

Effect of planar extension on the structure and mechanical properties of polystyrene–poly(ethylene-*co*-butylene)–polystyrene triblock copolymers

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Abstract

Two thermoplastic poly(styrene)–poly(ethylene-*co*-butylene)–poly(styrene) triblock copolymers containing either spherical or cylindrical poly(styrene) microdomains were pre-oriented through extensional flow. Small angle neutron scattering (SANS) measurements revealed that the pre-oriented triblock with a spherical microstructure adopts a body-centred cubic (bcc) structure with a [111] orientation along the flow direction. For the pre-oriented triblock with a cylindrical microstructure, the cylinder axis is aligned along the extensional flow direction. Investigation of the mechanical properties showed that Young's moduli of the pre-oriented copolymers are highly anisotropic. Specimens were then subject to uniaxial deformation along the extensional flow direction and at the same time microstructural changes induced by the deformation were investigated by SANS. It was found that the deformation of the bcc lattice is affine, and that the deformation of the microstructure is reversible. For the triblock copolymer with a cylindrical microdomain structure the deformation of the lattice was found to be non-affine. In this case, SANS patterns suggest a "micronecking" and a breaking of the cylindrical domains without any change in the domain spacing. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Thermoplastic elastomers have a wide range of commercial applications. A particularly important class of thermoplastic elastomers are the linear ABA triblock copolymers with two polystyrene endblocks and a midblock of rubbery polymer. By modifying the ratios and lengths of the different blocks in the copolymer it is possible to control the mechanical behaviour, i.e. the relative importance of rubbery and elastic response.

This class of triblock copolymer forms a number of microphase separated structures. At low polystyrene volume fraction, the polystyrene endblocks form spheres dispersed in the polybutadiene matrix. When the proportion of polystyrene end blocks increases, a progressive change from spherical to cylindrical and finally to lamellar structure is expected [1]. By applying extensional or shear flows, all these microphases can be macroscopically aligned.

Structural studies on oriented block copolymers have been reviewed recently by Honeker et al. [2]. The first experiments showing a macroscopic orientation under flow were performed on poly(styrene)–poly(butadiene)–poly(styrene) (SBS) triblock copolymers forming a hexagonal-packed cylinder microstructure [3]. Investigation of mechanical properties showed that Young's modulus is highly anisotropic with a modulus ratio (ratio of the tensile modulus measured parallel and perpendicular to the cylinders) of about 100 [4]. Small angle X-ray scattering (SAXS) measurements and transmission electron microscopy (TEM) revealed that the polystyrene cylinders were oriented parallel to the flow direction and formed a hexagonal lattice with a "single crystal" texture [5]. SAXS diffraction data revealed that for small strains, stretching applied in a direction normal to the cylinder axis induced the deformation of the hexagonal lattice and at high deformation strains, fracture of the "single crystal" structure [5] occurred. After these pioneering works, numerous studies focused on the effect of shear on the structure of SBS copolymer with cylindrical domain morphology [6–9] and on structural changes taking place during the extensional deformation

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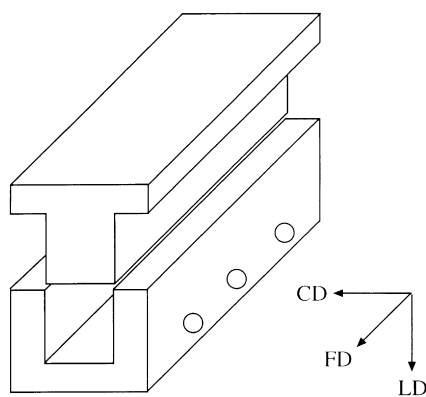


Fig. 1. Schematic of the channel die. The three directions indicated are the flow direction (FD), the loading direction (LD), and the constraint direction (CD).

of these pre-oriented copolymers. Tarasov et al. [10] investigated the effect of large tensile deformations ($>30\%$) perpendicular and parallel to the hexagonal-packed cylinders using SAXS. Results indicated that for strains below 100% , stretching normal to the cylinder axis caused a distortion of the unit cell. For higher strains, bending of the cylinders occurred and the crystal then adopted a flat zig-zag shape. Stretching in the direction of the cylinder axis resulted in the fracture of the cylinder into pieces about 1000 \AA long. Similar investigations were carried out by Pakula et al. [11] with SBS triblocks possessing a cylindrical microphase pre-oriented by shear flow. The deformation behaviour was investigated for uniaxial extensions applied perpendicular, parallel, and at 45° to the orientation of the polystyrene cylinders. When the deformation was applied perpendicular to the cylinders the change in domain spacing was affine up to the yield point. Above this point, yielding and breaking of the polystyrene domains occurred and localized regions relaxed into their unstretched domain spacing. However, the fragmented domains remained perpendicular to the deformation. For larger strains, reorientation of the broken domains was observed. When the stretching was applied parallel to the cylinders the deformation was found to be affine beyond the yield point. As the strain was increased further polystyrene domains underwent “micronecking” followed by breakage and finally for very large strains, microdomains were reoriented. For an extension at 45° to the cylinder orientation, macroscopic reorientation of the microdomains through a shearing process occurred for low strains. Then at higher strains, the polystyrene domains underwent a breaking process followed by further reorientation.

The effect of planar extension on the orientation of the polystyrene domains in a hexagonal-packed cylinder triblock has also been investigated [12]. Results from SAXS experiments showed that extensional flow can also induce a pronounced orientation of the polystyrene domains and lead to highly anisotropic mechanical properties. The polystyrene cylinder axis was found to be oriented in the flow direction.

Compression in a channel die of a triblock copolymer forming a lamellar structure has been shown using SAXS to lead to orientation of the lamellae in the plane of the sample with the lamellar normals perpendicular to the flow direction [12]. Both parallel and perpendicular orientations of lamellae with respect to the shear plane have been reported on the basis of SAXS experiments on semicrystalline diblock and triblock copolymers oriented in a channel die [13,14], depending on the temperature relative to the melting point of the crystalline block and on the compression ratio.

A number of previous studies have focussed on the effect of deformation on the microstructure of block copolymers forming poly(styrene) spheres in a rubbery matrix [15–17]. Inoue et al. investigated the effect of uniaxial extension on the orientation of SI and SIS (I = poly(isoprene)) diblock and triblock copolymers using SAXS and light scattering [15]. They found an affine deformation at small strains, but at larger strains, microvoid formation in the sample lead to density inhomogeneities. The deformation of the I midblock in an SIS triblock has been studied using small-angle neutron scattering (SANS) with contrast matching using a deuterated midblock [16]. Here, the molecular deformation was studied as a function of the uniaxial strain. The effect of roll-casting on the orientation of a poly(styrene)–poly(isoprene) diblock in mineral oil was probed using SAXS [17]. In addition, by measuring the change in domain spacing associated with certain reflections as a function of the strain, it was shown that the deformation was affine up to a 350% extension [17].

In this paper we report on the effect of planar extension on the orientation of two poly(styrene)–poly(ethylene-*co*-butylene)–poly(styrene) triblock copolymers forming either a cylindrical or a spherical microstructure, with poly(styrene) as the minority component. First, we investigated the mechanical properties of oriented triblocks which show that both triblocks are highly anisotropic. Then, samples were submitted to uniaxial tensile deformation and the structural changes during deformation were observed in situ using small-angle neutron scattering. Although previous results have been reported for block copolymers with a cylindrical structure, our experiments are the first to probe the nature of the extensional deformation process for block copolymers with a spherical morphology using small-angle scattering experiments. Furthermore, distinct deformation mechanisms for the spherical phase compared to the cylindrical phase are reported.

2. Experimental

2.1. Sample preparation and characterization

The two poly(styrene)–poly(ethylene-*co*-butylene)–poly(styrene) copolymers studied in this work were a gift from Shell Chemicals (UK). Literature from the

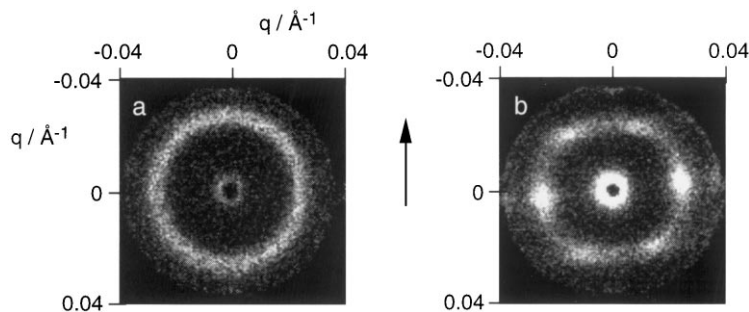


Fig. 2. Two-dimensional SANS patterns in the (CD, FD) plane for G1657 (a) dense sheet film and (b) for a processed (CR = 5.3). The arrow indicates FD.

manufacturer indicates that Kraton G1650 contains approximately 29% PS by volume and is expected to form a hexagonal-packed cylinder phase. Sample Kraton G1657 contains approximately 13% PS by volume and is thus expected to form a body-centred cubic (bcc) sphere morphology. The mass average molar mass determined from GPC in our laboratory, was found for G1650 to be $\bar{M}_w = 75\,000\text{ g mol}^{-1}$ with a polydispersity index $\bar{M}_w/\bar{M}_n = 1.12$ and for G1657 $\bar{M}_w = 70\,000\text{ g mol}^{-1}$ with a polydispersity index $\bar{M}_w/\bar{M}_n = 1.01$. Sample G1657 is stated to contain roughly 30 wt% diblock of half this molecular weight. The presence of diblock is not expected to influence the morphology of the triblock and thus has not been considered in this work.

Oriented samples were obtained by means of channel die compression which has been shown to be equivalent to planar extension [18]. The design of the channel die is illustrated schematically in Fig. 1. Prior to channel die compression, polymers were processed into dense sheet films by compression moulding in a plate press at approximately 150°C. Squares of films were then stacked into the centre of the lubricated channel die which was inserted in the plate press at 130°C. After allowing thermal equilibrium of the channel die, pressure was applied to squeeze the polymer. After compression, the channel die was held for 2 h at 130°C before cooling to room temperature by passing water through the plates. The compression ratio (CR) was then defined as the thickness of the dense sheet film divided by the thickness of the processed film.

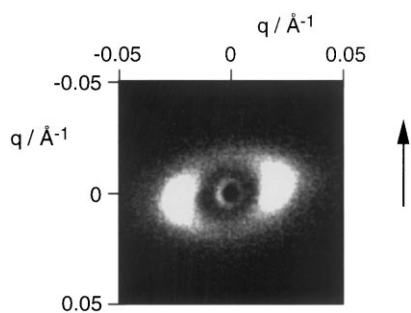


Fig. 3. Two-dimensional SANS pattern for a processed G1650 (CR = 4) in the (CD, FD) plane. The arrow indicates FD.

2.2. Techniques

Uniaxial stress–strain measurements were conducted on an Instron TT-CM. The crosshead speed was 2 cm/min for all samples. The stress is the drawing force divided by the cross-sectional area of the undrawn sample. All the experiments were carried out at room temperature.

SANS were performed at the SANS facility at Risø National Laboratory, Denmark using neutrons monochromated with a mechanical velocity selector to give $\lambda = 5.6$ or $\lambda = 7.7\text{ Å}$ wavelength neutrons ($\Delta\lambda/\lambda = 0.09$), and, a 6 m sample-to-detector distance. Samples were mounted on a stretching device which allows the sample to be uniaxially stretched by equal amounts from the centre of the sample. Only the central part of the sample was irradiated by the neutron beam. The stretching device has been described elsewhere [19].

3. Results and discussion

3.1. Structure of oriented films before drawing

Two-dimensional SANS patterns obtained for the dense sheet film specimen of G1657 and the channel die processed G1657 sample are shown respectively in Fig. 2a and b. The dense sheet film pattern shows a ring of scattering at $q^* = 0.026\text{ Å}^{-1}$. After processing through the channel die a six-fold anisotropic diffraction pattern is obtained with two strong equatorial reflections and four off-equatorial reflections. As a result of the orientation process the first order peak is shifted to a slightly smaller value at $q^* = 0.024\text{ Å}^{-1}$. The six reflections observed on the SANS pattern arise from the {110} reflections of a bcc structure with the [111] direction aligned with the extension direction. Patterns of similar symmetry have been already observed for block copolymers in solution forming a bcc phase [20] and a roll-cast poly(styrene)–poly(isoprene)–poly(styrene) triblock copolymer [17] and the indexation of the pattern is discussed elsewhere [20]. In the SANS data, the off-equatorial reflections are observed at $\sim (60 \pm 2)^\circ$ with respect to the equator, whereas they were previously observed at $\sim 55^\circ$ for the bcc phase in block copolymer solutions. This small difference is

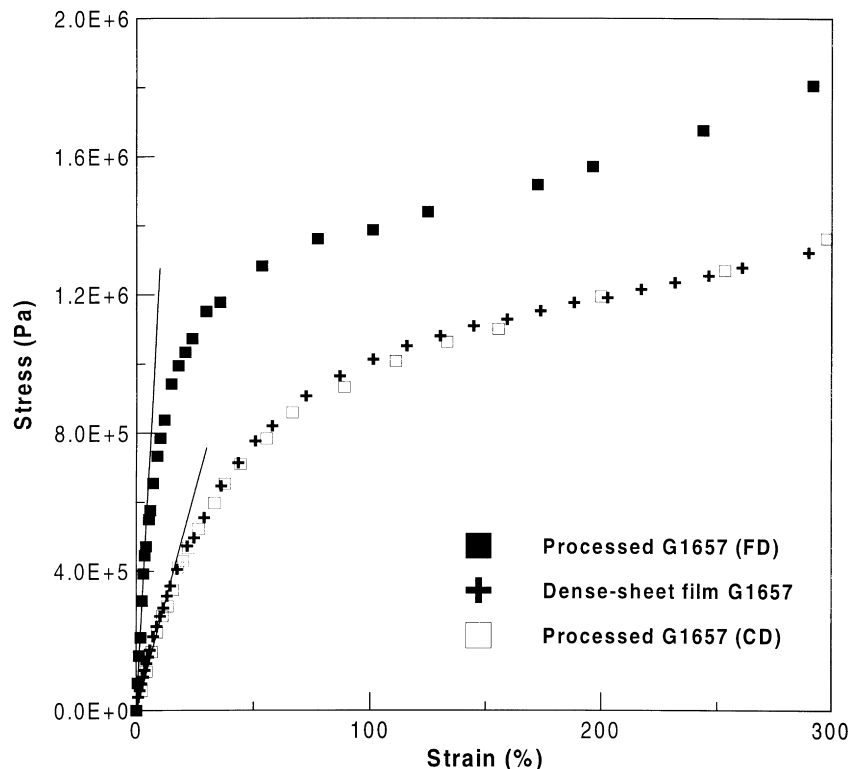


Fig. 4. Uniaxial stress–strain curves for dense sheet film G1657(+) and processed G1657 (CR = 8.7) for a deformation applied along FD(B) and along CDA.

probably due to distortions of the structure induced by compression. The essential feature is that the [111] direction lies along the flow direction and the bcc structure is highly twinned in {110} and {211} planes.

Fig. 3 shows the two-dimensional SANS pattern of the processed G1650. This anisotropic pattern is consistent with an orientation of the polystyrene cylinders parallel to the flow direction. The same orientation was reported previously with a similar Kraton triblock (PS = 29 wt%) oriented through extensional flow [12].

3.2. Mechanical properties

The effect of the uniaxial compression on the mechanical properties of the two Kraton polymers was investigated by measuring the stress–strain curves. Fig. 4 shows typical stress–strain data for the pre-oriented specimens of G1657 with the stress applied parallel to the flow direction FD and perpendicular to it. For comparison, the curve obtained with the dense sheet film is also shown. The three samples behave like rubbery materials and no yield stress is observed. The channel die processed G1657 film clearly exhibits an anisotropy of the mechanical properties. The polymer is stiffer when the strain is applied parallel to the flow direction in the channel die. Values of the small-strain elastic modulus or Young's modulus (E) obtained for strain along FD and along CD are $E_{FD} = 12.8$ and $E_{CD} = 2.5$ MPa, respectively giving a modulus anisotropy

$E_{FD}/E_{CD} \sim 5$. The mechanical behaviour of the dense sheet film is very similar to the processed film drawn perpendicularly to FD with $E = 3.1$ MPa. This result is quite surprising as a behaviour intermediate between the two cases would be expected for a sample without any orientation of the microdomains

Fig. 5 shows the evolution of Young's modulus as a function of the compression ratio (CR) for strains parallel and perpendicular to FD. We observe that the modulus along FD increases linearly with the compression ratio while the modulus along CD remains nearly constant.

Strain–stress data obtained with G1650 are shown in Fig. 6. As for G1657, processed G1650 displays an anisotropy of mechanical properties and the modulus along FD and along CD is respectively $E_{FD} = 42$ and $E_{CD} = 9.5$ MPa giving a modulus anisotropy $E_{FD}/E_{CD} \sim 4.5$. G1650 is stiffer along FD and exhibits a yield stress for a strain of about 5% while along CD the stress–strain is rather characteristic of a rubber-like behaviour. Unoriented G1650 has an intermediate behaviour. Fig. 7 shows the variation of Young's modulus as a function of the compression ratio. Data previously obtained with a similar Kraton copolymer pre-oriented by planar extension [12] are also reported in Fig. 7. Results clearly show that as for G1657 the mechanical anisotropy of the pre-oriented G1650 increases with the compression ratio. We also note that as expected Young's modulus of G1650 is higher than that of G1657. By increasing the fraction of PS, the stiffness increases.

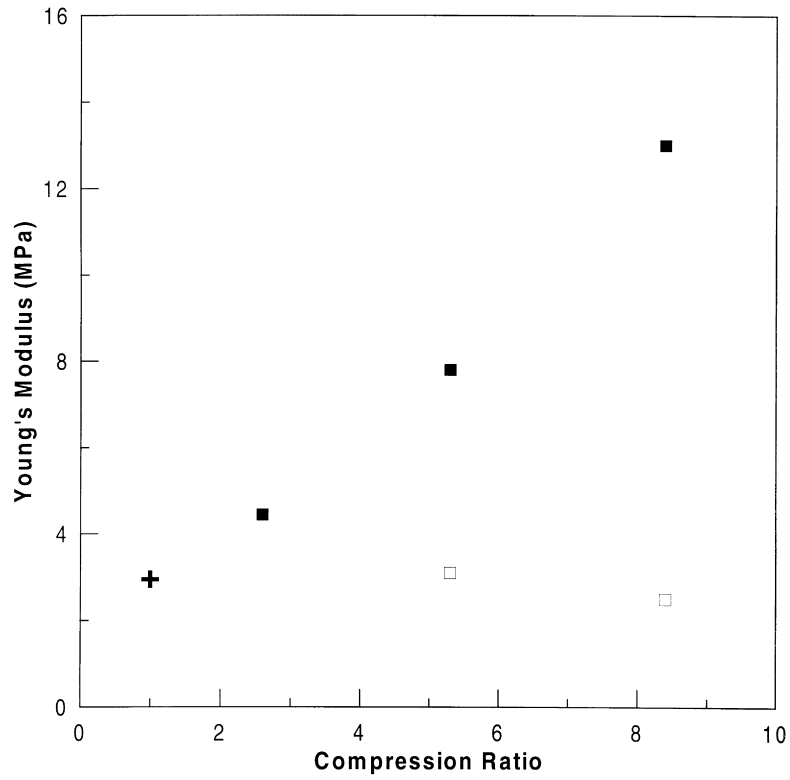


Fig. 5. Variation of Young's modulus versus the compression ratio CR for G1657. (B), deformation applied along FD; (A), deformation applied along CD. The point at CR = 1 corresponds to the dense-sheet film sample.

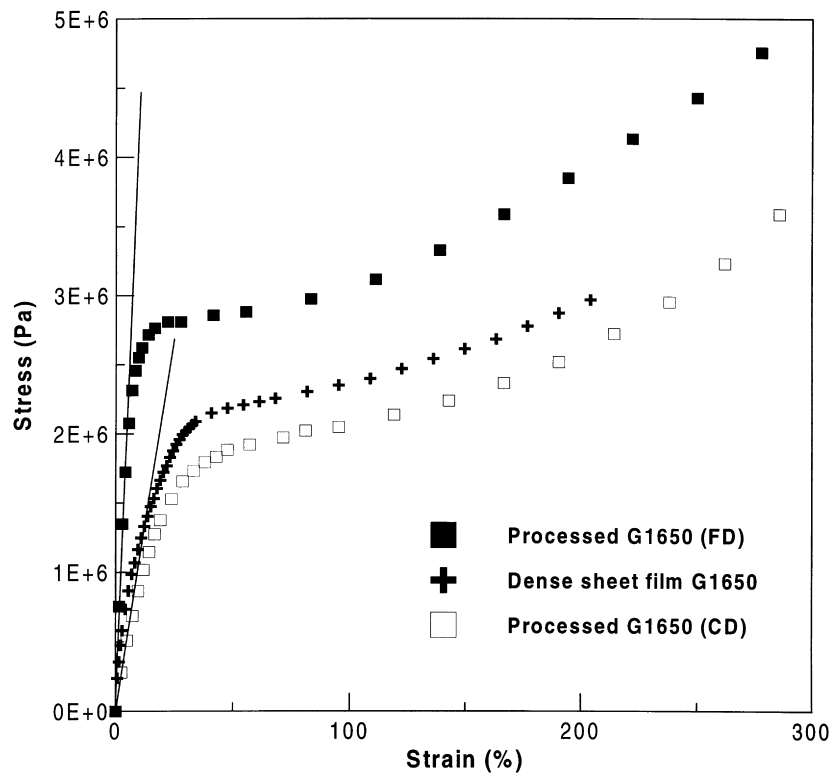


Fig. 6. Uniaxial stress–strain curves for dense sheet film G1650 (+) and processed G1650 (CR = 4) for a deformation applied along FD (B) and along CD (A).

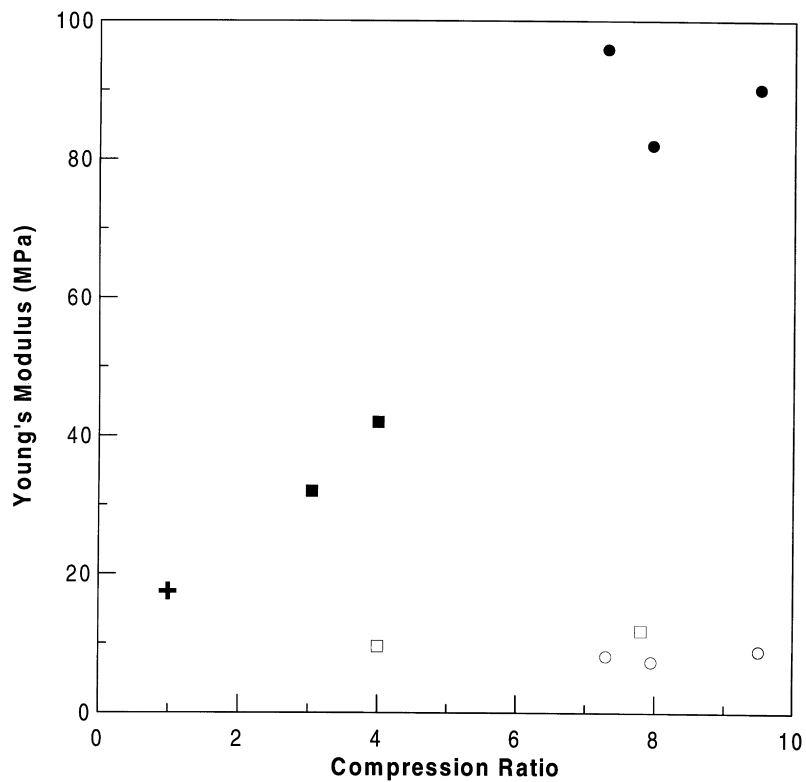


Fig. 7. Variation of Young's modulus versus the compression ratio CR for G1650. (B), deformation applied along FD; (A), deformation applied along CD. The point at CR = 1 corresponds to the dense-sheet film sample. (X, W): values of Young's modulus along FD and along CD, respectively (from Ref. [12]).

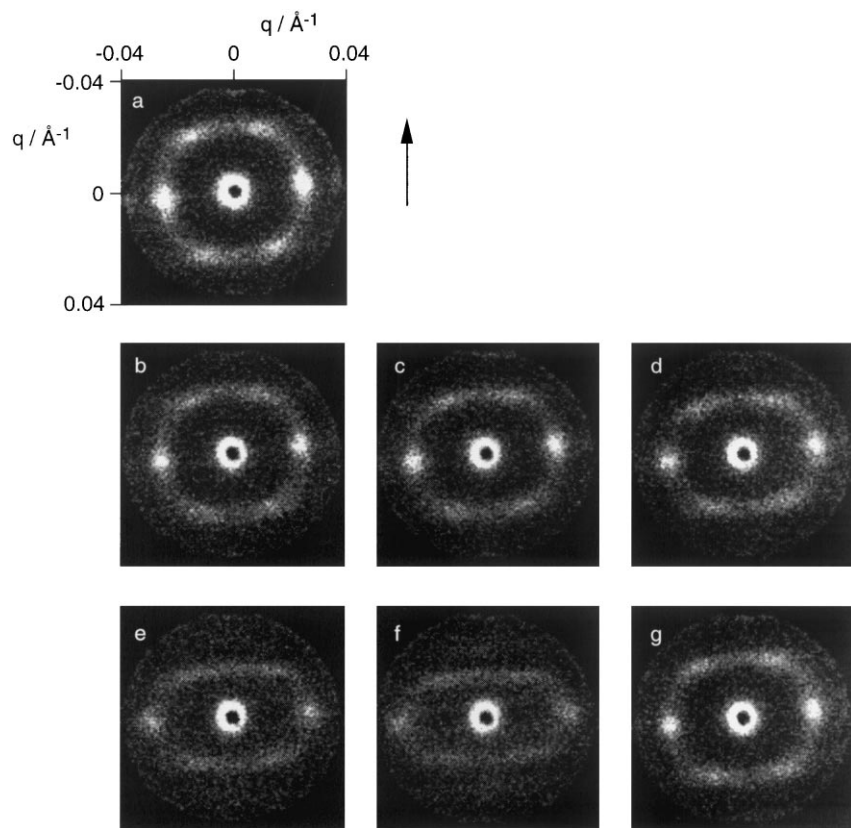


Fig. 8. Two-dimensional SANS patterns in the (CD,FD) plane for processed G1657 (CR = 5.3) at elongation ratios (a) 0, (b) 5, (c) 10, (d) 20, (e) 40, (f) 63, (g) 0%. The stretching direction (coincident with FD) is vertical.

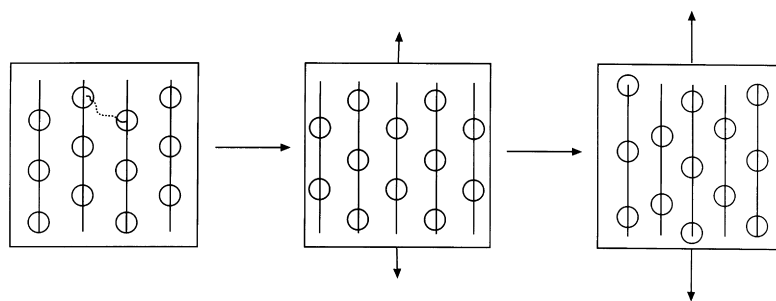
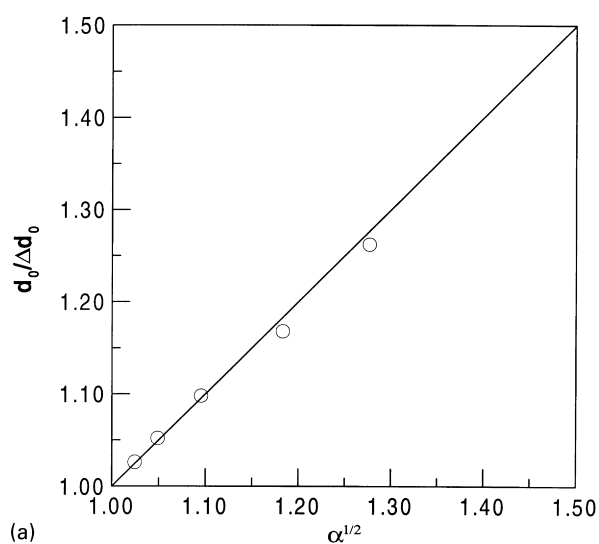
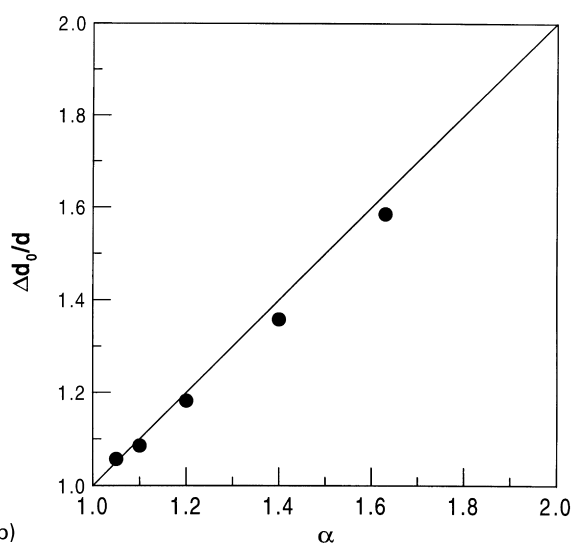


Fig. 9. Schematic of the structural transformations accompanying the affine deformation of the bcc phase under extension. Left: undeformed. Centre: decrease in domain spacing normal to the extension direction with increase in inter-sphere spacing in this direction. Right: further affine change in domain spacings, plus progressive de-correlation of “strings” of spheres oriented along the extension direction.



(a)



(b)

Fig. 10. (a) variation of the interdomain distance perpendicular to the deformation vs. contraction ratio of the sample, (b) variation of the interdomain distance parallel to the deformation vs. elongation ratio of the sample.

3.3. Structural changes during deformation

In order to investigate structural changes induced by large-strain deformations, channel die samples were subjected to in situ uniaxial elongation along the FD direction while SANS patterns were recorded with the beam along the LD direction.

Two-dimensional SANS patterns recorded at different strains at room temperature with processed G1657 are shown in Fig. 8. As the strain increases, the two equatorial $\{110\}$ reflections move away from the beam centre whilst the four other $\{110\}$ reflections move closer to the equator, also becoming more smeared out perpendicular to the extension direction. This suggests that the domain spacing along the drawing direction increases while the domain spacing perpendicular to the drawing direction decreases. A sketch of the change in structure consistent with these observations is contained in Fig. 9. This is purely schematic, since it does not allow for the detailed twinned structure of the bcc crystal. However, it illustrates the contraction of the domain spacing perpendicular to the extension direction, with a corresponding increase in inter-sphere spacing along the extension direction. We have also indicated that a fraction of spheres will be connected in pairs by bridging chains, although the fraction of bridged versus looped triblock chains is not known for the present samples. At the highest extension ratios the smearing out of the off-equatorial reflections normal to the extension direction indicates a de-correlation between “strings” of spheres along the extension direction, as indicated on the right-hand side of Fig. 9. When the load is removed, the high correlation is immediately recovered (Fig. 8g), although the structure is no longer strictly cubic.¹

For an affine deformation, the domain spacing distance increases by a factor α along the deformation direction and decreases by a factor $\alpha^{-1/2}$ in a direction perpendicular to the deformation, α being the relative deformation of the bulk material. The contraction ratio of the domain spacing,

¹ Similar behaviour has been observed for an oil-based gel of a poly(styrene)–poly(ethylene-co-butylene)–poly(styrene) triblock [21].

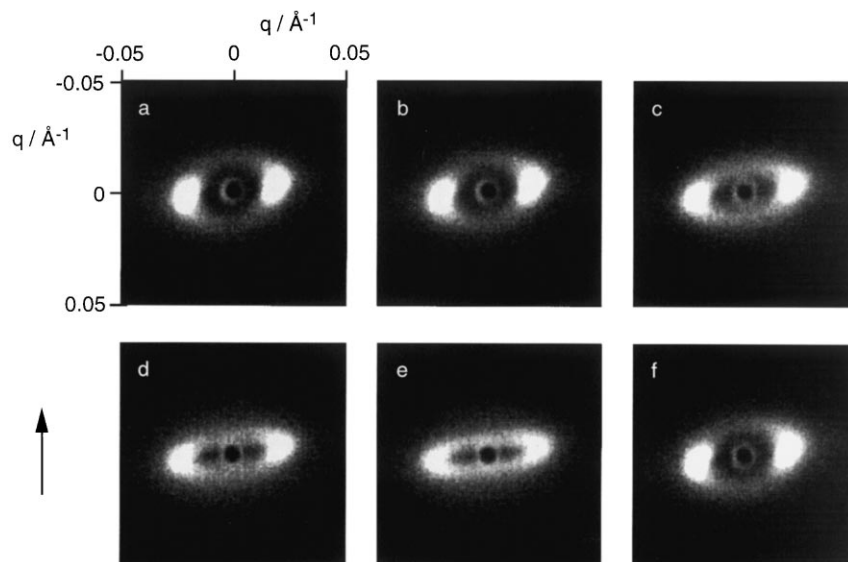


Fig. 11. Two-dimensional SANS patterns in the (CD,FD) plane for processed G1650 (CR = 4) at elongation ratios (a) 0, (b) 5, (c) 20, (d) 40, (e) 64, (f) 0%. The stretching direction (coincident with FD) is vertical.

d_0 , perpendicular to the applied deformation was determined from the position of the two equatorial reflections and is plotted in Fig. 10a against that of the bulk sample, $\alpha^{1/2}$. In Fig. 10b, the extension ratio of the domain spacing distance along the deformation direction is plotted against that of the macroscopic sample α . The extension ratio along the deformation direction was determined from the ordinates of the four off-equatorial reflections. As indicated by linear relationships, the change of the domain spacing distance is affine up to the maximum deformation applied, an extension of 63%. Furthermore, the value of the Poisson's ratio for deformations applied along the [111] direction is 0.54. Thus, in this respect the material behaves like a normal incompressible rubber although the SANS patterns indicate that the structure does not recover completely to its initial state.

The SANS patterns obtained for different deformations of pre-oriented hexagonal G1650 are shown in Fig. 11. When the sample is stretched parallel to FD or on average parallel to the cylinder axes, we observe the development of V-shaped lobes with conservation of the strong equatorial

scattering. For a 5% deformation, the intensity and the position of the equatorial reflection remain unchanged within experimental uncertainties. The initial structure of the sample is retained in the direction perpendicular to the cylinder axis. For deformations greater than the yield point, i.e. 5% according to Fig. 6, the equatorial reflection is shifted to a slightly higher peak position $q^* = 0.024 \text{ \AA}^{-1}$ and the intensity of the reflection decreases continuously with increasing strain. The increase of the scattering angle indicates a small reduction of the domain spacing perpendicular to the extension direction, and this reduction was found to be non-affine. The appearance of V-shaped lobes during deformation has been already reported previously for a poly(styrene)–poly(butadiene)–poly(styrene) triblock copolymer [11]. It was attributed to the “micronecking” followed by a breaking of the cylindrical domains that is correlated between adjacent cylinders, with fracture lines oriented at 30° to the stretching direction [11]. This angle corresponds to the envelope of the outer arms of the “V”. A similar mechanism is consistent with the SANS patterns in Fig. 11, and the corresponding structural changes within this

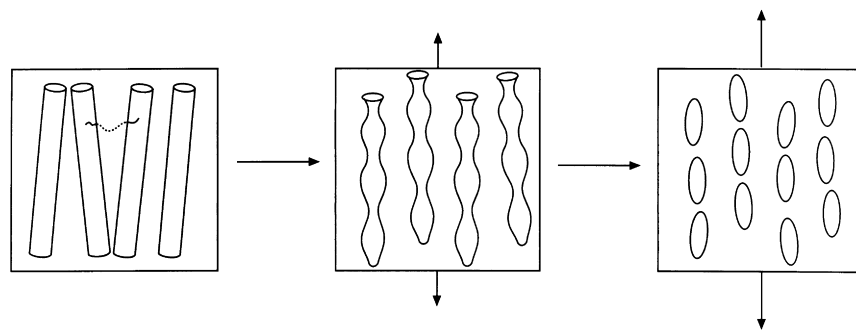


Fig. 12. Schematic of the structural transformations accompanying the non-affine deformation of the hexagonal phase under extension. Left: undeformed. Centre: correlated “micronecking” (undulations) of cylinders. Right: broken-up cylinders.

model are sketched in Fig. 12. The increase in off-equatorial intensity in stripes parallel to the equator in Fig. 11 is consistent with the development of structure along the cylinder axis. This intensity is initially rather diffuse, consistent with a “micronecking” or an undulation instability (Fig. 12, centre), but becomes much sharper (Fig. 11e), consistent with break-up of the cylinders into smaller anisotropic units (Fig. 12, right). Fig. 12 again emphasizes that there will be a finite fraction of bridging chains between rods. These cause the position of cylinder undulations to be correlated, which produces the V-shaped scattering lobes.

After breaking the rods a partial recovery of the diffraction patterns is observed when the load is removed. This result is consistent with electron microscopy observations reported by Odell and Keller [5] for similar samples. As the broken domains are very close to each other, the cylinders can reform through a diffusion process.

4. Summary

Two triblock copolymers forming a hexagonal-packed cylinder structure and a bcc-packed spherical structure were oriented through planar extension. SANS observations showed that for the triblock with a cylindrical morphology, planar extension induced an orientation of the cylinder axes along the flow direction. For the triblock with a spherical morphology planar extension resulted in an orientation of the [111] direction along the flow direction. For both triblocks, planar extension led to a large anisotropy of the elastic modulus, measured parallel and perpendicular to the flow direction. It was found that the anisotropy increases with the compression ratio of the processed specimens. The pre-oriented triblocks were then subjected to uniaxial extension along the flow direction and changes on structure were monitored in situ by SANS. It was found that for the copolymer in a bcc phase, the change in lattice spacing was affine with the macroscopic deformation of the sample up to 64% elongation. Furthermore diffraction data suggested a de-correlation of the polystyrene microdomains along the elongation direction. In contrast, the change in lattice spacing for the hexagonal phase triblock was found to be non-affine. Elongation along the cylinder axis lead to a “micronecking” followed by a breaking of the cylindrical domains. However, after removal of the strain, the cylinder microdomains were reformed. These conclusions for the

deformation of the sample containing cylindrical microdomains support the earlier work of Pakula et al. [11].

Acknowledgements

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