

Macromolecular orientation associated with shear bands in compressed polystyrene

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Small-angle neutron scattering (SANS) has been used to investigate macromolecular orientation associated with shear bands in compression-loaded partially deuterated polystyrene samples with single edge notches. Macromolecular orientation (within the shear band) and radii of gyration (along and perpendicular to these chain orientation directions) have been obtained. The variation of these extracted quantities has been investigated for a range of compression temperatures (293 K–363 K), strain values (7.5% and 12.5%) and strain rates ($5 \times 10^{-3} \text{ s}^{-1}$ and $5 \times 10^{-4} \text{ s}^{-1}$). The results indicate that glide mode is the predominant deformation mechanism in shear bands within the scope of the experiments.

(Keywords: shear band; small-angle neutron scattering)

Introduction

Small-angle neutron scattering (SANS) is well suited to the investigation of macromolecular orientation in hot-stretched^{1,2}, extruded³, and compressed^{4,5} partially deuterated polystyrene. For hot-stretched polystyrene, it was concluded that the molecular draw ratio follows the external draw ratio affinely (for high molecular weight polymer chains) up to moderately high extensions, beyond which their relation becomes nonlinear due to plastic deformations (mainly chain slippage).

Macromolecular orientation has also been investigated around shear bands in polystyrene by Lefebvre *et al.*^{4,5} The scope of the experiments reported here differs from these experiments^{4,5} in a few ways: (1) for Lefebvre *et al.*, the neutron scattering beam was perpendicular to the plane of propagation of the shear band whereas we chose another sample configuration whereby the neutron beam propagates along the plane of the shear band; (2) their higher compression temperature was not far from room temperature whereas this temperature was our lower choice; (3) our strains and strain rates were substantially higher than their values. To generate shear bands, Lefebvre *et al.* compressed (axially) notched cylindrical samples of partially deuterated polystyrene and then cut out thin (2 mm thickness) disks along the shear band propagation plane that they used for SANS measurements. They reported observing two main regimes corresponding to either an anisotropic glide within a coarse shear band (at lower temperatures) or to a diffusion-like homogeneous deformation (at higher temperatures). The range of our experimental parameters complements those reported by Lefebvre *et al.*^{4,5} in the sense that our compression temperatures, strains and strain rates are higher. For the experiments reported here, 2 mm thick samples that were single edge-notched were compression-loaded under different conditions. These samples were kept under compression during SANS data acquisition. This allows an observation of the shear bands in a plane perpendicular to their propagation plane.

Shear bands have been the subject of a large number of theoretical as well as experimental investigations. Their initiation is fairly well understood on a phenomenological

basis⁶ and is usually enhanced by the introduction of a small sharp notch. Their propagation has been thoroughly investigated by Kramer^{7,8}, among others. It is found that the shear-band packet propagates at a 38° angle to the compression axis and that there is formation of a diffuse shear zone, which propagates ahead of the band at about 45°. Optical birefringence has been the major tool for static (morphology) as well as dynamic (propagation) investigations of shear bands. However, a thorough microscopic (i.e. molecular) understanding of the way polymer chains yield locally under high external stresses has yet to be achieved.

Experimental

A thin (2 mm thickness) plaque of partially deuterated (5% by weight) polystyrene has been prepared by compression moulding. The molecular weight of the perdeuterated component has been determined (g.p.c.) as $M_w = 338\,000$ and $M_n = 239\,000$. The hydrogenated component has a close molecular weight but a high polydispersity yielding $M_w = 301\,000$ and $M_n = 130\,000$ for the mixture. Then a number of identical rectangular (4 cm × 2 cm) samples were cut out, sharply notched (notch was less than 1 mm deep), and compressed in the device shown in *Figure 1*. This compression device has thin aluminium windows, permitting 98% neutron transmission, and holes for the heating probes and controller thermocouples. Before and during the compression stage, each notched sample was kept at a constant temperature below the glass transition temperature. After compression, the strain was read off a graduation on the fixed part of the vice. Strain rates were not accurately monitored.

Three different displacement cases have been considered. Case 1 corresponds to a 'fast' strain rate (an approximate 3 mm displacement in 15 s) and a total strain of 7.5%. Case 2 corresponds to a 'slow' strain rate (an approximate 3 mm displacement in 2–3 min) and a total strain of 7.5%. Case 3 corresponds to a 'slow' strain rate as well (5 mm in 4–5 min) and a total strain of 12.5%. After the desired compression condition was reached, the

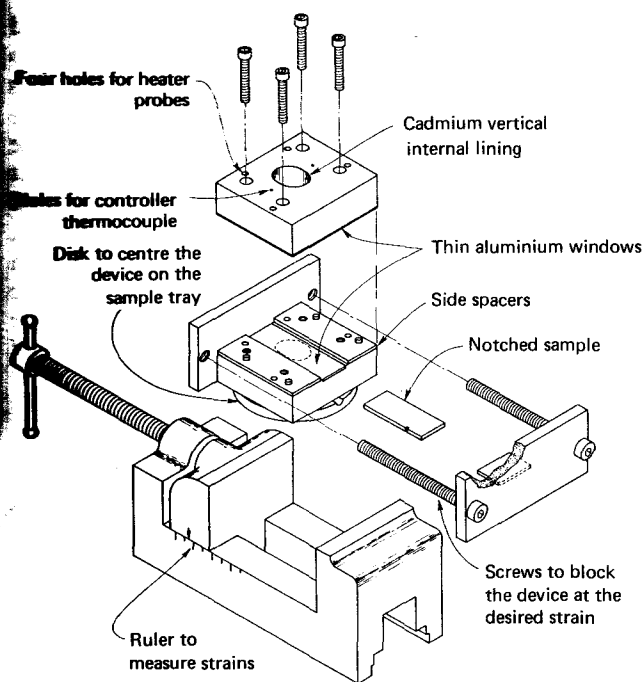


Figure 1 Compression device used to generate shear bands in partially deuterated polystyrene samples

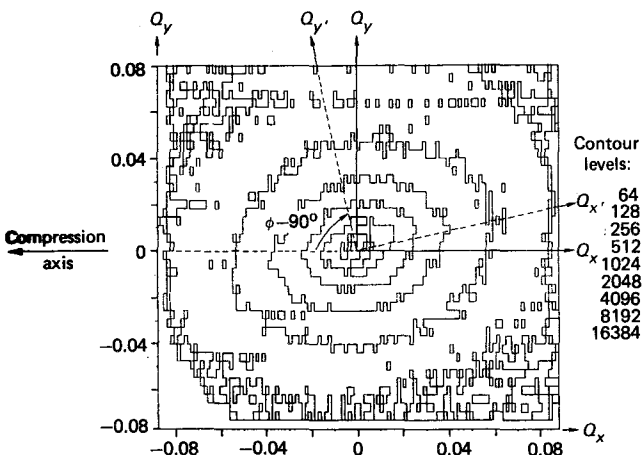


Figure 2 SANS isotensity contour plot for case 3 (strain of 12.5% and strain rate of $4.6 \times 10^{-4} \text{ s}^{-1}$) at 40°C

device was locked at this strain, cooled down to ambient temperature, and SANS data were taken.

The University of Missouri Research Reactor SANS instrument⁹ was used in the following configuration: neutron wavelength, 4.75 Å; sample to detector distance, 4.50 m; source and sample apertures, 2 cm and 1 cm (yielding good statistics for 8 h runs from which an empty compression device run (a background run with no sample in it) was subtracted). Reliable SANS data fall in the range $0.007 \text{ \AA}^{-1} < Q < 0.09 \text{ \AA}^{-1}$ with a resolution $\Delta Q \approx 0.005 \text{ \AA}^{-1}$.

SANS data were analysed in a way similar to that for the hot-stretched samples reported previously¹⁰, which consists of: (1) fitting the isotensity contours to confocal ellipses to extract an eccentricity ϵ and an orientation angle ϕ in each case; (2) elliptically averaging the raw data to obtain

$$I(Q^*R_g^*) = A + BS(Q^*R_g^*)$$

where a modified scattering wavenumber $Q^* = \sqrt{Q^2 + Q^2\epsilon^2}$ and radius of gyration $R_g^* = \sqrt{3}R_{g\parallel}$. The symbols \parallel and \perp represent the projections along (noted y' direction) and perpendicular (noted x' direction) to the direction of the orientation of the chains (defined by the angle ϕ in the scattering plane); (3) this intensity is then fitted to a Debye function for $S(Q^*R_g^*)$ and a constant (incoherent) background A , i.e.

$$S(Q^*R_g^*) = (2/X^2)[\exp(-X^2) - 1 + X]$$

with $X = Q^*R_g^*$. The extracted values for $R_g^* = \sqrt{3}R_g$ ($=\sqrt{3}R_{gy}$) and $\sqrt{3}R_{gx} = \sqrt{3}R_{g\parallel}\epsilon$ are apparent radii of gyration in the scattering plane. The factor $\sqrt{3}$ is introduced for normalization convenience. Corrections due to polydispersity or unmatched molecular weights have not been included. This method of using the full two-dimensional SANS data seems better suited than use of slices of the data parallel and perpendicular to the orientation direction.

Results and Discussion

Table 1 summarizes eccentricities ϵ and orientation angles ϕ corresponding to the different compression

Table 1 Macromolecular orientation of perdeuterated polystyrene chains in shear bands

Strain (%)	Strain rate (s ⁻¹)								
7.5	5×10^{-3}	Temperature (K)	363	353	343	333	323	313	293
		Eccentricity		0.90		0.90		0.90	
		Orientation angle (deg)		170		172		174	
		$\sqrt{3}R_{gy}$ (Å)		138		168		165	
		$\sqrt{3}R_{gx}$ (Å)		124		151		148	
		R_g (Å)		129		157		154	
7.5	5×10^{-4}	Eccentricity	0.82		0.84		0.82		0.82
		Orientation angle (deg)	169		168		168		174
		$\sqrt{3}R_{gy}$ (Å)	148		158		170		181
		$\sqrt{3}R_{gx}$ (Å)	131		133		139		148
		R_g (Å)	137		142		150		160
		12.5	4.6×10^{-4}	Eccentricity	0.74	0.72	0.74		0.73
Orientation angle (deg)	170			168	168		167	168	166
$\sqrt{3}R_{gy}$ (Å)	152			157	160		160	161	154
$\sqrt{3}R_{gx}$ (Å)	112			113	118		117	116	120
R_g (Å)	127			129	133		133	133	132

temperatures, strains, and strain rates considered. These were obtained by fitting SANS contour maps in the range $0.04 \text{ \AA}^{-1} < Q < 0.05 \text{ \AA}^{-1}$, but do not change much in other Q ranges in agreement with the observation of Lefebvre *et al.*⁴ Apparent radii of gyration $3R_{gy}$ and $3R_{gx}$ as well as the total $R_g = R_{gy} + 2R_{gx}$ have been included for each case. These correspond to the elongated, the lateral and the total statistical dimensions of labelled polystyrene chains in the shear band and are to be compared to a value around 154 \AA ($= 0.28 \sqrt{301000}$) for R_g before compression. Chain sizes in the transverse directions have been assumed to be of the same order (i.e. $R_{gx} \approx R_{gz}$). This may not be correct, but cannot be tested since the third direction is not directly accessible to SANS. The labelled chains are oriented at about 81° ($\phi - 90^\circ$) from the compression axis since the major axis of the contour plots are seen to be around $\phi = 171^\circ$ from the compression axis. The value of 81° is in agreement with the sum obtained from the typical shear-band packet propagation angle of 38° with respect to the compression axis and a molecular displacement of 45° within the shear band.

Close study of *Table 1* yields a few conclusions. Macromolecules participating in the shear band are oriented at about 81° from the compression axis regardless of compression conditions (temperature, strain and strain rate). Moreover, only glide modes of deformation of elongated molecular coils are observed in the shear band. This is at variance with the conclusion of Lefebvre *et al.*^{4,5} that at the compression temperatures considered here, diffusional modes should be the predominant deformation mechanism. However, it should be noted that the strain rates used cover only the higher part of the range used by Lefebvre *et al.*^{4,5} and the sample geometries are different. Our conclusion is also in conceptual agreement with that reached by Dettenmaier

*et al.*² from experiments performed on PMMA stretched at temperatures between 333 K and 373 K. *Table 1* also shows that the apparent total radius of gyration R_g (which is an indirect measure of the average volume of the labelled chains) is independent of temperature when the strain is not too high (7.5% case), which indicates that molecular deformations are highly non-affine, as expected in such plastic deformations. The components for R_g , however, do have a limited temperature dependence. In the higher strain (12.5%) case, nonlinear plastic deformations show saturation, causing both the components of R_g and R_g itself to become independent of temperature.

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References

- 1 Boue, F., Nierlich, M., Jannink, G. and Ball, R. *J. Physique* 1982, **43**, 137
- 2 Dettenmaier, M., Maconnachie, A., Higgins, J. S., Kausch, H. H. and Nguyen, T. Q. *Macromolecules* 1986, **19**, 733
- 3 Hadziioannou, G., Want, L. H., Stein, R. S. and Porter, R. *Macromolecules* 1982, **15**, 880
- 4 Lefebvre, J. M., Escaig, B. and Picot, C. *Polymer* 1982, **23**, 1751
- 5 Lefebvre, J. M., Escaig, B., Coulon, G. and Picot, C. *Polymer* 1985, **26**, 1807
- 6 Bowden, P. B. *Phil. Mag.* 1970, **22**, 455
- 7 Kramer, E. J. *J. Macromol. Sci.-Phys.* 1974, **B10**, 191
- 8 Kramer, E. J. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 509
- 9 Mildner, D. F. R., Berliner, R., Pringle, O. A. and King, J. S. *J. Appl. Cryst.* 1981, **14**, 380
- 10 Hammouda, B., Bubeck, R. A. and Mildner, D. F. R. *Polymer* 1986, **27**, 393