C–H bonds and four C–C bonds, corresponding to the "monomer" C_4H_8 in the chain; $\bar{V}$ is calculated on the same basis. Equation 9 is combined with eq 10 and 11 and evaluated with appropriate constants for polyethylene at 150 °C: $\bar{V} = 7160$ mm^3/mol,[16] $\kappa = 11 \times 10^{-10}$ Pa^{-1},[16] $I' = 1.58 \times 10^{-18}$ J (the value for n-heptane[19]), and $\alpha_{CH} = 6.5 \times 10^{-4}$ nm^3.[20] One thus obtains

$$\chi_{hd} = 1.14 \times 10^{-3} y^2 \tag{12}$$

Recall that this χ_{hd} is based on the number of C_4H_8 repeats in the polyethylene chain.

Consider first the limit for fully deuterated polyethylene, $y = 1$, mixed with normal PE of the same degree of polymerization, N. Adopting the convention that phase separation occurs at $\chi_{hd}N = 2$ for $\phi_d = 0.5$, single-phase behavior should be observed for molten polyethylenes when $N < 1750$ ($M < 98\,000$ g/mol). If ideal behavior is desired, i.e., $\chi_{hd} < 0.1/S(0)$ (see eq 5), then $N < 350$ ($M < 19\,700$ g/mol). This is a much more severe constraint, implying that excess forward intensity, $I(0)$, may be seen in "high concentration" blends of rather modest molecular weight PE and perdeuteriopolyethylene. It is possible that some of the problems encountered with "segregation" of crystallized polyethylene systems stemmed from concentration fluctuations in the melt. For example, Schelten et al.[21] studied a blend of $M = 140\,000$ g/mol perdeuteriopolyethylene in PE of $M = 100\,000$, $\phi_d = 0.1$. For this system, one predicts on enhancement of 2.0 for $I(0)$ in the melt state (compared to the ideal limit when $\chi_{hd} = 0$), nearly equal to the factor of 2.4 seen in the quench crystallized sample. This simple analysis fails, however, to explain the fact that no enhancement was seen for the same sample in the melt state;[21] it appears that more work is required to understand the isotope effect on SANS of labeled and unlabeled polyethylene mixtures. The proposal that excess SANS intensity from semicrystalline polymers may arise from χ_{hd} effects in the melt bears some similarity to the analysis of Wu and Wignall.[18]

Regardless of these uncertainties, it is obvious that the influence of χ_{hd} is smaller for $y < 1$. Considering the present studies, χ_{hd} is estimated from eq 12 to be 0.5×10^{-4} and 1.0×10^{-4} for $y = 0.2$ and 0.3, respectively. These values of the interaction parameter are calculated to affect $I(0)$ in Figures 2 and 3 by less than 3%.

Conclusions

A simple method for achieving significant H–D exchange on polyethylene is demonstrated. The exchange reaction performed over a heterogeneous catalyst labels all chains (large and small) with statistical uniformity. Undesired side reactions which change molecular weight, etc., are not serious problems. This technique for achieving partially labeled chains provides an additional degree of freedom in the preparation of SANS systems.

Such partially exchanged polymers are best suited to SANS studies of thermodynamic interactions between chemically unlike chains without complications from isotope effects ($\chi_{hd} \approx 0$). Experiments using blends of DPE with model copolymers are under way. This exchange method works equally well for copolymers of ethylene with 1-butene[12] and should be applicable to other copolymers and homopolymers of α-olefins such as polypropylene. The present reaction is not suitable for unsaturated polymers such as polybutadiene and polystyrene, as addition to double bonds will occur. With a proper solvent, this method may work for exchanging methylene sequences in polyethylene oxide, nylon 6, etc., though experiments should be done to ensure that backbone linkages are not affected.

Acknowledgment. This research was funded by the Gas Research Institute, Physical Sciences Division, Contract 5084-260-1051. The IPNS-SAD facility is supported by the US Department of Energy, BES-Materials Science, Contract W-31-109-Eng.38. We are indebted to Dr. G. VerStrate for molecular weight characterization and to Prof. R. L. Burwell for valuable discussions and advice on heterogeneous exchange reactions.

Registry No. PE, 9002-88-4; Rh, 7440-16-6; neutron, 12586-31-1.

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