Small angle neutron scattering study of the structure of a triblock copolymer of styrene and isoprene during extension

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A triblock copolymer with a styrene weight fraction of 0.41, has been examined at various extension ratios using small angle neutron scattering. The original 'polycrystalline' material with a face centred cubic arrangement of styrene domains acquires orientation as the extension ratio increases. Affine deformation is not obeyed at the supramolecular level and there is some evidence for non-uniform stress at this level.

Keywords Block copolymer; extension; neutron scattering; styrene; isoprene

INTRODUCTION

The structure and properties of styrene–diene block copolymers have occupied the interest of theoreticians and experimentalists for some years. This interest has been engendered by the variation of morphology with copolymer composition which results from the microphase separation of the two chemical entities in the copolymer. The minor component of the copolymer forms domains with spherical, cylindrical or lamellar morphology, the shape being determined chiefly by the composition.

The structural organization of these materials has been studied by electron microscopy, small angle X-ray scattering and small angle neutron scattering (SANS)[1–5]. In the main, these techniques have been used to determine the long range packing of the domains and the domain size, in addition SANS has been used in an effort to obtain the molecular size of the block sequences in the domains. Some discussions of the long range structure of these copolymers has been couched in the terms of liquid like structure factors using Ornstein–Zernicke theory, however it is apparent that a much more accurate description can be obtained by discussing the structure in the terms of a crystal lattice. This approach gives results which are in broad agreement with statistical thermodynamic theories[6,7] and furthermore, models generated on this basis are able to reproduce the observed SANS scattering profiles to quite good agreement[5].

By contrast with the work on the equilibrium state of these copolymers, little has been reported on the influence of stress on the structure. Apart from discussions on 'single crystal'[8,9] forms there appears to be only a brief mention of some electron microscope observations by Aggarwal, whilst Inoue et al.[10] discuss the results of a small angle X-ray and light scattering study. It is apparent that an examination of the structural changes induced by stress will be of help in the interpretation of the unique mechanical properties of styrene–diene copolymers, e.g. strain softening and rehardening. Some results of an

investigation of the influence of uniaxial extension on a triblock styrene–isoprene copolymer, with isoprene as the centre block, are presented here using small angle neutron scattering to investigate structural changes.

EXPERIMENTAL

Copolymer preparation

The triblock copolymer, SIS2, was prepared by sequential anionic polymerization in benzene under high vacuum conditions using *n*-butyl-lithium as initiator. Molecular weights were determined by gel permeation chromatography whilst the composition was determined by u.v. spectrometric analysis of a chloroform solution. Results of this characterization are given in *Table 1*.

Stress–strain properties

A small sheet of SIS2 was prepared by casting from toluene solution, after removal of solvent under vacuum, a specimen was taken from this sheet the remainder being used for neutron scattering experiments. Stress–strain data at room temperature were obtained using a laboratory model Instron tester and an extension rate of 5 cm min^{-1}. The specimen of SIS2 was extended to an extension ratio (length/original length, L/L_0) of 4, this was followed by decrease in extension at the same rate to the original dimensions.

Small angle neutron scattering

SANS data at room temperature ($\sim 20°C$) were collected for differing extension ratios using the D17

Table 1 Characteristics of styrene–isoprene block copolymer SIS2

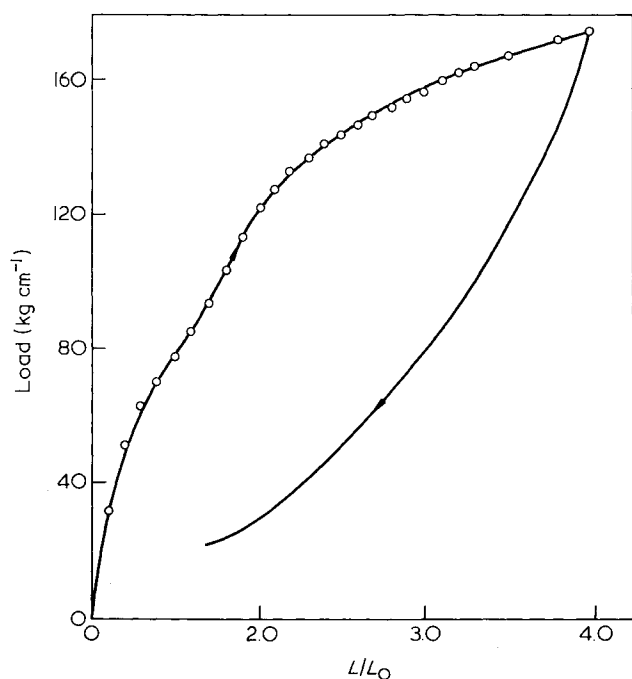| Weight fraction of styrene	0.41
$\bar{M}_w$ (g.p.c.)	97.27×10^3
$\bar{M}_n$ (g.p.c.)	90.65×10^3
Parent styrene block	
$\bar{M}_w$	22.49×10^3
$\bar{M}_n$	17.70×10^3

Figure 1 Load as a function of extension ratio for SIS2 with increasing and decreasing stress

diffractometer at the Institut Laue-Langevin, Grenoble, France. For this purpose the copolymer, in the form of a strip circa. $1.2 \times 3.0 \times 0.05$ cm^3, was mounted in a small stretching frame which allowed the application of uniaxial extension to the specimen. The incident neutron beam was shielded from all but the sample by using a large sheet of cadmium, thus preventing spurious neutron beam reflections from the frame. Scattered neutrons were detected by a two dimensional position sensitive detector which has been described in the literature[11], the range of scattering vector, $Q\left(\dfrac{4\pi}{\lambda}\sin\dfrac{\theta}{2}\right)$, was $0 \leqslant Q(\text{Å}^{-1}) \leqslant 7 \times 10^{-2}$ and the neutron wavelength 12 Å $\pm 10\%$.

RESULTS

The stress–strain curves for both increasing and decreasing uniaxial extension are shown in *Figure 1*. In view of the rapid extension rate, the considerable stress hysterisis observed is not surprising. However, this extension rate most closely approaches that used in the SANS measurements. The copolymer was stretched as rapidly as possible to the desired extension ratio and the scattered intensity measured for 20 min at each selected value of L/L_0. The distribution of scattered intensity on the detector is shown as a series of contour plots for each extension ratio in *Figures 2a–f*. The contour plot for the unstressed copolymer is perfectly circular, indicative of no preferred orientation in the sample. As L/L_0 increases, this circular pattern becomes ellipsoidal with the semi-minor axis parallel to the extension direction. With continued extension the major feature of the diffraction pattern is a series of distinct spots. Radial intensity distributions as a function of scattering vector Q were calculated with the aid of data analysis programmes available at ILL[12]. The data at each extension ratio were analysed in two ways. Firstly, the scattering in the meridional direction was analysed by using a rectangular area of the detector.

Secondly, the scattered intensity at an azimuthal angle of 70° was analysed by using sectors which enclosed these diffraction maxima. *Figure 3* shows schematically the areas used for constructing the radial distribution of intensity. These data were corrected for background
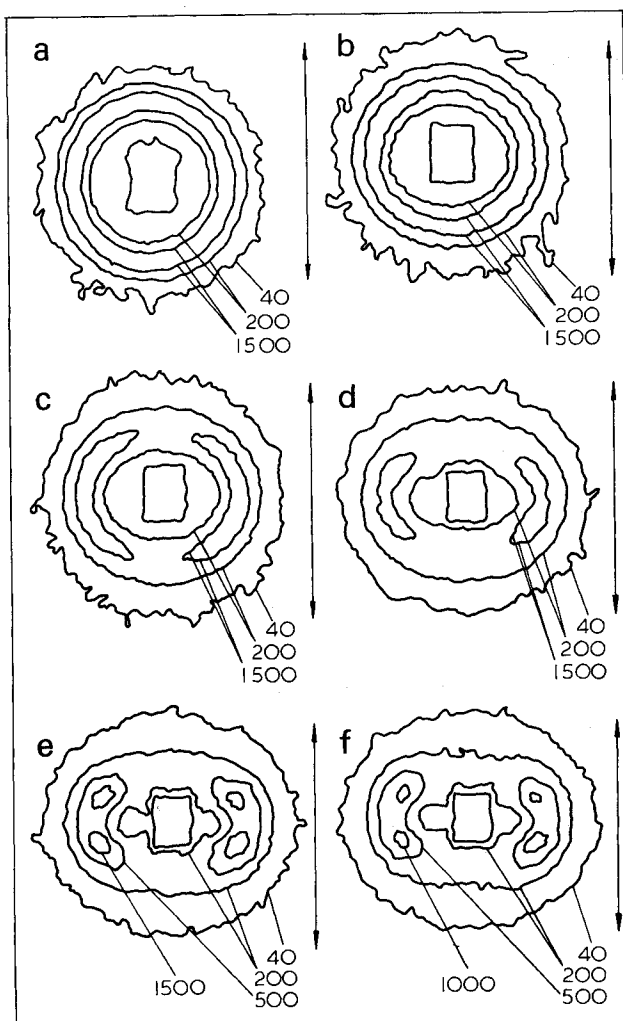

Figure 2 Contour plots of scattered neutron intensity for various extension ratios. (a) 1.0 (b) 1.1 (c) 1.2 (d) 1.5 (e) 2.0 (f) 3.0. Rectangular area is the outline of the beam stop. Neutron count as indicated, arrow indicates direction of stretch
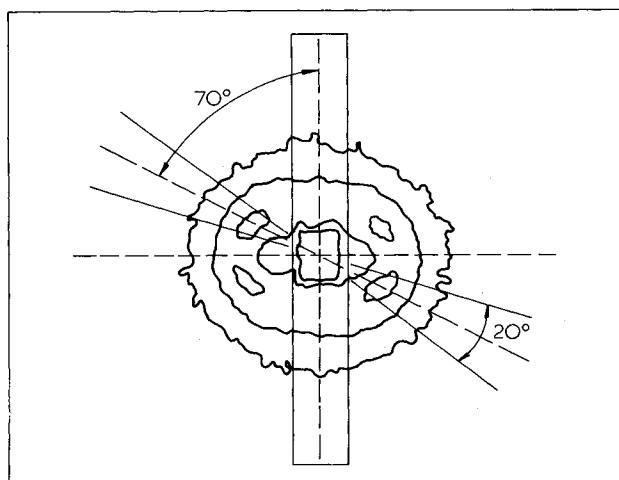

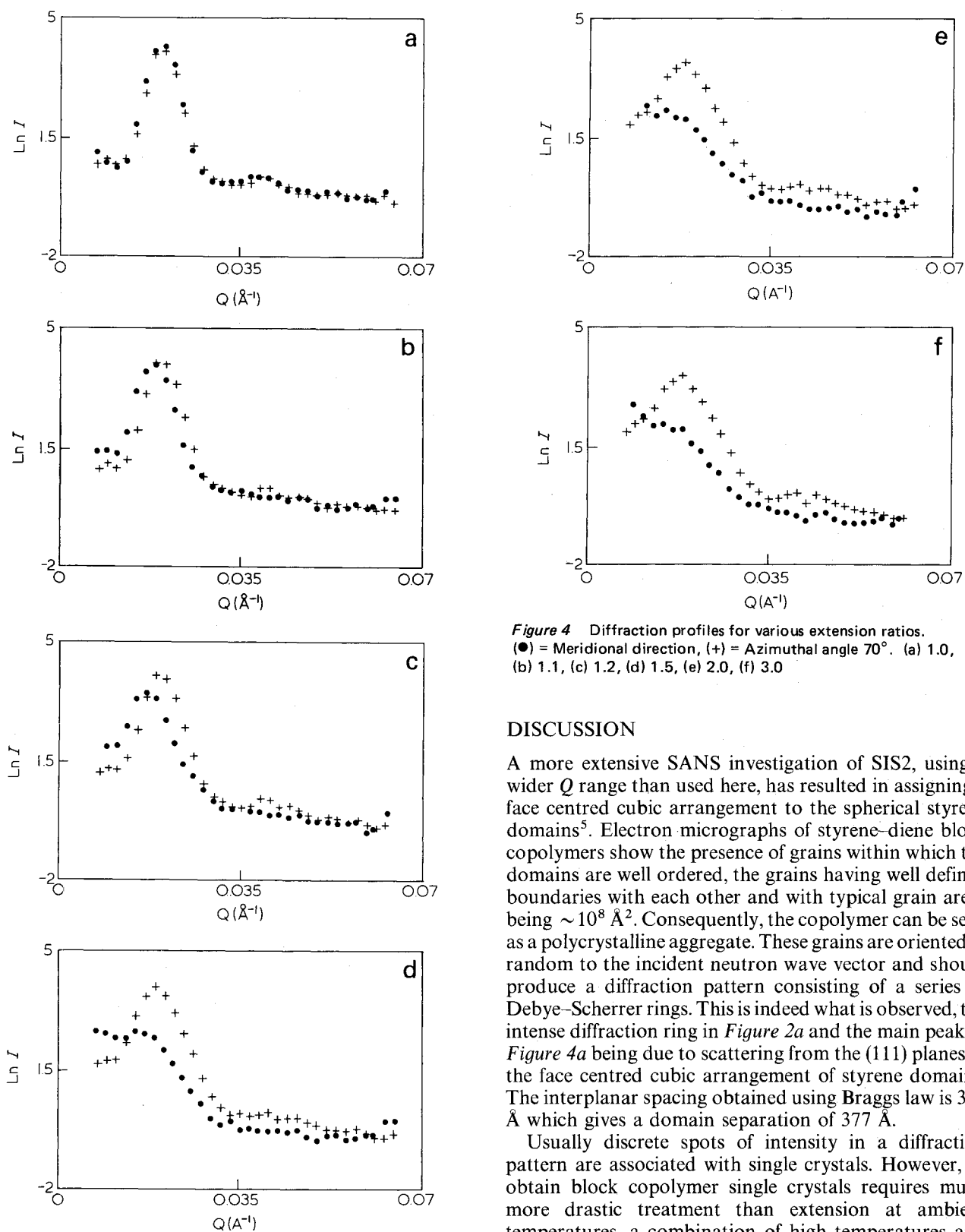*Figure 3* Sketch of the areas used for calculation of diffraction profiles

Figure 4 Diffraction profiles for various extension ratios. (●) = Meridional direction, (+) = Azimuthal angle 70°. (a) 1.0, (b) 1.1, (c) 1.2, (d) 1.5, (e) 2.0, (f) 3.0

DISCUSSION

A more extensive SANS investigation of SIS2, using a wider Q range than used here, has resulted in assigning a face centred cubic arrangement to the spherical styrene domains[5]. Electron micrographs of styrene–diene block copolymers show the presence of grains within which the domains are well ordered, the grains having well defined boundaries with each other and with typical grain areas being $\sim 10^8$ Å^2. Consequently, the copolymer can be seen as a polycrystalline aggregate. These grains are oriented at random to the incident neutron wave vector and should produce a diffraction pattern consisting of a series of Debye–Scherrer rings. This is indeed what is observed, the intense diffraction ring in Figure 2a and the main peak in Figure 4a being due to scattering from the (111) planes in the face centred cubic arrangement of styrene domains. The interplanar spacing obtained using Braggs law is 307 Å which gives a domain separation of 377 Å.

Usually discrete spots of intensity in a diffraction pattern are associated with single crystals. However, to obtain block copolymer single crystals requires much more drastic treatment than extension at ambient temperatures, a combination of high temperatures and shearing forces is usually required[8,9]. We do not envisage such a structure being responsible for the observed scattering at large value of L/L_0. By comparison with investigations of the influence of stress on polycrystalline metals it seems likely that extension of the copolymer introduces deformation texture into the specimen, due to the slip and rotation of the grains as a result of the extension. Grains then have a preferred orientation with respect to the extension direction producing a discontinuous Debye–Scherrer ring as observed here.

scattering and normalized to the scattering from water. The diffraction profiles are shown in Figures 4a–g. It appears that the meridional 'Bragg' peak (parallel to the direction of extension) moves to lower Q and decreases in intensity as L/L_0 increases, whereas those peaks at an azimuthal angle of 70° show a much smaller shift to lower Q, no change in intensity but a distinct broadening of the Bragg peaks.
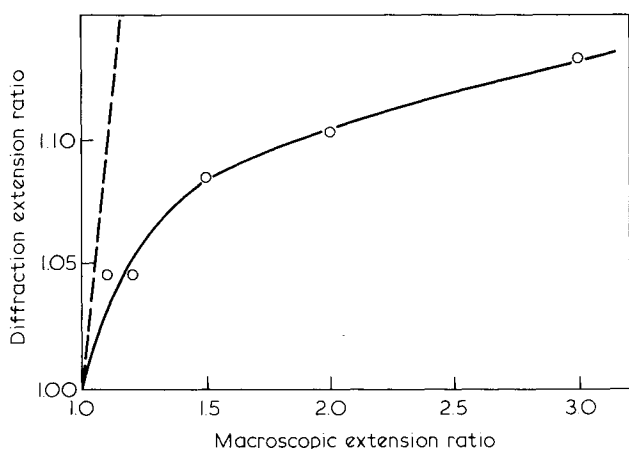
Figure 5 Extension ratio calculated from (111) plane separations as a function of macroscopic extension ratio. Dashed line-affine deformation line

Complete specification of the orientation of crystal plane direction requires a pole diagram and such data are not available for the copolymer SIS2 used[13]. Nonetheless, from the azimuthal angle of the diffraction spots, 70°, and the scattering angle with respect to the incident wave vector it seems that the most probable orientation is that with the [111] crystallographic direction parallel to the direction of stress. Furthermore it appears that the [111] direction is a fibre axis for the specimen, a phenomenon which has also been observed for cast metal sheets[13].

Consequently, the separation of the (111) crystallographic planes in the copolymer should increase as the extension ratio increases if the strain is transmitted affinely to the level of the domains. The extension ratio calculated from the separation of these planes is plotted against macroscopic extension ratio in *Figure 5*. Clearly the affine deformation principle is not obeyed and indeed the observed correspondence between macroscopic and supramolecular extension ratios is much weaker than that noted at a molecular level for homopolymers[14,15]. The broadening of the diffraction peak with extension ratio apparent in *Figure 4* indicates that the strain is not uniform across the (111) planes. Apart from deformation in the grains themselves, this may be due to incomplete orientation of the grains with their [111] crystallographic directions parallel to the extension direction.

Whilst the results presented here suggest that the major relief of stress in styrene–diene block copolymers takes place at grain boundaries, with slippage and rotation of the grains, the spherical domains themselves may distort without a significant change in the separation of their centres of mass and this mechanism may constitute an important contribution to the mechanical properties of block copolymers. Such a mechanism has apparently been observed by electron microscopy[16], observation by SANS calls for experimental arrangements to be significantly different from those used here. A factor that must be borne in mind is the fact that the SANS measurements were of the stop–go type and not continuous as in the stress–strain measurements. However with current neutron source luminosities, this type of SANS measurement is the closest approach to the conditions used in the stress–strain measurements.

ACKNOWLEDGEMENTS

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