

SELECTED PAPERS ON HIGH-POLYMER PHYSICS

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Neutron-scattering studies of bulk polyethylene at intermediate Q values

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We report SANS studies of bulk polyethylene (PE) samples crystallized from the melt at different rates. All samples contained both protonated and deuterated PE. Substantial isotopic concentration fluctuations are present in slow-cooled samples. This is seen as large differences in the low-angle (low- Q) SANS. At larger Q values, the SANS data from both materials is approximately identical. We interpret this in terms of an exponential radial correlation function for composition fluctuation whose correlation length is comparable to lamellar dimensions. Numerical calculations show that concentration fluctuations have minimal effect in the intermediate Q region.

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Small-angle neutron scattering (SANS) is a powerful new tool for the study of bulk polymers. Protonated and deuterated analogs of a given polymer are mixed to form specimens. Neutron-scattering cross sections for protons and deuterons are substantially different. Consequently, such specimens scatter neutrons according to dilute solution scattering laws, although the specimens retain all the other characteristics of bulk polymers.

Several groups have studied polyethylene, PE, by SANS: Schelten, *et al.*,¹ Sadler and Keller,² and King *et al.*³ SANS data suggests that chain-folded lamellae with regular or "adjacent" reentry predominate in solution-crystallized PE, and that lamellae with irregular or "switchboard" reentry are the dominant species in melt-crystallized PE. Bank and Krimm,⁴ using ir methods, have concluded that adjacent reentry occurs in both solution-crystallized and melt-crystallized PE. Yoon and Flory⁵ have calculated SANS patterns for PE with either adjacent or switchboard reentry.

It has been observed that "concentration fluctuations" or "segregation" exists in bulk specimens containing both protonated and deuterated PE. This was seen in Zimm plots of SANS data which gave unrealistically large values for the apparent molecular weight. Stehling, Ergos, and Mandelkern⁶ found that deuterated PE has a melting point some 4.8 °C lower than protonated PE. Presumably this melting-point difference reflects isotopic variations in molecular force fields which produce compositional heterogeneities in the mixed specimens. Uncertainties about the magnitude of concentration fluctuations and their influence on SANS have raised questions about conclusions drawn from SANS experiments on polyethylene.

We report SANS studies of bulk PE emphasizing (i) the issue of adjacent versus switchboard reentry and (ii) the

possibility that isotropic concentration fluctuations obscure SANS data about this question. Experimental SANS data on PE samples bulk crystallized by different methods are given. We also report some rudimentary calculations of the SANS in PE. Our conclusions are as follows:

(1) Concentration fluctuations, when they are present, strongly influence SANS intensities at low Q . This is reflected in Zimm plots of SANS data (Schelten, Wignall, Ballard, and Longman⁷). However, concentration fluctuations have a minimal effect at higher Q .

(2) Because of this, the most meaningful SANS data for distinguishing adjacent and switchboard reentry occur at higher Q values; specifically where Q^{-1} is less than lamellar dimensions.

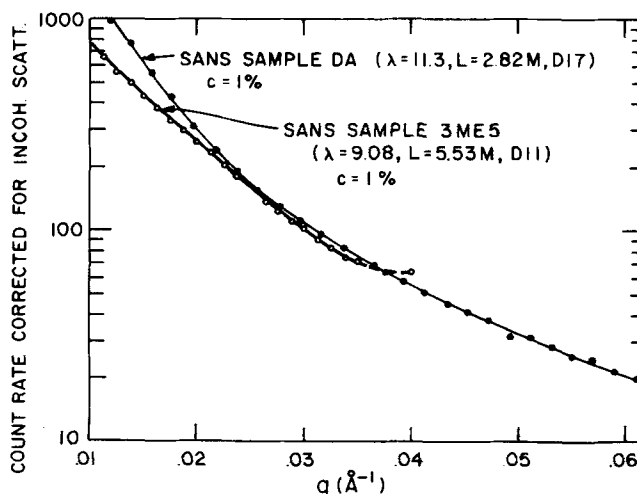


FIG. 1. Coherent SANS results of slow-cooled (DA) and quenched-cooled (3ME5) polyethylene samples with deuterated polyethylene concentration $C=0.01$.

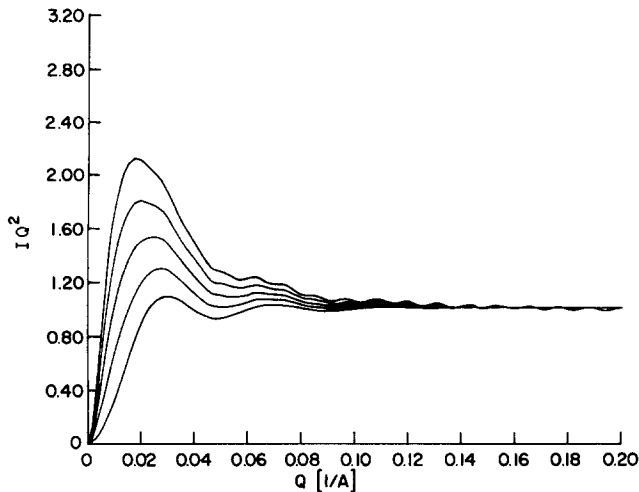


FIG. 2. Calculated values of $I = \alpha I_D + (1 - \alpha) I_C$ plotted as IQ^2 versus Q . I_C corresponds to a PE crystalline whose lamellar thickness is 160 Å. L , the correlation length in Eq. (3), was taken to be 75 Å. The curves, from top to bottom, correspond to $\alpha = 0.04, 0.03, 0.02, 0.01$, and 0.00, respectively. Note that IQ^2 becomes insensitive to α at higher Q values.

Figure 1 shows the SANS intensity I plotted against $Q = (4\pi/\lambda) \sin \frac{1}{2} \theta$, where λ is the wavelength of the neutron and θ is the scattering angle. All the targets contained 1% perdeuterated polyethylene ($M_w = 97\,140$, $M_w/M_n = 1.61$) in a matrix of protonated polyethylene ($M_w = 78\,700$, $M_w/M_n = 5.76$). The sample marked DA was slow cooled from the melt, producing substantial isotopic concentration fluctuations. The 3ME5 sample was quench cooled, prepared by dropping a heated mold into a large volume of cold water. The SANS measurements were done at the Institut Laue-Langevin. Previous research^{2,7} has shown that concentration fluctuations are minimized by rapid quenching. As shown in Fig. 1, the 3ME5 and DA samples have different intensities at low Q , but the intensities superimpose at higher Q . (We attribute the upturn in $I(Q)$ for 3ME5 near $Q = 0.036 \text{ \AA}^{-1}$ to detector correction uncertainties at the time the 3ME5 data was taken.) As reported by Schelten, Wignall, Ballard, and Longman,⁷ intensity difference at low Q translates into a large difference in the apparent molecular weight when a Zimm plot is constructed. However, the intensity superposition at higher Q suggests that concentration fluctuations do not compromise SANS data in this Q region.

Numerical calculations support this contention. We calculated the SANS from a rectangular array or platelet. Following Yoon and Flory,⁵ we chose 28 rows of 128 elements. The distance between elements in a row was 1.25 Å; the spacing between adjacent rows was 5.0 Å. The scattering intensity I_C was obtained from

$$I_C(Q) = 1 + \left(\frac{2}{N}\right) \sum_{j=1}^{N-1} (N-j) \left\langle \frac{\sin(Qr_j)}{Qr_j} \right\rangle. \quad (1)$$

N is the total number of scattering elements. Next, following Debye, Anderson, and Brumberger,⁸ the scattering from concentration fluctuations I_D was obtained from

$$I_D(Q) = \int_0^\infty \gamma(r) r^2 \left(\frac{\sin(Qr)}{Qr} \right) dr, \quad (2)$$

where

$$\gamma(r) = \exp(-r/L). \quad (3)$$

This correlation function obtains for a Markov distribution⁸ of composition fluctuations which we assume to be present in the partially deuterated PE. Finally, the intensities were summed with a weighting factor, α ($0 < \alpha < 1$),

$$I = \alpha I_D + (1 - \alpha) I_C. \quad (4)$$

For the present purposes, α can be viewed as an arbitrary parameter relating the relative intensities of concentration fluctuations and molecular scattering. Summerfield, King, and Ullman⁹ have related α to the mean square concentration fluctuation in the targets. Results with $L = 75 \text{ \AA}$ are shown in Fig. 2 plotted as IQ^2 versus Q . We see that concentration fluctuations have minimal effect at $Q > 2\pi/L$. If one associates the spatial correlation length of concentration fluctuations with the dimensions of crystalline and amorphous regions in PE, 75 Å appears to be a lower bound for reasonable L values. The curves shown in Fig. 2 represent a "worst case" on this basis since large L values produce even smaller effects in the higher- Q region.

Figure 3 shows the results of a similar superposition for a single rod containing 128 elements. This would correspond to the extreme case of a PE chain passing once, and only once, through a lamella. Again, concentration fluctuations have minimal effect at large Q .

We performed calculations for rectangular arrays (platelets) of varying dimensions. Changing the number of rows, while keeping the number of elements per row constant, mimics completely adjacent reentry with chains of varying molecular weight. Increasing the number of elements in a row, while keeping the total number of elements constant, mimics the increase in lamellar thickness with annealing. The results of these calculations, not shown, resemble Fig. 2. With larger platelet dimensions, the variations from $IQ^2 = 0$ to $IQ^2 = \text{const}$ occurs at progressively lower Q values.

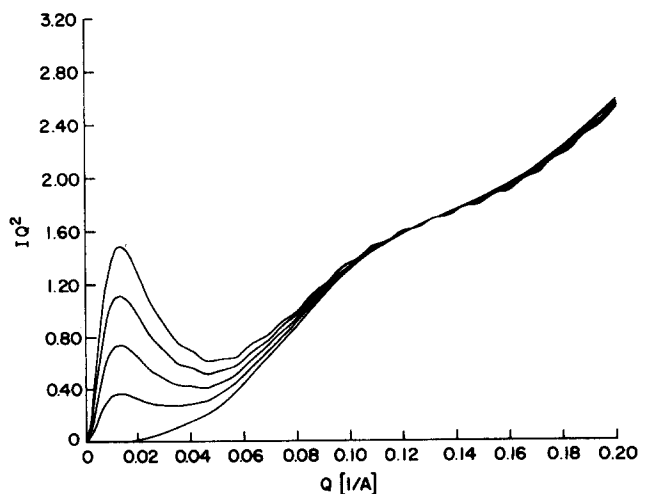


FIG. 3. Calculated values of $I = \alpha I_D + (1 - \alpha) I_C$ plotted as IQ^2 versus Q . I_C corresponds to a single PE stem 160 Å long in crystalline background. L was taken to be 75 Å. The curves, from top to bottom, correspond to $\alpha = 0.04, 0.03, 0.02, 0.01$, and 0.00, respectively.

The magnitude of IQ^2 in the plateau region (at higher Q) is independent of lamellar dimensions and reflects the number of scattering elements per unit area in the platelet.² As shown in the numerical calculations of Yoon and Flory,⁵ the magnitude of IQ^2 in the plateau region decreases as one goes from (1) completely adjacent reentry to (2) situations where a chain passes through a platelet many times with a variable distance between reentry sites. In the latter case, the number of scattering elements per unit area is decreased from the former situation.

In the present context, the main point is that the magnitude of the IQ^2 plateau is basically unaffected by composition fluctuations whose influence is most pronounced at lower Q values. Comparisons of experimental and theoretical values of IQ^2 in the plateau region are reserved for future publications.

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