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Investigation of Chain Folding in Polyethylene Melts by Diffuse Neutron Scattering†

J. Schelten* and M. Stamm

Institut für Festkörperforschung der Kernforschungsanlage Jülich,
D 5170 Jülich, West Germany.

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ABSTRACT: Melts of polyethylene and n-hexatriacontane consisting of 50% deuterated and 50% protonated molecules were investigated by neutron scattering in a Q range between 0.09 and 3.25 Å^{-1}. A comparison of the measured scattering patterns with calculated scattering functions based on Gaussian chains in the melt yields no evidence for back-folding in polyethylene as proposed by Pechold. Deviations of the scattering function from the Debye function are observed. They are explained by effective intramolecular monomer–monomer interactions at the Θ temperature and are estimated from calculations based on molecular conformations obtained by Monte Carlo methods.

Introduction

There are essentially two models for the conformation of polymer molecules in the melt which are still under discussion. According to the random coil model proposed by Flory,[1] the molecular conformations in the melt and in a Θ solvent are identical, and to a first approximation the spatial distribution of two chain segments is Gaussian at large distances. For this distribution Debye developed an analytical expression for the scattering function.[2] The scattering function of single chains can be obtained by neutron scattering. With remarkable consistency it has been shown for PMMA, PS, PE, PP, and n-alkanes that the radii of gyration deduced from neutron small-angle scattering experiments in the melt are of the same magnitude as in Θ solvents.[3–7] In addition, the measured scattering functions in the glassy state and the melt can well be described by the Debye function within a certain Q range. Deviations from the Debye function are expected for polymers such as PE and PS for large Q values, e.g., $Q \geq 0.4$ Å^{-1}, due to influences of molecular geometry.[8] Experimentally, a Debye behavior is observed for $Q \leq 0.4$ Å^{-1}. For PMMA, on the other hand, strong deviations at much smaller Q values have been observed. By numerical calculations of scattering functions of PMMA based on the isomeric state theory it was shown that the deviations are caused by the molecular geometry.[9] Thus the experimental results from neutron scattering on polymers in the melt and in the glassy state give strong evidence that the random coil model is a good description of the polymer conformation in the melt and glassy state.

A very convincing argument for the random coil model is presented by de Gennes.[18] Intrachain and interchain forces are acting on each polymer segment. Because of the homogeneous density in amorphous polymers, the sum of both forces is independent of the molecular conformations. Therefore, the molecules coil unperturbedly and the distances between chain segments are Gaussian distributed, apart from molecular geometry effects. Despite the independence of the total segment interactions on the molecular conformation, there may exist a nonzero effective intrachain interaction, as will be discussed in the last part of the paper.

Besides this random coil model, which denies any order in the amorphous or molten state of polymers, folding models have also been proposed, e.g., the meander model of Pechold.[10,11] The essential feature of this folding model is the formation of bundles of parallel chain segments. To obtain orientational isotropy a superfolding was introduced, leading to a meander shape of the bundles. With the aid of this model it is easy to understand that polymers can crystallize rapidly since long-range diffusive motions are not necessary and that during crystallization the density changes only slightly, e.g., 14% in the case of polyethylene. Similar density differences are found for nonpolymeric organic solids. According to the random coil model, larger density differences are expected for polymers if no tendency for parallel packing of polymer segments is introduced.

In order to describe the neutron scattering experiments with polymer melts[3–8] by the meander model, a certain amount of back-folding had to be incorporated into the model (see Figure 1). The probability for back-folding is given by the Boltzmann factor $\exp(-E_f/k_BT)$. The folding energy E_f has recently been calculated on the basis of empirical interatomic potentials and a back-folding probability was obtained with which the neutron results could be explained.[12] This model is based theoretically on a few hypotheses, of which one, the cluster entropy hypothesis, cannot be proven to be either right or wrong. Up to now experimental results do not exist which are in contradiction with this model. The purpose of this paper is to present new experimental results by which a decision between the two models can be made. The basic idea of the experiments is to measure the additional scattering due to back-folding by diffuse neutron scattering from mixtures of deuterated and protonated polyethylenes in the melt. As will be shown later, this scattering should result in a halo centered at a position corresponding to the distance between neighboring chain segments.

In the theoretical section the various contributions to the scattering cross section of a polymer mixture are calculated, with emphasis on the contribution due to

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† The scattering experiments were performed at the Institute Laue Langevin (ILL), Grenoble, France.

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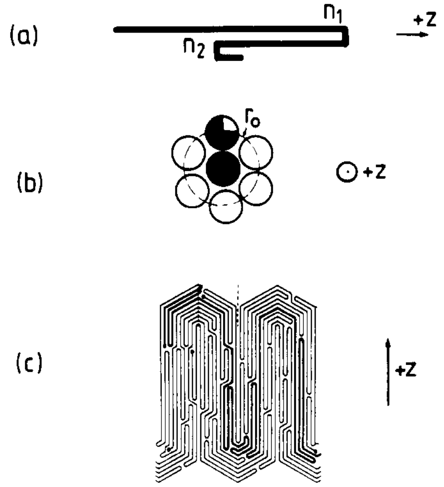

Figure 1. (a) Back-folding of a one-dimensional chain; n_1 and n_2 are the numbers of consecutive steps in the $+z$ and $-z$ directions, respectively. (b) Nearest-neighbor arrangement perpendicular to the z direction with a deuterated chain at the origin. (c) Meander model in the melt with back-folding of the chains within bundles as proposed in ref 12.

back-folding. Sample preparation and data evaluation are described in the Experimental Section. Finally, the experimental results are presented and discussed with respect to the random coil and meander models.

Scattering Theory

In order to estimate the additional scattering cross section due to back-folding, a model one-dimensional chain is considered which progresses successively n_1 steps in the $+z$ direction, n_2 steps in the $-z$ direction, etc. as indicated in Figure 1a. Each step in the $+z$ direction is the equivalent of progressing another monomer unit in the chain direction without the occurrence of back-folding into a neighboring site beside the chain. The probability of n_1 consecutive steps in one direction and of back-folding in the n_1 + first step is given by

$$p(n_1) = (1 - p_f)^{n_1} p_f \tag{1}$$

where p_f is the back-folding probability of one step.

The probability $p(n)$ is used to calculate the mean fraction of the chain which is accompanied by a back-folded part of the chain. If we consider only one fold, the fraction is $w = n_2/n_1$ if $n_1 \geq n_2$ and $w = 1$ if $n_1 < n_2$. Thus the mean fraction is

$$\bar{w} = \sum_{n_1,n_2} p(n_1)p(n_2)\frac{\min(n_1,n_2)}{n_1} \tag{2}$$

In a straightforward calculation one obtains in the limit of infinitely long chains

$$\bar{w} = (1 - p_f) \ln (2 - p_f) + p_f \tag{3}$$

The essential feature of (3) is that $\bar{w}$ increases monotonically with p_f from $\bar{w} = \ln 2 \approx 0.7$ at $p_f = 0$ to $\bar{w} = 1$ at $p_f = 1$.

Thus, the mean fraction $\bar{w}$ depends only slightly on the back-folding probability p_f. Note, however, that the mean number n_1 of consecutive steps in one direction is very sensitive to p_f ($n_1 = (1 - p_f)/p_f$) and that $\bar{w}$ is essentially the ratio of two such numbers. Therefore, to a first approximation $\bar{w}$ is independent of p_f.

From a knowledge of $\bar{w}$ one can calculate pair correlations due to back-folding in a polymer melt consisting of deuterated and protonated molecules. It is assumed that the fractions of the two components are 50% ($c_D = c_H = 0.5$) and that the two components are randomly distributed. Starting from an arbitrarily chosen monomer at the origin which may be deuterated, the number of deuterated monomers which occupy nearest-neighbor sites perpendicular to the chain direction is calculated. The number of such possible sites may be ν. In Figure 1b ν is assumed to be six. Two cases must be considered: the deuterated chain at the origin folds back to one of these sites. This case has a probability $\bar{w}$ and the number of deuterated chains on the neighboring sites is $1 + {}^1/_2(\nu - 1)$, if one assumes as a first approximation a random occupancy of the remaining $\nu - 1$ sites by deuterated monomers. The other case is that none of the neighboring sites is occupied by the back-folding chain at the origin. The probability for this case is $1 - \bar{w}$ and the number of deuterated chains is ${}^1/_2\nu$. Thus the conditioned probability p_{DD} of finding a deuterated monomer at a neighboring site if there is a deuterated monomer at the origin is

$$p_{DD} = \tfrac{1}{2} + \tfrac{1}{2}(\bar{w}/\nu) \tag{4}$$

The conditioned probability p_{DD}, which for a random distribution of deuterated and protonated monomers is equal to ${}^1/_2$, determines the magnitude of the first Cowley order parameter α:

$$\alpha = (p_{DD} - 0.5)/0.5 = \bar{w}/\nu$$

The order parameter and its relation to the diffuse scattering are as defined by Guinier.[17]

With the aid of α, the scattering cross section per monomer, $d\sigma/d\Omega$, due to back-folding is given by

$$\frac{d\sigma}{d\Omega}(Q) = c_D c_H |F_D - F_H|^2 \left\{ 1 + \alpha \int s(r) \frac{\sin (Qr)}{Qr} 4\pi r^2 \, dr \right\} \tag{5}$$

Q is the scattering vector and F_D and F_H are the form factors of deuterated and protonated monomers.

In eq 5 $s(r)$ is the pair correlation density whose volume integral over the nearest-neighbor distance results in ν. Since $s(r)$ is sharply peaked, the integration in eq 5 can be performed, leading to the expression

$$\frac{d\sigma}{d\Omega}(Q) = c_D c_H |F_D - F_H|^2 \left\{ 1 + \bar{w} \frac{\sin (Qr_0)}{Qr_0} \right\} \tag{6}$$

where r_0 is the nearest-neighbor distance, which is approximately 5 Å for polyethylene.

For reasons which will be outlined later in the text, the difference $\Delta(d\sigma/d\Omega)(Q)$ of the scattering cross section of a polymer with and without back-folding will be quantitatively discussed.

$$\Delta(d\sigma/d\Omega)(Q) = c_D c_H |F_D - F_H|^2 \bar{w} \frac{\sin (Qr_0)}{Qr_0} \tag{7}$$

For polyethylene with $c_D c_H |F_D - F_H|^2 = 1.07$ barn and $\bar{w} = 0.7$, $\Delta(d\sigma/d\Omega)(Q)$ reaches its minimum value of -0.16 barn at $Q = 1.4\pi/r_0 = 0.88$ Å^{-1} and its maximum value of $+0.1$ barn at $Q = 2.46\pi/r_0 = 1.55$ Å^{-1}. $\Delta(d\sigma/d\Omega)$ is zero at $Q = \pi/r_0$, i.e., at $Q = 0.63$, 1.25 and 1.88 Å^{-1}.

It should be noted that the calculated cross section difference given by (7) underestimates the additional scattering due to back-folding, according to Pechold's meander model, since only nearest-neighbor correlations have been considered and since for $\bar{w}$ the smallest value has been inserted.

In the following, all the other contributions to the neutron scattering cross section of such a two-component polymer system are described. For this purpose the liquid structure factor $\tilde{S}(Q)$

$$\tilde{S}(Q) = \frac{(2\pi)^3}{v}\delta(Q) + \tilde{s}(Q) \qquad (8)$$

is introduced, where v is the monomer volume. The structure factor $\tilde{s}(Q)$ is known from X-ray scattering experiments. The Fourier transform of eq 8 results in the pair correlation function

$$S(r) = 1/v + s(r) \qquad (9)$$

where $s(r)$ approaches 0 as $r \to \infty$ since at large distances $S(r)$ becomes identical with the mean number density $1/v$. The function $H(r)$ is also introduced to describe correlations between monomers of the same chain. Starting from a monomer, the probability of finding a monomer of the same chain at a distance r is given by $H(r)$. Its Fourier transform, $H(Q)$, is proportional to the scattering function of the single chains. The total neutron scattering cross section per monomer of a polymer mixture in the melt consists of the following contributions:

(i) The scattering cross section of the liquid:

$$\frac{d\sigma_1}{d\Omega}(Q) = (c_D F_D + c_H F_H)^2 \tilde{s}(Q) \qquad (10)$$

In eq 10 the scattering amplitude per monomer is the averaged form factor of the two components.

(ii) The diffuse scattering:

$$\frac{d\sigma}{d\Omega}(Q) = c_D c_H |F_D F_H|^2 \int S(\mathbf{r}) \cdot H(\mathbf{r}) e^{i\mathbf{Q}\mathbf{r}}\, d_3\mathbf{r} \qquad (11)$$

Equation 11 can be derived from first principles by assuming a random distribution of molecules and identical intramolecular correlations $H(r)$ for both components. Equation 11 splits into two terms by applying the faltung theorem and using eq 8

$$\frac{d\sigma_2}{d\Omega} = c_D c_H |F_D - F_H|^2 \frac{1}{v} \tilde{H}(Q) \qquad (12)$$

and

$$\frac{d\sigma_3}{d\Omega} = c_D c_H |F_D - F_H|^2 \frac{1}{(2\pi)^3} \tilde{H}(Q) * \tilde{s}(Q) \qquad (13)$$

In small-angle neutron scattering experiments with polymer melts only $(d\sigma_2/d\Omega)(Q)$ is usually considered. This is justified by the fact that the other term of the diffuse scattering cross section is negligible at small scattering vectors Q. However, for Q values of the order of π/r_0 both contributions are of the same order of magnitude and at $2\pi/r_0$, where the liquid structure factor has its first maximum, $(d\sigma_3/d\Omega)(Q)$ becomes larger than $(d\sigma_2/d\Omega)(Q)$. For a perfect crystal $\tilde{s}(\mathbf{Q})$ is a sum of δ functions

$$\tilde{s}(\mathbf{Q}) = \sum_{\tau} \delta(\mathbf{Q} - \tau)$$

with τ any reciprocal lattice vector. This leads to

$$\frac{d\sigma_3}{d\Omega}(\mathbf{Q}) = \sum_{\tau} \frac{d\sigma_2}{d\Omega}(\mathbf{Q} - \tau)$$

and implies that the strong Q dependence at the origin is also found at any reciprocal lattice point. These arguments make it clear that the folding term $(d\sigma_3/d\Omega)(Q)$ must appear in a description of the diffuse scattering. For the data interpretation this term is crucial.

(iii) The incoherent scattering is mainly determined by the exceptionally large incoherent scattering cross section of hydrogen, σ_H. It is superimposed on the other three coherent contributions.

$$\frac{d\sigma_4}{d\Omega}(Q) = c_D \frac{2\sigma_D}{4\pi} + c_H \frac{2\sigma_H}{4\pi} \qquad (14)$$

This contribution is independent of Q and is of the order of 6.6 barn per monomer for a 50% polyethylene mixture.

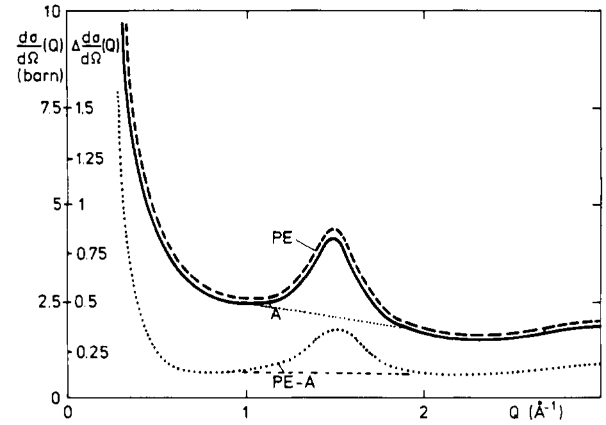

Figure 2. Calculated differential cross sections, $(d\sigma/d\Omega)(Q) = d\sigma_1/d\Omega + d\sigma_2/d\Omega + d\sigma_3/d\Omega$, of a 50% mixture of polyethylene (PE) and of an n-alkane (A) in the melt vs. the scattering vector Q. The difference in scattering cross section (PE-A) is plotted on an extended scale.

For a calculation of the scattering cross section of a 50% polyethylene mixture, the liquid structure factor $s(Q)$ was taken from Yoda.[13] For $(c_D F_D + c_H F_H)^2$ a value of 0.874 barn was used for all Q values, which is a good approximation for $Q \lesssim 1$ Å^{-1}. Furthermore, the single-chain scattering function $H(Q)$ is well approximated by the Debye function $D(Q)$; i.e., $H(Q) = NvD(Q)$, where N is the number of monomers per chain and v is the volume per monomer unit ($v \approx 25$ Å^3). The Debye funtion has the form

$$D(Q) = \frac{2}{Z^2}(e^{-Z} - 1 + Z) \qquad (15)$$

with $Z = (R_g Q)^2$ and $R_g = \beta N^{1/2}$.

The radius of gyration, R_g, is determined by the experimental value of $\beta = 1.65$ Å. Again, for $c_D c_H (F_D - F_H)^2$ a Q-independent value of 1.07 barn was used.

We dismiss possible arguments that the Debye approximation is very poor for a calculation of the scattering cross section for Q values of about 1 Å^{-1} for the following reasons. For PE it was shown experimentally that the Debye function is an excellent representation of the single-chain scattering for values up to 0.4 Å. It was also argued that at Q about $2\pi/r_0 \approx 1$ Å^{-1}, the major contribution of the diffuse scattering is the folding term $(d\sigma_3/d\Omega)(Q)$. Its value is mainly determined by $H(Q)$ at small Q values. In the folding integral the tail of $H(Q)$ has a negligible contribution. Therefore, in particular at Q values about the liquid structure factor maximum ($Q \approx 1$ Å^{-1}), accurate scattering cross sections are obtained if H is approximated by the Debye function.

The calculated scattering cross section, $d\sigma_1/d\Omega + d\sigma_2/d\Omega + d\sigma_3/d\Omega$, is shown for polyethylene ($N = 3000$) and an n-alkane ($N = 36$) in Figure 2. In the plotted Q range the difference between the scattering functions of polyethylene and n-alkane is very small and is therefore shown with an extended scale (dotted curve). Only at small Q values the difference is very large, due to the different molecular weights, and at $Q = 0$ it amounts to 3170 barn. There are contributions to the peaks in the scattering functions of

PE and A both from eq 10 and 13, whereas the peak of PE-A is caused entirely by the contribution described by eq 13. The incoherent scattering $(d\sigma_4/d\Omega)(Q)$ is the same for PE and A and cancels when the difference is taken.

So far, only the random coil model has been discussed. The introduction of back-folding, according to Pechold, would result in an additional term $(d\sigma_5/d\Omega)(Q)$, already discussed in eq 6.

Back-folding has to be considered only for long-chain molecules, however, and is not present in n-alkanes. Small-angle neutron scattering results of n-$C_{16}H_{34}$ and n-$C_{36}H_{74}$ in the melt and in solution obtained by Dettenmaier[19] agree well with scattering functions calculated on the basis of the rotational isomeric state theory. In this theory back-folding as discussed by Pechold has an extremely small probability in comparison with other rotational states which lead to unperturbed coil conformations. Since the observed radii of gyration in melt and in Θ solvents are also in good agreement with rotational isomeric state calculations, a random coil conformation can be assumed for n-alkanes.

Because of this difference between PE and n-alkanes, it is advantageous to investigate the difference in scattering functions PE-A. The contribution of back-folding is then given by eq 7 and other large scattering contributions cancel each other, which makes the method more sensitive for an observation of back-folding.

Experimental Section

Deuterated polyethylene was obtained from Merck. The degree of deuteration is stated to be 99%. The molecular weight was measured by GPC to be $M_w = 38\,800$ with $M_w/M_n = 4.7$, and the branching ratio was measured by IR methods to be <0.5 CH_3 per 100 CH_2 groups. For protonated polyethylene an NBS standard material (SRM 1475) was used, as this has already been well characterized:[14] $M_w = 53\,000$, $M_w/M_n = 2.90$ (light scattering and GPC), 0.15 CH_3 per 100 CH_2 groups, $\rho = 0.978\,44$ g cm^{-3}. The 50% mixtures of deuterated and protonated polyethylenes were prepared by dissolving the two components in tetrachloroethylene at 121 °C and crystallizing the mixed solute at 15 °C followed by a filtration and vacuum-drying procedure. The resulting powder was then melted at 150 °C and poured into the aluminum sample container.

The deuterated hexatriacontane ($C_{36}D_{74}$) was obtained from Merck Sharp and Dohme and had a degree of deuteration of 99%. $C_{36}H_{74}$ was supplied by Hoch-Light Laboratories. The 50% mixtures were prepared by mixing the components directly in the melt. The mole concentrations were $c_D = 0.47$ and $c_D = 0.50$ for polyethylene and n-hexatriacontane, respectively.

The wide-angle neutron scattering experiments were performed on the D1B instrument at the high-flux reactor of the Institute Laue Langevin in Grenoble. A multicounter system consisting of 400 cells and covering an angular range of $2\theta = 80°$ was used.

The wavelength was 2.52 Å (graphite monochromator) and the diffraction pattern was recorded for the 2θ range $2 < 2\theta < 82°$, corresponding to a scattering vector Q of $0.09 < Q < 3.25$ Å^{-1}. The samples were heated in a furnace under a helium atmosphere to 148 ± 4 °C. There were two heat shieldings to ensure temperature homogeneity in the sample, which was heated from the top and bottom. The illuminated sample volume was 50 × 10 × 1 mm^3. The sample was placed in the beam at an angle $\alpha = 30°$ between sample normal and incident beam. Thus, within the investigated 2θ range, shielding effects are avoided and attenuation is minimized. The measuring time per scattering pattern was of the order of 10 h.

The recorded scattering patterns were normalized to a constant neutron flux at the specimen and the scattering from the aluminum container was subtracted. Then the scattering patterns were normalized to the same sample weight and corrected for attenuation of the neutron flux. The attenuation was mainly due to incoherent scattering and depends on the angles 2θ and α because the path length of the neutron beam changes as a function of 2θ and α. Finally the intensities were changed into cross sections per monomer by assuming that at the largest measured Q value ($Q = 3.25$ Å^{-1}) the scattering cross section is the sum of the incoherent scattering per monomer and the coherent scattering of all atoms per monomer. This assumption would be correct for very large Q. At $Q = 3.25$ Å^{-1} it leads to a fairly good absolute calibration because of the relatively large and Q-independent incoherent scattering. The accuracy can be estimated to be ±15%.

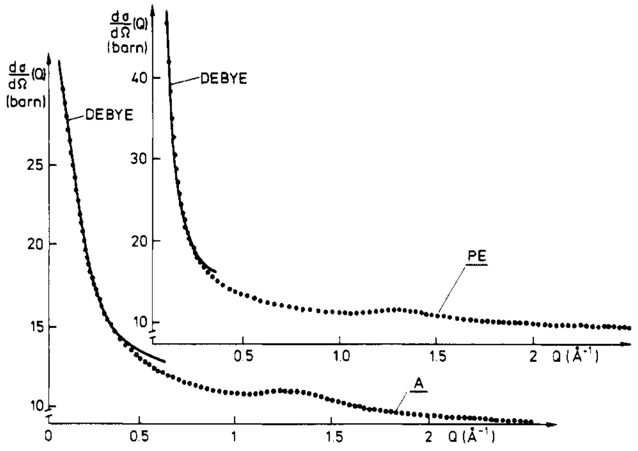

Figure 3. Measured differential scattering cross section per monomer vs. scattering vector for 50% mixtures of deuterated and protonated polyethylene (PE) and n-alkane (A) melts. The solid lines are Debye functions according to eq 15, fitted to the data at small Q.

In Figure 3 the measured scattering functions of a 50% mixture of polyethylene and of a 50% mixture of an n-alkane in the melt are shown. The strongly decreasing part of the scattering function at small Q can well be described by a Debye function fitted to the data. The first liquid structure factor maximum at $Q = 1.3$ Å^{-1} is barely discernible.

Results and Discussion

In this section the experimental results will be discussed with respect to two aspects: the back-folding of the chains and the detailed differences between the conformations of polyethylene and n-alkane in the melt.

In the theoretical section it has already been shown that back-folding is best resolved at Q values between 1 and 2 Å^{-1}. The scattering data presented in Figure 3 are plotted on an enlarged scale in Figure 4. The peak at 1.35 Å^{-1} arises mainly from two contributions, the scattering of the liquid described by eq 10 and the diffuse scattering, eq 13. Back-folding would contribute to this peak according to eq 6.

The scattering patterns of polyethylene and the n-alkane are very similar since contributions to the scattering cross sections, such as the liquid structure factor and the incoherent scattering, are identical in both cases and contributions from the diffuse scattering are nearly identical. In Figure 5 the difference pattern is shown and may be compared with the dotted line in Figure 2. The strong decrease of the difference of the scattering cross sections, $\Delta(d\sigma/d\Omega)$, at small Q in Figure 5 is caused by the difference of intramolecular long-range correlations. A similar Q dependence has been obtained in Figure 2, where the long-range correlations have been described by the Debye function. However, the experimental $\Delta(d\sigma/d\Omega)$ of Figure 5 becomes negative in contrast to the calculated $\Delta(d\sigma/d\Omega)$ of Figure 2. This indicates that the Debye function is not a completely correct description of molecular conformations in the melt. An explanation for this deviation will be given at the end of this section. On the other hand, in accordance with the calculations, a peak at 1.35 Å^{-1} is observed in the experimental difference pattern of Figure 5. Comparing the peak heights of Figures 2 and 5 in ab-

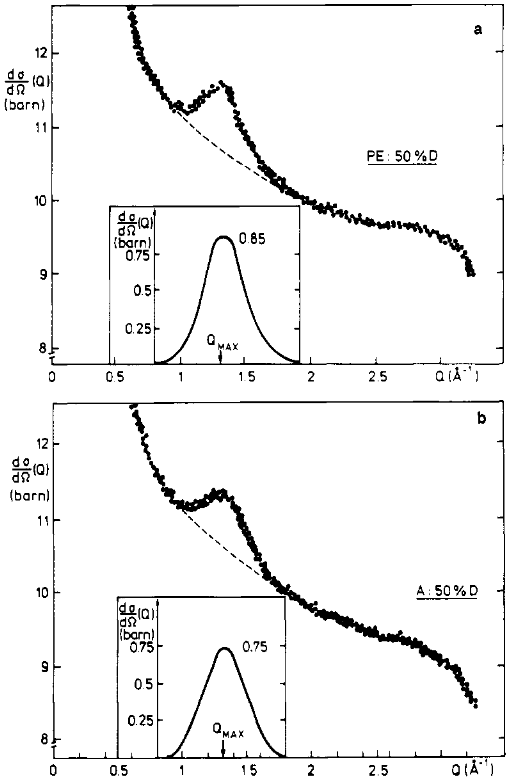

Figure 4. Measured differential scattering cross section per monomer vs. scattering vector Q for 50% mixtures of deuterated and protonated polyethylene (a) and n-alkane (b) melts. In the inserts the peaks at 1.35 $Å^{-1}$ obtained from the difference between the measured curve (●) and the dashed "background" line are plotted with an extended scale.

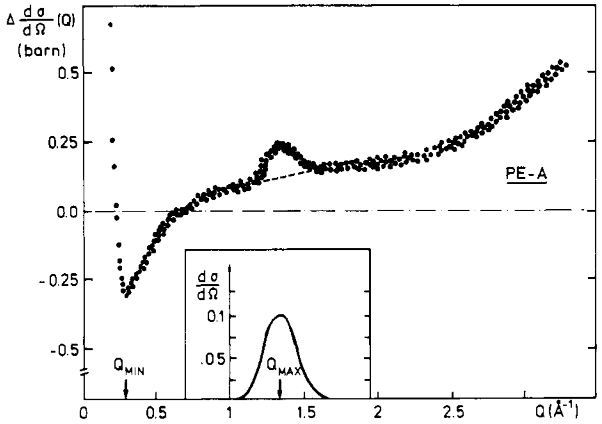

Figure 5. Difference scattering cross section per monomer vs. scattering vector Q (PE-A = data of Figure 4a minus data of Figure 4b).

solute units, one finds that the calculated cross section is about a factor of 2 larger than the experimental value. The calculated cross section is too large because the Q dependence of the form factors F_D and F_H has not been included. An additional uncertainty arises from the experimentally determined liquid structure factor $S(Q)$ which was used in the calculation. It should also be recalled the normalization of the neutron scattering data to absolute intensities is only accurate to ±15%.

Because of the discrepancy of the absolute peak intensities, only intensity ratios are discussed below. The ratio of the peak heights of the calculated difference pattern (PE-A) and of the calculated scattering pattern PE is 0.1. This compares well to a value of 0.12 ± 0.01 obtained from the corresponding experimental peak heights of Figure 5 and Figure 4.

Thus, it is clearly demonstrated that the small peak at 1.35 $Å^{-1}$ in Figure 5 is caused by diffuse scattering of eq 13 which is known to be solely responsible for the peak in the calculated PE-A curve of Figure 2. Thus no indication of back-folding can be deduced from this peak. On the other hand, the remaining slightly increased difference in scattering cross sections of Figure 5 in this Q range is not consistent with back-folding for the following reasons: (i) According to eq 7, a sinusoidal modulation with a minimum at 0.88 $Å^{-1}$ and a maximum at 1.55 $Å^{-1}$ is to be expected. (ii) The cross section should rise by a value of at least 0.26 barn from minimum to maximum.

These two features are not observed in Figure 5. The Q dependence of the difference pattern does not show the expected modulation and the rise of $\Delta(d\sigma/d\Omega)$ from 0.80 to 1.55 $Å^{-1}$ is only 0.05 barn, which is at least 5 times smaller than the increase expected from back-folding.

It is still necessary to explain why the scattering of the n-alkane exceeds the scattering of polyethylene at Q values of the order of 0.25 $Å^{-1}$. Such a behavior cannot be explained by a Debye function, where for all Q values a positive PE-A difference is obtained. The observed negative difference in cross sections is very small. At $Q_{\min}$ it is 2% of the coherent scattering cross section of polyethylene. This relative difference also cannot be explained by the small difference in concentration c_D of polyethylene and n-alkane because the prefactor $c_D(1 - c_D)$ of the diffuse scattering changes only by a relative fraction of 0.003 upon going from $c_D = 0.47$ (PE) to $c_D = 0.50$ (A). In addition, the observed difference cannot be explained by the small difference of the isothermal compressibility ($\bar{s}(Q)$ for $Q \rightarrow 0$) of n-alkane and polyethylene.

Because of the great similarity in the scattering functions of polymers in the melt and in Θ solvents, it is reasonable to assume, that conformations in the melt are determined by an *effective* intrachain monomer–monomer interaction. This interaction certainly has a strong repulsive part at small distances caused by the hard-core interaction of monomers. It then must have an attractive part at larger distances since otherwise one would have observed excluded-volume effects in the melt. With such an effective interaction between chain segments, the negative difference of the scattering function (PE-A) at large Q values can be understood. In real space this difference means that the probability of finding a pair of monomers belonging to the same chain at small distances, $r < 20$ Å, is slightly larger for short chains than for long chains. To understand this behavior let us consider two monomer units at a distance $r < 20$ Å. They are attracted by other monomers surrounding them and belonging to the same chain. These long-range forces result in an increase in the monomer distances. In the case of polyethylene the number of surrounding monomers is much larger than that in an n-alkane. Therefore the separation between chain segments of polyethylene is larger than in an n-alkane. This means that the pair correlation function of polyethylene is slightly smaller at distances $r < 20$ Å than that of n-alkanes. Consequently, the difference of the PE-A scattering function becomes negative at corresponding Q values, which has experimentally been found.

The behavior of scattering functions and pair correlation functions of short chains and long chains was studied by Baumgärtner[15,16] with a dynamic Monte Carlo method using a Lennard-Jones potential to describe the effective intrachain monomer–monomer interaction. Calculated scattering functions (ref 16, Figure 4b) clearly show that the difference between long and short chains (e.g., PE-A) becomes slightly negative at large Q values. The crossover from a positive to a negative difference occurs at $Q \simeq 2/R_{gA}$, where R_{gA} is the radius of gyration of the short chain. At much larger Q the difference goes to zero. This occurs in the calculation at $Q \simeq 1/l$, where l is of the order of the monomer bond length. A quantitative comparison of the calculated and the experimental scattering function is not possible since only the diffuse scattering contribution of eq 12 is known from the Monte Carlo calculations and the detailed chain geometry is not taken into account. The atomic structure of the PE and A chains is, however, the same and it should cancel out by taking the difference scattering function (PE-A). The change of the sign of the experimentally determined $\Delta(d\sigma/d\Omega)$ occurs at the Q value predicted by the Monte Carlo calculations, which may serve as an indication for the validity of the simplifications used here.

In summary, the discussion of the measured scattering functions of polyethylene and n-alkane melts has shown that no evidence for back-folding of the polyethylene chains was found. Furthermore, details of the molecular conformations in the melt have been explained by effective intramolecular interactions which are attractive at large distances.

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Stress–Strain Behavior of Thin ABA Poly(styrene-*b*-isoprene) Films

G. C. Meyer* and J. M. Widmaier

Ecole d'Application des Hauts Polymères, 67000 Strasbourg, France.

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ABSTRACT: The stress–strain behavior of thin ABA poly(styrene-*b*-isoprene) films (SIS) was examined as a function of total molecular weight and polyisoprene (PI) content. The Young's modulus was found to increase classically with decreasing PI content, whereas the tensile strength goes through a maximum corresponding to the limit of filmability of the SIS copolymer.

We are currently investigating the adhesive properties of ABA poly(styrene-*b*-isoprene) triblock copolymers (SIS).[1] They are used as heat-activated thin films in simple overlap joints. Their tensile strength and their tensile shear strength have been studied in regard to the molecular characteristics of the SIS copolymers and several other parameters.[2]

The mechanical properties of a joint, mainly its resistance to various acting forces, depend not only on the adhesive forces developed between the adhesive and the substrate but also on their rheological properties. In our work, only undeformable (for the stresses involved) substrates (glass, steel, aluminum, and wood) were used. Therefore the mechanical properties of only the adhesive film could play a role in the overall behavior of the bonded joint. This consideration led us to investigate the tensile properties of thin films of SIS.

In the related literature, the mechanical properties of SIS copolymers have been extensively studied.[3-6] Interest has been mainly in block copolymers of the thermoplastic elastomer type which have over 60% polydiene content. In these copolymers, the polystyrene domains act as cross-linking points, thus reinforcing the mechanical resistance of the materials. Especially stress-strain properties have been investigated on several-millimeter-thick standard test samples. Much less work has been done on SIS with a rigid matrix[5] and, hence, a high Young's modulus. In turn, to our knowledge, there are no investigations on thin copolymer films.

In this paper, we report stress–strain measurements on some 30 thin SIS films (about 0.1 mm). Their tensile strength has been studied as a function of their molecular characteristics.

Experimental Section

Synthesis and Characterization of Block Copolymers. SIS copolymers were prepared in the pilot plant of our Institute[7] by the now classical three-step anionic polymerization, in benzene at 50 °C, using n-butyllithium as initiator. Molecular characteristics were determined by gel permeation chromatography (GPC, Waters, in THF) and by ultraviolet spectroscopy (Cary 1501) and appear in Table I. Each copolymer is characterized by its total molecular weight, M_{tot}, and its elastomer content, % I.

Obtention of Films and Test Samples. SIS films were obtained by compression molding for 2 min at 180 °C, followed by rapid cooling. Dumbells (0.1-mm thick) for stress–strain ex-