

Macromolecular orientation in hot stretched and injection moulded polystyrene

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(Received 16 July 1985)

Small-angle neutron scattering (SANS) and optical birefringence measurements were used to investigate a wide range of macromolecular orientation in hot stretched and injection moulded polystyrene samples. These two techniques show similar trends even though each is sensitive to different forms of macromolecular orientation. The hot stretched samples are found to deform nonaffinely in relation to the external drawing (for draw ratios higher than 3). The cold condition injection moulded samples showed more orientation than the hot condition injection moulded samples, which were not birefringent even though they did have a residual orientation as seen by SANS. SANS is evidently sensitive to factors controlling orientation at extremes for which birefringence is not.

(Keywords: small-angle neutron scattering; macromolecular orientation; optical birefringence)

INTRODUCTION

A detailed understanding of macromolecular orientation in polymeric substances is valuable since this microscopic structural property affects some mechanical properties (anisotropic mechanical behaviour). This paper concerns the macromolecular orientation of polymer chains in hot stretched and in injection moulded polystyrene plastic samples. Among the possible techniques to measure polymer orientation in the bulk, we have chosen to use small-angle neutron scattering (SANS) on partially deuterated samples and optical birefringence on the same samples. Results from these two methods are analysed and compared.

Studies on macromolecular orientations associated with uniaxially stressed and solid state extruded plastic samples have been reported in the literature¹⁻⁷. In both cases, the goal was to find out whether the polymer chains follow affinely the external deformation imposed by the experimental conditions. It has been demonstrated¹ that chains deform affinely when their lengths are not too short and are given insufficient time to relax. Whether this affine property is followed or not also depends on the experimental conditions such as the stretching rate and temperature, and the rate of cooling of the sample. In the experiments reported here, polystyrene samples were hot stretched under very narrow conditions. In order to extract the radii of gyration both parallel and perpendicular to the stretch axis, we fit the elliptically averaged^{8,9} SANS data to a Debye function with a modified argument. This procedure assumes that chain portions deform uniformly. Another more familiar approach¹⁻⁷ was also used in which an estimate of the

molecular draw ratio (*MDR*) is made from the eccentricity of the iso-intensity contour plots provided that the chain volume is assumed constant during deformation. With our experimental conditions, it was found that the molecular draw ratio is a nonlinear function of the external draw ratio (*EDR*), i.e. chains do not deform affinely to the external stretching for draw ratios higher than 3. Birefringence data are also taken on the same samples and are found to reproduce similar trends to the SANS data.

Injection moulding is the most widely used method for the processing of polymer articles¹⁰. It is characterized by high repetition rates and high precision of the fabricated shapes. During the injection, packing and cooling stages of the moulding, flow and thermal stresses develop resulting in preferential orientation of the polymer chains. Our goal here is to quantify this macromolecular orientation at different spots in differently shaped samples and at different layers inside the sample. Here also, SANS (elliptical averaging of the data) and birefringence techniques are used.

HOT STRETCHED POLYSTYRENE

Experiments

Deuterated atactic polystyrene of $M_w = 338\,000$, $M_n = 239\,000$ has been synthesized and characterized by g.p.c. Deuteration is needed to enhance the SANS coherent scattered signal. A 5% fraction by weight was mixed to normal polystyrene of approximately the same molecular weight. The mixture was also characterized by g.p.c. and showed $M_w = 301\,000$ and $M_n = 130\,000$. This small deuterated fraction has negligible effect on the birefringence measurements whereas it creates a high contrast in SANS measurements. The partially deuterated

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mixture was then compression moulded into bars which were hot stretched in an Instron machine for stretching ratios from 1 to 4 under conditions listed in Table 1. Sample thicknesses were around 2 mm. Birefringence data were taken on these samples. Small-angle neutron scattering (SANS) measurements were performed at the University of Missouri Research Reactor (MURR). The SANS data were taken with the following instrumental configuration⁸: source and sample apertures were of diameters 2 cm and 1 cm respectively, placed 450 cm apart, with a sample-to-detector distance of 450 cm, and a wavelength of 4.75 Å, giving a measured scattering number range of 0.007 < Q < 0.09 Å⁻¹ and a resolution ΔQ ≈ 0.005 Å⁻¹. A beam open background has been subtracted from each (5 hour) run.

Data analysis

A method based on fitting all the two-dimensional SANS data over all of the available Q range was used. For the sake of comparison, a more common path¹⁻⁷ used to analyse azimuthally asymmetric SANS data was also followed.

The first method is based on a simple model (see Appendix) which assumes that polymer chains are Gaussian and deform uniformly in both the parallel and perpendicular directions to the stretch axis¹². The main assumption in this model is that the deformation parameters ε_{||} and ε_⊥ do not depend on the length of the chain portion that is considered, i.e., they do not depend on i and j in the following expressions:

$$\langle r_{ij}^2_{||} \rangle = \epsilon_{||}^2 \langle r_{ij}^2 \rangle \quad ; \quad \langle r_{ij}^2_{\perp} \rangle = \epsilon_{\perp}^2 \langle r_{ij}^2 \rangle$$

where r_{ij} is a vector joining monomers i and j belonging to the same chain and the brackets <...> denote an ensemble average over chain configuration. The subscript symbols || and ⊥ define directions parallel and perpendicular to the stretch direction.

Our data analysis proceeds as follows: First we average the two-dimensional SANS data elliptically (ellipses taken in the Q range 0.02 Å⁻¹ ≤ Q ≤ 0.03 Å⁻¹), by a least squares refinement, to extract an eccentricity ε and an orientation angle relative to the deformation direction. We obtain the dependence of the intensity I(Q*R_g^{*}) on Q* where we define a modified scattering number Q* = √(Q_{||}² + Q_⊥²ε²) and a modified radius of gyration R_g^{*} = √3R_{g||}. Here also the symbols || and ⊥ have the same meaning. We then fit

Table 1 Hot stretched conditions

Sample	Load (lbs)	Stretch rate (inch/min)	EDR ^a	Temperature ^b (°C)
CDS1	12.8	10	2.0	110
CDS2	15.1	10	1.5	110
CDS3	11.0	10	2.75	110
CDS4	10.0	5	4.0	110
CDS5		10	1.75	110

^aThe external draw ratio (EDR) is defined as the length of the sample after the stretch relative to its length before the stretch

^bUpon reaching the desired extension, the samples were quenched in water at 23°C

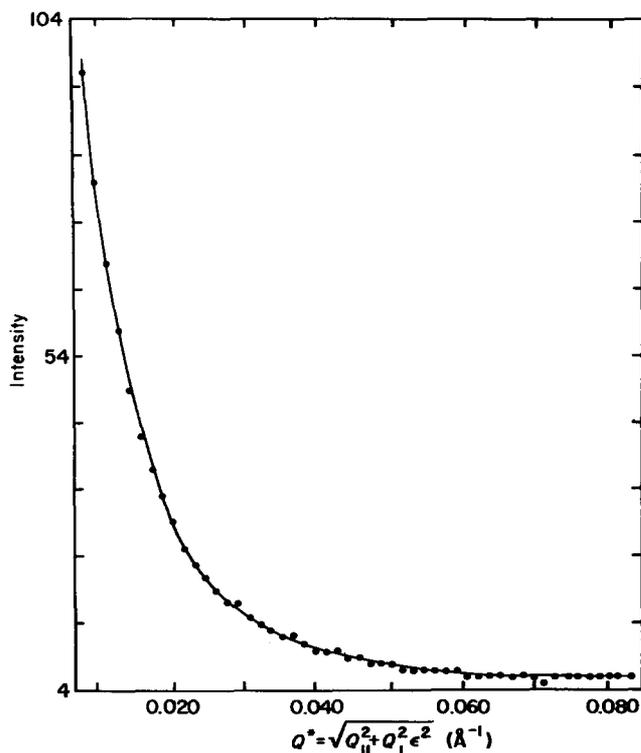


Figure 1 SANS intensity (arbitrary units) I(Q*R_g^{*}) vs. Q* = √(Q_{||}² + Q_⊥²ε²) for the hot stretched sample CDS2 (points) fitted to a Debye function (solid curve)

this curve to a Debye form plus a constant (incoherent) background (Figure 1 is an example).

$$I(Q^*R_g^*) = A + B[\exp(-Q^{*2}R_g^{*2}) - 1 + Q^{*2}R_g^{*2}]/Q^{*4}R_g^{*4}$$

The extracted values for R_g^{*} = √3R_{g||} and √3R_{g_x = √3R_{g||}ε (reported in columns 4 and 5 of Table 2) are apparent radii of gyration (they have not been corrected for the 5% concentration, for polydispersity or for the fact that deuterated and normal polystyrene chains do not have exactly the same lengths) in the directions parallel and perpendicular (R_{g_x} = R_{g⊥}/√2) to the stretch axis. The overall radius of gyration}

$$R_g = \sqrt{R_{g||}^2 + R_{g\perp}^2} = \sqrt{\epsilon_{||}^2 R_g^2 + \epsilon_{\perp}^2 R_g^2} = R_g^* \sqrt{1 + 2\epsilon^2} / \sqrt{3}$$

is reported in column 6 of Table 2.

The second method that we used to fit SANS data is a familiar one based on the assumption that intramolecular deformations conserve the chain volume, i.e. √3R_{g||} = (MDR)R_{g0} and √3R_{g_x} = R_{g0}/√(MDR). In this notation it is assumed that the parallel direction is along a z axis and the perpendicular direction in the (x-y) plane. Also, R_{g0} is the unperturbed radius of gyration, MDR is the molecular draw ratio, and the factor √3 has been introduced for normalization convenience. In this method, SANS two-dimensional data are also averaged elliptically to extract an eccentricity ε and an orientation angle relative to the deformation direction. Consequently, values for MDR (=ε^{-2/3}) as well as √3R_{g||} = (MDR)R_{g0} and √3R_{g_x} = R_{g0}/√(MDR) were obtained and reported in columns 7, 8 and 9 of Table 2. An overall radius of gyration R_g = √(R_{g||}² + R_{g⊥}²) is also reported in column 10 and seen to

Table 2 SANS (columns 3–10) and birefringence (column 11) results for the hot stretched polystyrene samples

Sample	EDR	ϵ	SANS-method 1			SANS-method 2				Birefringence $\times 10^3$
			$\sqrt{3}R_{g_{ }}$ (Å)	$\sqrt{3}R_{g_x}$ (Å)	R_g (Å)	MDR	$\sqrt{3}R_{g_{ }}$ (Å)	$\sqrt{3}R_{g_x}$ (Å)	R_g (Å)	
CDS1	2	0.45	249	112	170	1.73	247	108	168	5.74
CDS2	1.5	0.75	170	127	143	1.21	176	132	148	1.78
CDS3	2.75	0.33	293	97	187	2.05	293	100	188	6.83
CDS4	4	0.30	330	99	207	2.33	332	93	206	10.02
CDS5	1.75	0.54	214	116	155	1.54	220	116	158	4.21

agree well with the one in column 6. An unstretched value (143 Å) for R_g has been used for R_{g_0} of the sake of comparison with the first method (which does not require an unstretched radius of gyration). Birefringence data (in column 11 of Table 2) are seen to agree qualitatively with the SANS data.

A plot of the external draw ratio (EDR) vs. the extracted (MDR) in Figure 1, shows a nonlinear behaviour (above EDR = 3) which means that chains do not follow affinely to the external drawing. This might be expected for hot stretched samples for which the molecular chains have time (and space) to rearrange their conformations by disentanglement and slippage past each other to lesser constrained states before being cooled down to the water bath temperature.

INJECTION MOULDED POLYSTYRENE

A series of the same partially deuterated (5%) atactic polystyrene samples were injection moulded in the cold (notation 4C) and hot (notation 5H) forms. Small disks (samples 4CD and 5HD) of 5 cm diameter and bars (samples 4CB and 5HB) 16 cm long and 1.5 cm wide were moulded; all samples had 3 mm thickness. Table 3 shows the injection moulding conditions.

Birefringence measurements were performed at the Dow Chemical Research Center at different spots (1, 2, 3, 4, 5 and 6) on the disks and bars as shown in Figure 3. Birefringence numbers reported in Table 4 have been averaged over sample thickness.

SANS data (Table 5) were taken (at MURR) at different spots (A, B, C, D and Z) on the same samples. Here also 1 cm spot sizes were chosen. Because these samples showed little orientation they were run for 10 h to obtain reliable statistics. A beam open background has also been subtracted from each run. The same program was then used to fit the two-dimensional data to confocal ellipses and extract eccentricities and orientation angles. In order to observe surface and core orientations and increase sample transmission, the original samples were thinned by machining. Either one surface was milled (from 3 mm down to 1.5 mm on one side as in spots A, B, C, D) so that a surface layer was left intact, or a core layer was obtained by milling (from 3 mm down to 1.5 mm as in spot Z) both of the surface layers. Values corresponding to spots 1 and A, 2 and B, 3 and C, and 4 and D can be compared to see that birefringence and SANS data follow the same trends, especially for disk 4CD.

A comparison of the data at the different spots shows that a number of obvious conclusions can be drawn: there is more macromolecular orientation close to the injection gate than away from it, close to the surface than deep inside the sample (compare spots A, B, C, D, to spot Z) and

Table 3 Injection moulding conditions

Cold conditions	
Melt temperature	167°C
Pressure	3700 psi
Injection time	8 s
Cool time	30 s
Band temperature	176°C
Mould temperature	24°C
Hot conditions	
Melt temperature	229°C
Pressure	2500 psi
Injection time	8 s
Cool time	30 s
Band temperature	246°C
Mould temperature	65°C

Table 4 Birefringence results for the injection moulded samples averaged over the sample thickness

Spot	1	2	3	4	5	6
Birefringence $\times 10^3$ for Disk 4CD	1.387	0.843	0.642	0.886	–	–
Birefringence $\times 10^3$ for Bar 4CB	0.750	0.595	0.755	0.869	0.881	0.800

Table 5 SANS data for the injection moulded samples

Disk 4CD	Eccentricity, angle ^a	Bar 4CB	Eccentricity, angle ^a
Spot A	0.63, 5°	Spot A	0.60, 2°
Spot B	0.77, 9°	Spot B	0.76, 6°
Spot C	0.87, 24°	Spot C	0.78, 2°
Spot D	0.79, 38°	Spot Z	0.87, 1°
Spot Z	0.92, 40°		
Disk 5HD	Eccentricity, angle ^a	Bar 5HB	Eccentricity, angle ^a
Spot A	0.89, 8°	Spot A	0.88, 8°
Spot B	0.90, 5°	Spot B	0.87, 4°

^a Higher eccentricity numbers correspond to SANS iso-intensity elliptical contours that are closer to circular and therefore to less orientation. The stated angle (in the scattering plane) corresponds to the mean orientation angle of the polymer chains relative to the direction of injection

in open parts of the sample than in corners. Also, cold injection moulding produces more orientation than hot injection moulding.

Each one of these two diagnostic techniques has both advantages and drawbacks. The main advantage of

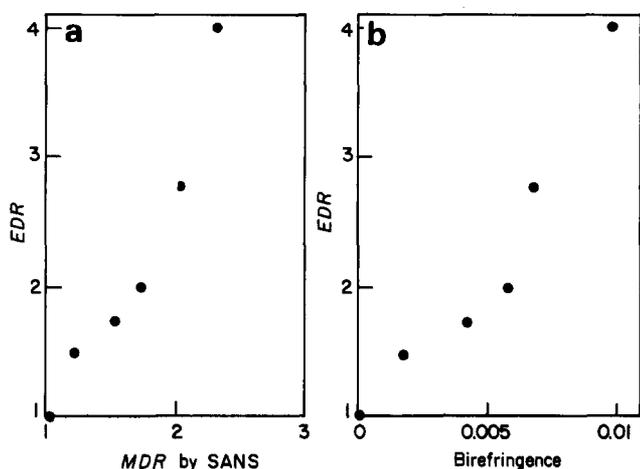


Figure 2 Non-linear variation (a) of the external draw ratio (*EDR*) with the molecular draw ratio (*MDR*) extracted from SANS measurements and (b) of the *EDR* with the birefringence data for a set of five hot stretched samples and one compression moulded sample (*EDR*=1)

birefringence is that it can be used on thick samples (provided that they are optically transparent) at small spots. SANS, on the other hand, can be used on optically opaque samples and seems to be more sensitive to low levels of orientation. For instance, SANS shows macromolecular orientation for the hot injection moulded samples whereas these do not present measurable birefringence. To give confidence that the macromolecular orientation obtained for the hot injection moulded samples is real and not an artifact due to beam crossfire, misalignment, or to the finite size of the rectangular detector cells, analysis of data scattered from glassy carbon (a strong azimuthally symmetric isotropic scatterer) gave eccentricities higher than 0.95. A compression moulded sample also gave an eccentricity of 0.95.

As an oversimplified picture, we can say that birefringence observes orientation of chain portions belonging to different chains whereas the orientation extracted from SANS measurements is purely a single chain property, i.e. the orientation of one chain within a uniform background. The fact that spot B on samples 4CB and 5HB shows similar eccentricities may suggest that this low residual orientation is independent of the rate of quench of the sample.

CONCLUSIONS

Macromolecular orientation has been investigated in hot stretched and injection moulded polystyrene samples by SANS and birefringence.

Given the preparation conditions for our hot stretched samples, we found that polymer chains in these samples did not deform affinely to the external drawing for draw ratios higher than 3. As noted in Table 1, sample CDS4 (*EDR*=4) had a lower stretch rate and therefore showed a highly non-affine behaviour. SANS and birefringence data agreed qualitatively.

These two diagnostic techniques have also been applied to injection moulded samples and shown to agree except for those which were hot injection moulded; these showed a residual orientation by SANS whereas they did not present detectable birefringence. This may be due to the fact that the two techniques are sensitive to different forms

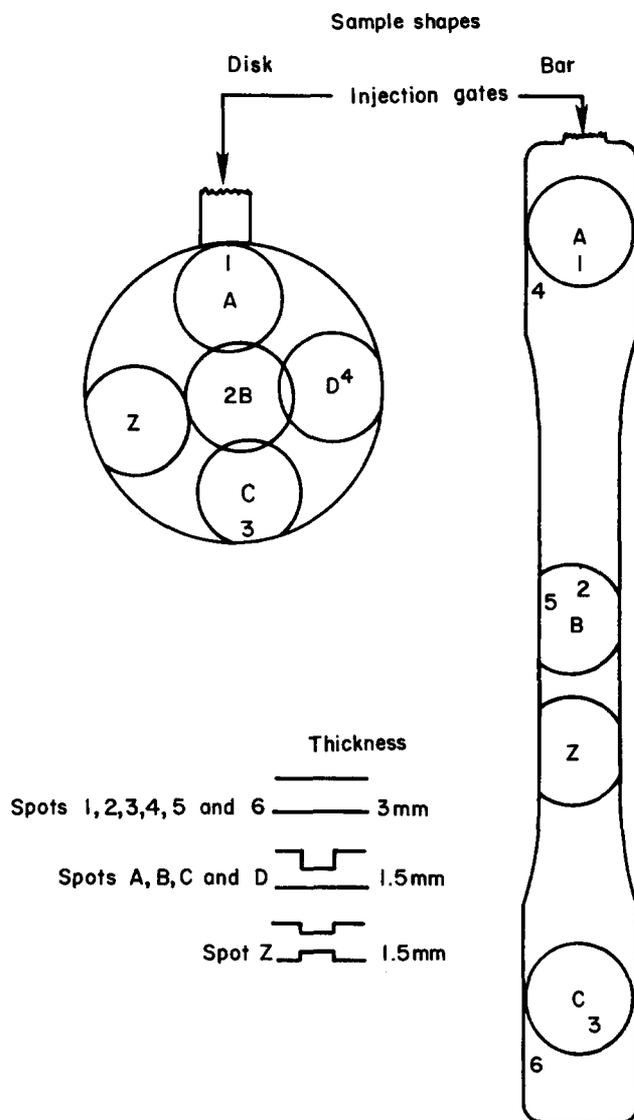


Figure 3 Injection moulded samples. Birefringence measurements were taken at spots 1, 2, 3, 4, 5 and 6 while SANS data were taken at A, B, C, D and Z

of chain orientation. Birefringence detects an orientation of chain portions averaged over all adjacent chain portions, whereas SANS (supplemented by the partial deuteration technique) can 'see' the overall orientation of a chain. Further investigations, varying the moulding conditions or using other polymer chains which are stiffer, may be worth pursuing and may yield a better understanding of the relationship between chain structure (and conformation) and polymeric systems material properties.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Dr Mike Malanga in the polymerization and characterization of our polystyrene samples, Mr Chris Weber in the injection moulding of the samples, and Mr Steve Nolan in taking the birefringence data. This research was supported by a grant from The Dow Chemical Company.

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average (in the case of deformed chains) is being approximated by the usual Gaussian average. It is assumed that the chain portions deform uniformly:

$$\langle r_{ij\parallel}^2 \rangle = \varepsilon_{\parallel}^2 \langle r_{ij}^2 \rangle \quad \text{and} \quad \langle r_{ij\perp}^2 \rangle = \varepsilon_{\perp}^2 \langle r_{ij}^2 \rangle$$

i.e. that ε_{\parallel} and ε_{\perp} are independent of i and j . Moreover, $R_{g\parallel} = \varepsilon_{\parallel} R_g$ and $R_{g\perp} = \varepsilon_{\perp} R_g$ with $\varepsilon_{\parallel}^2 + \varepsilon_{\perp}^2 = 1$. The isotropic case is recovered if $\varepsilon_{\parallel} = \varepsilon_{\perp} / \sqrt{2} = 1/\sqrt{3}$. The ensemble averages in the parallel and perpendicular directions can be performed separately to yield:

$$S(Q) = \sum_{i,j}^N \exp \left[-Q_{\parallel}^2 \varepsilon_{\parallel}^2 \left\langle \frac{r_{ij}^2}{2} \right\rangle \right] \exp \left[-Q_{\perp}^2 \varepsilon_{\perp}^2 \left\langle \frac{r_{ij}^2}{2} \right\rangle \right]$$

If the chain portions are assumed to be ideal ($\langle r_{ij}^2 \rangle = b^2|i-j|$), conventional manipulations can be used to obtain the familiar Debye function,

$$S(X) = \frac{2}{X^2} [\exp[-X] - 1 + X]$$

with an argument:

$$X = Q^{*2} R_g^{*2}$$

where Q^* and R_g^* are defined, viz.

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

$$R_g^* = \sqrt{3} \varepsilon_1 R_g$$

and introduced $\varepsilon = \varepsilon_x / \varepsilon_{\parallel} = \varepsilon_{\perp} / (\sqrt{2} \varepsilon_{\parallel})$ as the eccentricity of the elliptically averaged data. A least squares refinement of the intensity $I(Q^* R_g^*)$ vs. Q^* data to a Debye function with three adjustable parameters (two of them being a baseline and an intercept) gives a value for R_g^* which yields an apparent (not concentration of polydispersity corrected) radius of gyration $R_g = R_g^* \sqrt{1 + 2\varepsilon^2} / \sqrt{3}$.

APPENDIX

Elliptical averaging of scattering data from deformed Gaussian polymer coils

In this Appendix, the structure factor for a deformed Gaussian coil representing polymer chains in the bulk is derived. Consider a polymer chain oriented along the z direction (parallel to the scattering plane) of a Cartesian system. The scattered intensity is proportional to the static form factor:

$$S(Q) = \sum_{i,j}^N \langle \exp[iQ \cdot r_{ij}] \rangle$$

where r_{ij} is the vector joining two monomeric units i and j , N is the degree of polymerization and the bracket $\langle \dots \rangle$ represents an ensemble average over the equilibrium distribution which, in this case, is assumed to be the product of two Gaussians in the directions parallel and perpendicular to z with variances $\langle r_{ij\parallel}^2 \rangle$ and $\langle r_{ij\perp}^2 \rangle = \langle r_{ij}^2 \rangle = \langle r_{ij\perp}^2 \rangle / 2$. Note that a non-equilibrium