

## Treatment of SANS Data from Hot Stretched Polystyrene Chains

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(Received 27 March 1989; accepted 8 August 1989)

### Abstract

The small-angle neutron scattering technique is applied to a hot stretched 5% perdeuterated polystyrene sample in order to investigate the residual macromolecular orientation at various length scales. The observed orientation is left over after fast quenching (in ice water) of the hot stretched sample. Previous investigations focused on how much polymer chains follow the external stretching. It is found that, even when macromolecules follow the external stretching affinely on the average, they do not deform uniformly. Moreover, over the time scale of the temperature quench, small chain portions relax more rapidly than large ones.

### Introduction

The small-angle neutron scattering (SANS) technique is very sensitive to macromolecular orientation (Benoit *et al.*, 1975; Boue, Nierlich, Jannink & Ball, 1982; Brown, 1985; Clough, Maconnachie & Allen, 1980; Dettenmaier, Maconnachie, Higgins, Rausch & Nguyen, 1985; Hadziioannou, Wang, Stein & Porter, 1982; Hammouda, Mildner, Bubeck & Malanga 1986) when used on partially deuterated samples. This technique is applied here to investigate the residual macromolecular orientation in hot stretched (and ice-water quenched) polystyrene. Previous SANS investigations on macromolecular orientation in hot stretched samples focused on whether polymer chains follow the external stretch-

ing 'affinely', *i.e.* whether the extracted molecular draw ratio (MDR) is comparable to the external draw ratio (EDR). It was found that macromolecules follow the external drawing affinely until nonlinear effects (chain slippage, for example) dominate, therefore limiting further increase of the MDR. The onset of such nonlinear effects depends on molecular weight and on hot stretching conditions (temperature, cooling rate, *etc.*) and was estimated (Boue *et al.*, 1982) to be around  $EDR = 3$  for molecular weights about 300 000, with a hot stretching temperature of 383 K and when the sample was immediately quenched in ice water. The purpose of the present study is to investigate whether polystyrene chains deform uniformly at various length scales in the linear-response (so-called affine) region.

SANS data were taken at the University of Missouri Research Reactor (MURR), at the National Institute of Standards and Technology Reactor (NISTR) and at the Intense Pulsed Neutron Source (IPNS) for comparison and for a wider range of scattering vector. Various data analysis schemes are discussed.

### Experiments

A sample of 5% by weight perdeuterated polystyrene and 95% hydrogenated polystyrene was prepared and characterized by gel permeation chromatography (GPC) which yielded  $M_r = 338\ 000$  and  $M_n = 239\ 000$  for the perdeuterated chains and  $M_r = 299\ 000$  and  $M_n = 124\ 000$  for the hydrogenated chains. The specimen was hot stretched at 383 K (at a rate of  $25.4\ \text{cm min}^{-1}$ ) to an extension ratio of 1.6 and then quenched in ice water (cold-water jets were

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turned on automatically as soon as the desired extension was reached). A non-stretched sample of the same thickness (1.5 mm) was also measured in order to determine the unperturbed radius of gyration.

Data were taken on the SANS instruments at MURR, NISTR and IPNS. Sample widths were 2.0 cm for the nonstretched and 1.55 cm for the hot stretched one. The MURR-SANS instrument (Mildner, Berliner, Pringle & King, 1981) was used in the following configuration: sample-to-detector distance of 450 cm, source and sample apertures of 2 and 1 cm respectively, wavelength of 4.75 Å ( $\Delta\lambda/\lambda = 4\%$ ) yielding reliable data in the momentum transfer range  $0.007 < Q < 0.09 \text{ \AA}^{-1}$  with a flat resolution of  $\Delta Q = 0.0045 \text{ \AA}^{-1}$ . The NISTR-SANS instrument (Glinka, 1988) was used with a sample-to-detector distance of 360 cm, source and sample apertures of 1.8 and 0.8 cm respectively and neutron wavelength of 7.1 Å ( $\Delta\lambda/\lambda = 25\%$ ) yielding reliable data in the momentum transfer range  $0.007 < Q < 0.1 \text{ \AA}^{-1}$ . The IPNS-SANS instrument (Epperson, Thiyagarajan & Klippert, 1988), on the other hand, uses a distribution of wavelengths between 1 and 14 Å, sample-to-detector distance of 150 cm, source and sample apertures of 1.2 and 0.4 cm respectively, therefore giving a wide reliable  $Q$  range of  $0.007 < Q < 0.24 \text{ \AA}^{-1}$ . On the IPNS-SANS instrument, the short wavelengths were used since that region is characterized by high intensities. Sensitivity corrections were made for the two reactor-based instruments (MURR, NISTR) by rescaling the data so that a water run gave a flat  $Q$ -independent signal and for the IPNS instrument by rescaling the data taken from a well characterized coherent scatterer (Jayasuriya, Tcheurekdjian, Wu, Chen & Thiyagarajan, 1988) such as an aluminium sample containing radiation-induced voids; this is to avoid annoying inelasticity corrections for water at short wavelengths. Counting times were 8 h on MURR-SANS, 2 h for NISTR-SANS and 2 h on IPNS-SANS. These last two instruments have higher fluxes because of the use of cold sources. Background runs (with no sample in the beam) were taken and subtracted from the raw data in each case.

### Data analysis for the non-stretched sample

Polystyrene chains follow random-walk statistics in the bulk state. Unperturbed Gaussian chains can be described with a Debye function for the structure factor  $S(Q)$ , where

$$\begin{aligned} S(Q) &= (1/N) \sum_{i,j} \langle \exp(i\mathbf{Q} \cdot \mathbf{r}_{i,j}) \rangle \\ &= (2N/U^2) [\exp(-U) - 1 + U] \end{aligned}$$

and  $r_{i,j}$  is the distance between monomers  $i$  and  $j$ ,  $U = Q^2 R_g^2$ ,  $R_g^2 = Nb^2/6$  is the radius of gyration

Table 1. *Fit of the SANS data from non-stretched polystyrene*

Parameter	MURR-SANS	NISTR-SANS	IPNS-SANS	
$B$	105	175	0.39	0.30
$A$	9580	11923	93	86
$R_g$ (Å)	145	145	154	146
$Q$ range of the fit ( $\text{\AA}^{-1}$ )	0.008–0.09	0.011–0.0089	0.006–0.18	0.006–0.1

squared,  $N$  is the total number of monomers per chain and  $b$  is the statistical segment length. A fit of the scattered intensity to

$$I(Q) = B + AS(Q)$$

yields a background (mainly incoherent scattering) value  $B$ , an intercept  $A$  and an apparent radius of gyration  $R_g$ , summarized in Table 1. Since no purely hydrogenated polystyrene sample was measured, incoherent scattering was assumed to be flat and introduced as a  $Q$ -independent fitting parameter  $B$ . As shown in Table 1, fits of MURR and NISTR data agree well. The small discrepancy between the signal-to-noise ratios ( $A/B$ ) from the two instruments occurs because unweighted fits have been performed. Changing the range of the fits changes  $B$  slightly while keeping the radii of gyration unchanged. The IPNS instrument, which uses a wide distribution of wavelengths, yields a different signal-to-noise ratio because of inelasticity effects which modify the background value  $B$ , so that IPNS data are treated with a  $Q$ -dependent scaling factor. After rescaling, data taken on the three SANS instruments yield similar structure factors (Fig. 1). Since the purpose of these investigations is not to extract a precise  $R_g$ , but rather to observe its anisotropy upon hot stretching, refining corrections such as those for polydispersity and mismatched molecular weights have not been included.

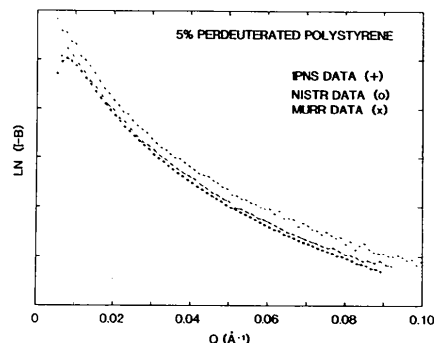


Fig. 1. SANS data from non-stretched polystyrene taken on the MURR-SANS, NISTR-SANS and IPNS-SANS instruments. Intensities have been rescaled to arbitrary units so as to fit on the same scale (these are not absolute intensities).

### Structure factor for uniaxially oriented Gaussian chains

Consider a chain containing  $N$  monomers interacting through a Gaussian monomer–monomer pair distribution and following random-walk statistics. Uniaxial stretching affects intermonomer distances  $r_{ij}$  differently in the parallel and perpendicular directions to the stretch axis:

$$\begin{aligned}\langle r_{ij\parallel}^2 \rangle &= \varepsilon_{\parallel}^2(i,j) \langle r_{ij}^2 \rangle \\ \langle r_{ij\perp}^2 \rangle &= \varepsilon_{\perp}^2(i,j) \langle r_{ij}^2 \rangle,\end{aligned}$$

such that the ellipticities  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  depend in general on the intermonomer distance  $r_{ij}$ . If chain deformations are uniform (same deformation at various length scales), these ellipticities are constant and their ratio

$$\varepsilon = \varepsilon_{\perp} / \varepsilon_{\parallel}$$

is the eccentricity that can be obtained from equal-intensity contour maps. For affine deformations,  $\varepsilon = \Lambda^{-3/2}$  where  $\Lambda$  is the EDR. These contour maps, however, show a residual  $Q$  dependence in reciprocal space implying an  $r$  dependence of the eccentricity in configuration space,

$$\varepsilon(i,j) = \varepsilon_{\perp}(i,j) / \varepsilon_{\parallel}(i,j).$$

$\varepsilon(i,j)$  is expected to be a decreasing function of  $r_{ij}$ , going from a value close to unity at distances less than the entanglement length to its minimum value imposed by the external draw ratio. A momentum-space variable,

$$Q^* = [Q_{\parallel}^2 + \varepsilon^2(Q) Q_{\perp}^2]^{1/2},$$

and a configuration-space variable,

$$r^* = [r_{\parallel}^2 + \varepsilon^{-2}(r) r_{\perp}^2]^{1/2},$$

can be defined. These two variables are canonical conjugates of each other, *i.e.* a Fourier transform pair. The variation of  $\varepsilon(r)$  with  $r$  could be obtained numerically by Fourier transforming the 2D raw data and observing the  $r$  dependence of the eccentricity of the equal-level maps of the monomer–monomer pair distribution function.

Note that a Debye function for the structure factor,

$$\begin{aligned}S(Q) &= (1/N) \sum_{ij} \langle \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}) \rangle \\ &= (1/N) \sum_{ij} \exp[-Q_{\parallel}^2 \varepsilon_{\parallel}^2(i,j) \langle r_{ij}^2 \rangle / 2] \\ &\quad \times \exp[-Q_{\perp}^2 \varepsilon_{\perp}^2(i,j) \langle r_{ij}^2 \rangle / 2],\end{aligned}$$

could be derived only when  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  are assumed independent of  $r_{ij}$ . For other explicit dependences on

Table 2. Treatment of SANS data from the hot stretched sample

Intensities within sectors are fitted to a Debye function for the structure factors.

		MURR-SANS	NISTR-SANS
		$0.01 < Q < 0.08 \text{ \AA}^{-1}$	$0.012 < Q < 0.07 \text{ \AA}^{-1}$
Direction			
parallel to the stretch axis	$10^\circ$ sectors	$A$ $B$ $R_{g\parallel} (\text{\AA})$	16824 300 116
perpendicular to the stretch axis	$10^\circ$ sectors	$A$ $B$ $R_{g\perp} (\text{\AA})$	2657 (7000*) 117 (151) 138 (253)

\* In order to extrapolate the data lost underneath the beam stop in the parallel direction, the intercept  $A$  for this direction is fixed equal to the value obtained for the perpendicular direction. Corresponding values of  $B$  and  $R_g$  (in parentheses) are results of the fit with fixed  $A$ .

$r_{ij}$ , the ensemble average  $\langle \dots \rangle$  would have to be performed numerically.

### Data analysis for the stretched sample

#### Sector averaging

A common data treatment scheme used to analyze anisotropic SANS data is to bin the raw data into sectors along and perpendicular to the stretch axis. Intensity data  $S(Q_{\parallel})$  and  $S(Q_{\perp})$  are then analyzed to extract radii of gyration  $R_{g\parallel}$  and  $R_{g\perp}$ . The eccentricity  $\varepsilon = R_{g\perp} / R_{g\parallel}$  can be compared with the external draw ratio  $\Lambda$ . Affine deformations are characterized by  $R_{g\parallel} = \Lambda R_{g0}$  and  $R_{g\perp} = R_{g0} / \Lambda^{1/2}$ . This standard data treatment method was followed here for the hot stretched partially deuterated polystyrene sample. Table 2 shows fits to Debye functions along the  $\parallel$  and  $\perp$  directions choosing (arbitrarily)  $10^\circ$  sectors. The sector size can change the estimate of  $R_g$  appreciably. This is partly because when sectors are too thin, intensity counts are low, whereas when sectors are made wide, a circular averaging scheme within the sectors is performed even though equal-intensity contours have elliptical shapes.

Note that this data analysis scheme corresponds to setting either  $Q_{\parallel} = 0$  or  $Q_{\perp} = 0$  in the general expression for  $Q^*$ . Use of a Debye function to fit 1D sector data therefore assumes constant ellipticities  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$ , *i.e.* uniform intermonomer deformations. Data along the parallel direction have a steeper variation and are harder to extrapolate. As Table 2 shows for the NISTR-SANS data, the intercept  $A$  in the parallel direction has to be fixed to a constant value (7000) equal to that obtained for the perpendicular direction in order to obtain reasonable radii of gyration

(253 Å). This is done because of the requirement  $S(Q_{\parallel}) = S(Q_{\perp})$  at the zero- $Q$  (thermodynamic) limit.

### Elliptical binning

As shown in Fig. 2, equal-intensity contour maps show elliptical shapes. In order to determine their eccentricity and orientation angle, elliptical bins of constant  $Q^* = (Q_{\parallel}^2 + \varepsilon^2 Q_{\perp}^2)^{1/2}$  are formed. Minimization of the variance

$$\langle (C - \langle C \rangle)^2 \rangle,$$

involving counts  $C$  in each detector cell and their average  $\langle C \rangle$  within the elliptical bins yields the best eccentricity  $\varepsilon$  and orientation angle for a specified  $Q^*$  range. Changing the  $Q^*$  range gives a variation  $\varepsilon(Q)$  shown in Fig. 3. This  $Q$  dependence implies an  $r$  dependence in configuration space which could be obtained by performing an elliptical binning of the Fourier transform (monomer-monomer pair distribution function) of the 2D raw data. Moreover, it was found that deformations are cylindrically symmetric around the stretch axis.

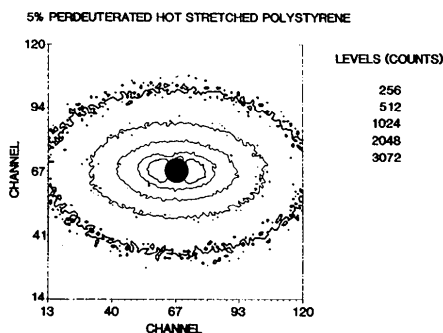


Fig. 2. Equal-intensity contour maps for the stretched polystyrene sample. Data shown were taken on the NISTR-SANS instrument. Data underneath the beam stop (center of the figure) are unreliable.

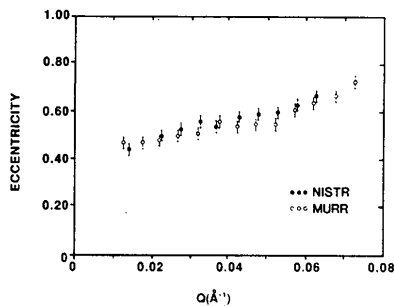


Fig. 3. Variation of the eccentricity  $\varepsilon$  with momentum transfer  $Q^*$ . Data shown were taken on the MURR-SANS and the NISTR-SANS instruments.

Note that the elliptical averaging method introduced to make asymmetric SANS data treatment more efficient uses an average (constant) value for the eccentricity. This method consists of elliptical binning of the data to a Debye function to extract radii of gyration along and perpendicular to the stretch axis. These values are averaged quantities since no  $Q^*$  dependence of the eccentricity is included.

As an alternative approach to the elliptical averaging method, one could use a direct nonlinear least-squares fit of the raw data to a 2D Debye function with an argument  $Q^* = [Q_{\parallel}^2 + \varepsilon^2(Q)Q_{\perp}^2]^{1/2}$  and model behavior for  $\varepsilon(Q)$ .

### Summary and discussion

SANS data from a non-stretched and a hot stretched 5% perdeuterated polystyrene sample were taken. Structure factors extracted from these data for the unstretched sample were compared and found to agree well. When the fits are taken within the same  $Q$  range, radii of gyration obtained from the three instruments agree well.

SANS data from the hot stretched sample were analyzed using the sector averaging method and a nonlinear least-squares fitting of the 2D raw (*i.e.* non-averaged) data to a Debye function. Isointensity contour maps show elliptical shapes with a slightly  $Q$ -dependent eccentricity which has been plotted experimentally. The slight increase of  $\varepsilon(Q)$  in reciprocal space or slight decrease of  $\varepsilon(r)$  in direct space imply that small chain portions relax faster (within the time of quench) than the whole macromolecule. The sector averaging method yields structure factors in the directions parallel and perpendicular to the stretch axis. Fitting these structure factors to a Debye function to extract radii of gyration assumes a  $Q$ -independent eccentricity, *i.e.* uniform deformations within the sample. Elliptical averaging within the sectors was found to improve this data treatment method.

This research was supported by a grant from The Dow Chemical Foundation. Allocation of beam time on the NISTR and IPNS SANS instruments is greatly appreciated.

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