

SANS from Hot-Stretched Polystyrene Revisited

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SYNOPSIS

Small-angle neutron scattering (SANS) has been used to investigate macromolecular orientation of uniaxially hot-stretched partially deuterated polystyrene. Principle radii of gyration and degree of eccentricity were measured over a range of hot-stretch temperatures, strain rates, and external draw ratios (EDR). Results show affine deformation for EDR < 4 and an increase in the degree of local molecular orientation with increasing rate of strain and decreasing stretching temperature. It also is found that although the macromolecules follow the external stretching affinely on average, they do not deform uniformly.

Keywords: neutron scattering (SANS) from hot stretched polystyrene • polystyrene, hot stretched, SANS study of • chain deformation in hot stretched polystyrene, SANS study of

INTRODUCTION

Small-angle neutron scattering (SANS) is a valuable diagnostic tool to investigate the morphology of polymers in the solid state. When used on partially deuterated samples, SANS is very sensitive monitor of single-chain conformations over a wide range of correlation distances and is thus capable of providing direct information about the size of the whole polymer molecule down to the average statistical segment. As a result, the technique can be particularly useful for characterizing the response of individual molecules to macroscopic deformation as an example.¹⁻¹⁰

Previous SANS studies³⁻⁸ of hot-stretched (partially deuterated) polystyrene have focused on finding out whether polymer chains deform affinely with respect to macroscopic deformation of the sample (i.e., whether the extracted molecular draw ratio (MDR) is comparable to the external draw ratio (EDR) of the sample). Results indicate the limit of affine deformation is at an approximate external draw ratio of between 2 and 3 for samples having an average molecular weight around 300,000 when

deformed slightly above the glass transition temperature (T_g).^{4,9} Below this extension limit, the molecular draw ratio is found to vary linearly with the external draw ratio (elastic deformation) while above it, nonlinear (viscoelastic) effects tend to dominate. The purpose of the present study is to characterize the molecular draw ratio of polystyrene under various deformation conditions (different extension ratios, hot-stretching temperatures, and strain rates) and to determine whether polystyrene chains deform uniformly at various length scales.

EXPERIMENTS

Sample Preparation and Characterization

Normal hydrogenated polystyrene (HPS) and pre-deuterated polystyrene (DPS) were first synthesized, then characterized by gel permeation chromatography and dilute solution viscosity. These materials were subsequently solution blended to yield a weight ratio of 80% HPS/20% DPS (corresponds to a 81.15% HPS/18.85% DPS by monomer density). After the solvent was evaporated, a solid homogeneous, partially deuterated polystyrene (PDPS) blend was obtained. Samples were compression molded into bars 2 mm thick and then

hot-stretched using an Instron tensile tester having a specially designed oven equipped with cold water jets for rapid quenching. The samples were uniaxially deformed to different degrees of deformation over a range of temperatures and strain rates. Blank samples (HPS) were also prepared under identical molding and hot-stretching conditions. Immediately after reaching the desired external draw ratio, the samples were rapidly quenched to room temperature by spraying with cold water. Strain rates ranged from 1.27 to 25.4 cm/min which corresponds to stretching times from 5 min down to 15 s. All samples were then characterized by SANS at room temperature.

Data Acquisition and Reduction

All SANS data were taken at the University of Missouri Research Reactor (MURR) in the usual instrument configuration:¹¹ sample-to-detector matched distance of 450 cm, source and sample apertures of 2 and 1 cm, respectively, and wavelength of 4.75 Å giving a scattering wavenumber range of $0.00675 \text{ \AA}^{-1} < Q < 0.09 \text{ \AA}^{-1}$. Measurements were made on both hydrogenated polystyrene and partially deuterated polystyrene (PDPS) blends. The measurement spot was at the center of the bar for all samples except for samples PDPS8A, B, C for which three measurement spots were chosen (spot A is near the clamped end of the sample, spot C is near the center of the bar, and spot B is half way between the two). Measurement times ranged from 6 hours for thick samples to 12 hours for thin ones. Beam-open background (BOB) and beam-blocked background (BBB) runs were taken as well in order to correct for background scattering not associated with the sample.

Theoretical transmission values for all samples were computed $T = \exp(-\Sigma_s t)$ using the macroscopic scattering cross sections Σ_s (Table I). The standard data reduction method to obtain the static structure factor was followed:

$$S(Q) = k[(I_{\text{PDPS}}/T_{\text{PDPS}} - I_{\text{BOB}})/t_{\text{PDPS}} - (1 - c_{\text{DPS}})(I_{\text{HPS}}/T_{\text{HPS}} - I_{\text{BOB}})/t_{\text{HPS}}]$$

where I is the measured SANS intensity for the PDPS, HPS, and BOB runs, T is the sample transmission, and t is the sample thickness. K is a proportionality constant (machine constant) and c_{DPS} is the deuterated monomer fraction in the PDPS sample. Here, $c_{\text{DPS}} = 18.85\%$. A test of the blank sample subtraction scheme for all hydrogenated HPS samples was performed by checking that the quantity $(I_{\text{HPS}}/T_{\text{HPS}} - I_{\text{BOB}})/t_{\text{HPS}}$ for all hydrogenated HPS samples is constant. This will be true provided that the measurement spot size remains constant from sample to sample. Subtraction of the BBB (sometimes referred to as "dark current") did not make an appreciable difference on the final results and was therefore not performed. This reduction method resulted in data files containing the extracted structure factor $S(Q)$ which is used in further data analysis. Figure 1 shows the SANS scattered intensity for unstretched partially deuterated polystyrene PDPS.

DATA ANALYSIS

One main purpose of these experiments is to investigate the extent of macromolecular orientation at various length scales during hot stretching. In the detector plane, this translates into a dependence of the equal-intensity contour maps on Q (especially at intermediate Q). This dependence was obtained by fitting the SANS equal intensity contour plots to elliptical bins of fixed width (0.01 \AA^{-1}) at various scattering wavenumber Q^* ranges. Here

$$Q^* = (Q_{\parallel}^2 + \epsilon^2 Q_x^2)^{1/2}$$

is a natural variable given the elliptical symmetry. Q_{\parallel} and Q_x are the projections of the scattering wavevector along and perpendicular to the hot-stretching

Table I. Molecular Weight and Thermal Neutron Scattering Macroscopic Cross Sections

	HPS	DPS	PDPS
Density (g/cm ³)	1.05	1.131	
Monomer molecular weight (g/mol)	104	112	
Polymer molecular weight (g/mol)	$M_w = 305,000$	$M_w = 290,000$	
Molecular weight distribution	1.1	1.3	
Monomer macroscopic scattering cross section (cm ⁻¹)	4.227	0.6396	3.522

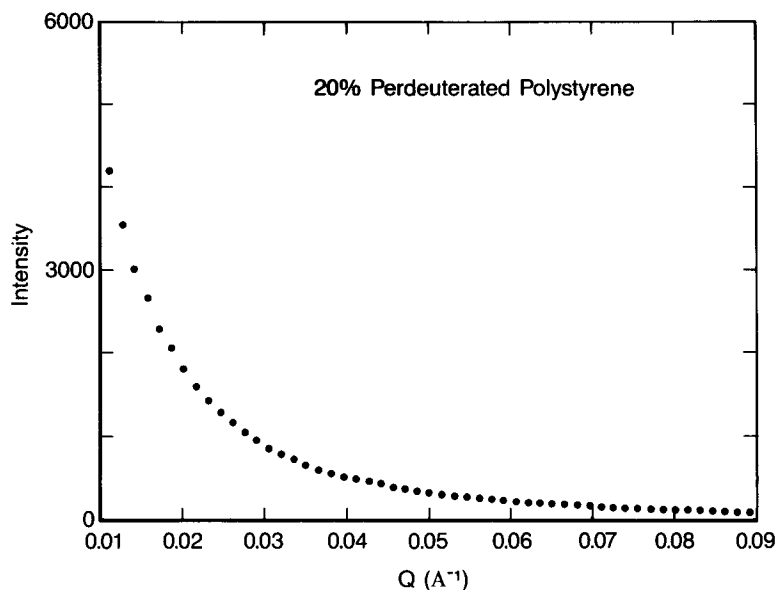


Figure 1. SANS scattered intensity (arbitrary units) from unstretched partially deuterated polystyrene after incoherent and beam-open background corrections.

axis, respectively. Best fits gave an eccentricity ϵ and an orientation angle ϕ in each case.

In order to extract partial radii of gyration, anisotropic SANS data were grouped into sectors both parallel and perpendicular to the symmetry axis to yield intensities $S(Q_{||})$ and $S(Q_x)$. A further elliptical binning of the data within each sector (the $\epsilon(Q^*)$ dependence obtained above is used explicitly

here) was performed to help keep the extracted radii of gyration independent of sector size. The sector-binned data (30° sectors) were then fitted to a Debye function (Gaussian coil model):

$$S(Q_{||,x}) = 2 [\exp(-Q_{||,x}^2 R_{g||,x}^2) + Q_{||,x}^2 R_{g||,x}^2 - 1] / Q_{||,x}^4 R_{g||,x}^4$$

Table II. Hot-Stretch Conditions and SANS Results of Polystyrene

Sample	EDR ^a	$\dot{\gamma}$ (cm/min)	Temp. (°C)	$R_{g }$	R_{gx}	MDR ^b		ϵ^c	
							x	a	b
PDPS	1.00	25.4	110	145	147	1.00	1.000		
PDPS1	1.50	25.4	110	202	117	1.39	0.801	0.486	2.92
PDPS2	2.00	25.4	110	248	110	1.71	0.684	0.299	3.89
PDPS3	3.00	25.4	110	325	85	2.24	0.582	0.137	5.13
PDPS4	4.00	25.4	110	367	81	2.53	0.555	0.095	5.12
PDPS5	2.00	12.7	110	260	103	1.79	0.705	0.275	4.63
PDPS6	2.00	2.54	110	248	105	1.71	0.719	0.291	5.38
PDPS7	2.00	1.27	110	234	105	1.61	0.719	0.327	5.15
PDPS8	2.00	25.4	115	255	109	1.76	9.746	0.289	5.46
PDPS9	2.00	25.4	120	232	108	1.60	0.740	0.350	4.90
PDPS10	2.00	25.4	125	234	105	1.61	0.774	0.406	4.85
PDPS8A	2.00	25.4	115	243	102	1.68	0.700		
PDPS8B	2.00	25.4	115	253	100	1.74	0.685		
PDPS8C	2.00	25.4	115	255	109	1.76	0.746		

^a EDR is the ratio of the length of the sample after hot stretching to that before stretching.

^b MDR is R_g (stretched)/ R_g (unstretched).

^c $\epsilon = a + bQ^*$.

from which radii of gyration (z-average) were extracted and reported in Table II. If chain deformation is affine, then the radii of gyration of the two principal axes should be related to the radius of gyration of the undeformed chain (R_{g0}), i.e.,

$$R_{g\parallel} = \lambda R_{g0}$$

and

$$R_{gx} = R_{g0}/\lambda^{1/2}$$

where λ is the extension ratio. Since our main interest is in the anisotropy of the radii of gyration rather than on their absolute values, no polydispersity corrections were performed.

RESULTS AND DISCUSSION

As a first test of the data, neutron transmission measurements of the hydrogenated PS samples and

deuterated blends were made and found to be within 5% of predicted transmissions value (Table I).

Table II summarizes the main results when PS is uniaxially hot-stretched over a wide range of extension ratios, shear rates, and temperatures. An unperturbed $R_{g0} = 146 \text{ \AA}$ (EDR = 1) was within 2% of the value 148 \AA obtained¹² from $R_g = 0.275 (M_w)^{1/2}$. Principal radii of gyration, measured in the direction of hot stretching ($R_{g\parallel}$) and transverse to the deformation direction (R_{gx}), are listed in columns 5 and 6, respectively. Results clearly show that the degree of molecular orientation is significantly influenced by deformation imposed on the macroscopic scale.

In Figure 2 the molecular draw ratio (MDR $= R_{g(\text{stretched})}/R_{g(\text{unstretched})}$) is plotted against the external draw ratio (EDR) of hot-stretched PS at 110°C . The data indicate that with increasing macroscopic deformation, the degree of molecular ori-

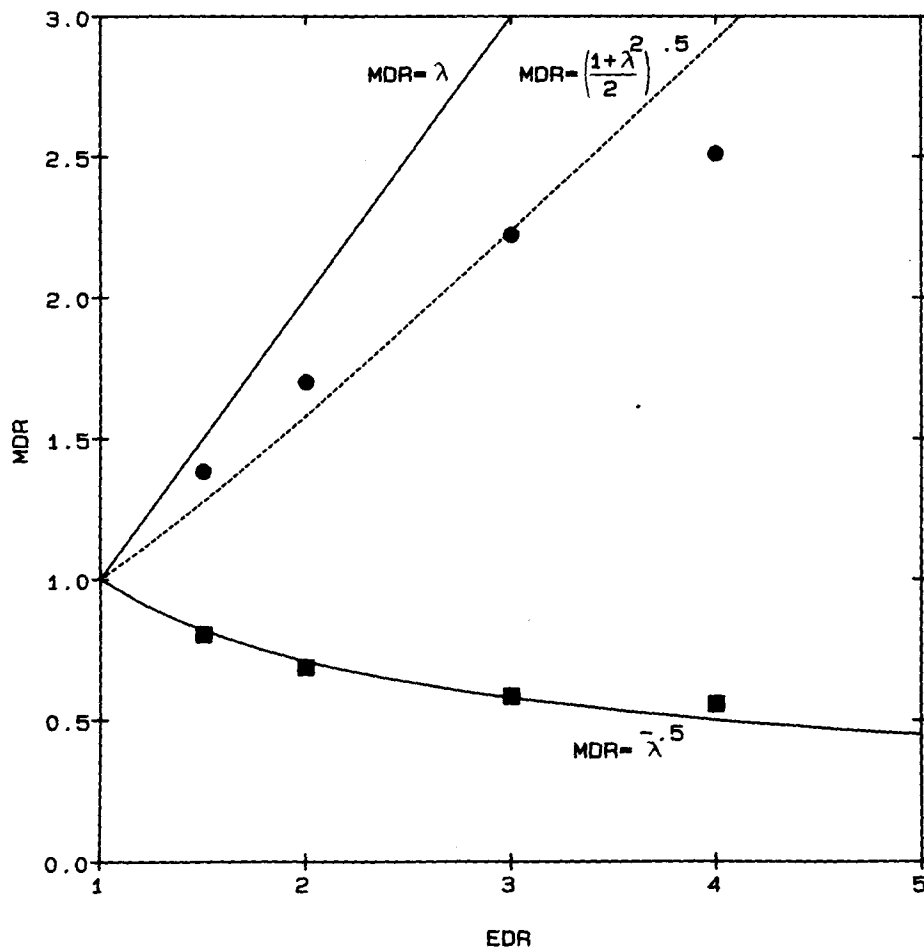


Figure 2. Plot of longitudinal and transverse molecular draw ratio as functions of sample elongation. See text for explanation of the theoretical curves.

orientation in the longitudinal direction ($MDR_{||}$) increases while the degree of alignment in the transverse direction (MDR_x) decreases. Deformation of PS chains transverse to the direction of macroscopic orientation is found to be in close agreement with the predicted behavior of $R_g = \lambda^{-1/2}$ over the range of EDRs studied. However, molecular orientation parallel to the stretching direction is observed to increase as expected but not according to a uniformly affine transformation for which the line $MDR = \lambda$ holds. The experimental points also do not appear to follow the line corresponding to $MDR = [(1 + \lambda^2)/2]^{1/2}$, the dependence predicted for junction affine behavior.¹³ Thus, these results are in qualitative agreement with previous findings,² and suggests that none of the current models are capable of properly describing the effects of deformation on the molecular scale.

The effects of various deformation processes on the degree of local chain orientation were measured

and the results are summarized in columns 9 and 10 of Table II. The data have been analyzed by linear least-squares regression ($\epsilon = a + bQ^*$) and indicate that the ellipticity ϵ depends upon the characteristic length scale of measure and the conditions of deformation. Figure 3 is a plot of eccentricity against Q^* for samples deformed to different extension ratios. Results shows a linear dependence over most of the specified momentum transfer range for all samples examined. This Q dependence implies a dependence in configuration space which means that localized chain relaxation of different characteristic lengths is occurring during deformation, even at high strain rates. This dependence tends to become independent of hot-stretching conditions at high Q where small chain portions (smaller than R_g) are being probed. The data show (Table II) that the average degree of eccentricity decreases with increasing EDR, with increasing strain rate, and with decreasing temperature.

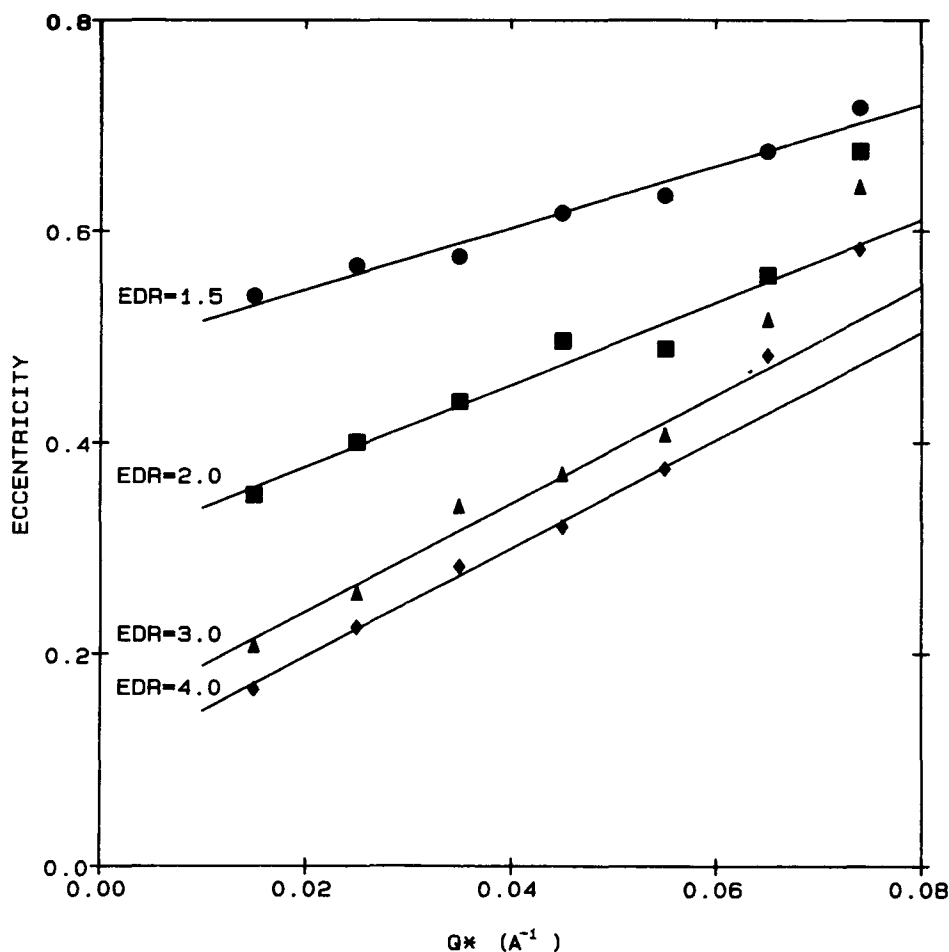


Figure 3. Linear least-squares fit of eccentricity versus Q^* for samples deformed to different external draw ratios.

Our polystyrene samples were hot-stretched according to well-controlled conditions, then rapidly quenched with cold water to minimize sample relaxation. The slight increase of $\epsilon(Q)$ in reciprocal space or slight decrease in direct space implies that small chain portions relax faster (within the time of quench) than the whole molecule. Results indicate that higher hot-stretching temperatures are equivalent to lower strain rates ($\dot{\gamma}$), that is, longer times for molecular relaxation during the stretching process. This effect is reminiscent of the Williams-Landel-Ferry time-temperature superposition principle, which involves the molecular relaxation in the rubbery region following a step stress (relaxation time is measured at fixed stress).¹⁴ However, single eccentricity master curves for both temperature and shear rate were found to yield shift factors that are in poor agreement with what would be predicted. This lack of agreement may be due to such factors as the molecular weight distribution, sample preparation, etc. One possible improvement would be to monitor the chain relaxation behavior of hot-stretched PS which had experienced a fixed stress relaxation period before quenching.

Finally, measurements taken at three spots on the polystyrene sample DHPS8 show that the molecular draw ratio does not change substantially (see Table II) along the hot-stretched bar.

This work has been funded by a grant from the Dow Chemical Company Corporate Research Program. Help by Dr. M. Malanga and R. Peters is greatly appreciated.

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Received December 15, 1989

Accepted April 22, 1991