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Polymer 41 (2000) 2577–2582

polymer

# Correlation of lattice deformation with macroscopic strain for the hexagonal-packed cylinder phase of a triblock copolymer

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Received 4 January 1999; received in revised form 16 April 1999; accepted 21 May 1999

## Abstract

The deformation of a lattice of hexagonal-packed cylinders has been correlated to the applied oscillatory strain via time-resolved simultaneous small-angle X-ray scattering (SAXS) and rheology experiments. Kraton-type poly(styrene)–poly(ethylene-*co*-butylene)–poly(styrene) (PS–PEB–PS) triblocks were pre-aligned in the hexagonal-packed cylinder phase formed in the melt. Specimens were then subjected to oscillatory strain (7%, i.e. small but in the non-linear viscoelastic regime) with the cylinder axis parallel or perpendicular to the shear axis at room temperature (where PS is glassy). At the same time, SAXS was used to probe the change in domain spacing during one cycle of shear with a time resolution down to 2 ms. It was found that the lattice deforms in phase with the applied strain (although the stress is out-of-phase). However, the deformation is not affine. The observed change in domain spacing for the cylinders was significantly smaller than the applied strain for both the perpendicular and parallel orientation. The deviation from affine behaviour was greatest for the parallel orientation. This non-affine behaviour is ascribed to the take-up of strain by initially poorly oriented grains. Rheology data obtained concurrently with the SAXS indicates a two-step relaxation of the dynamic shear modulus. The initial fast process may be due to the realignment of grains, whereas the slower process may be due to the perfection of lattice order resulting from non-linear viscoelastic strains.

*Keywords*: Triblock copolymer; Lattice deformation; X-ray scattering

## 1. Introduction

It is well known that extensional and shear flows can be used to macroscopically align microphase-separated structures formed by block copolymer melts. The first experiments to demonstrate flow-induced alignment were conducted on poly(styrene)–poly(butadiene)–poly(styrene) (PS–PB–PS) triblock copolymer melts, using commercial Kraton copolymers forming a phase of hexagonal-packed PS cylinders (28% PS, Kraton TR1102) [1]. Small-angle X-ray scattering (SAXS) together with transmission electron microscopy (TEM) was used to confirm long-range hexagonal order of rods oriented along the flow direction by extrusion.

More recently, there has been much work showing that shear can be used to generate highly aligned "monodomains" of various microphases (lamellar, hexagonal-packed cylinder, body-centred cubic, bicontinuous cubic gyroid). This subject has been reviewed recently [2–4]. Less attention has been devoted to the effect of extensional flows. A review [5] of the effect of orientation of triblock copolymers on their mechanical properties includes a discussion of previous tensile deformation experiments. SAXS and TEM have been performed [6] on pre-aligned samples of Kraton TR1102. A tensile deformation perpendicular to the cylinders was found to be affine up to 20% strain, whereas in the direction parallel to the cylinders, the deformation was affine up to only about 3% strain, above which the polymer yielded [6]. The deformation behaviours of Kraton TR1102 and another Kraton triblock during extension were studied using SAXS by Pakula et al. [7]. Two orientations of pre-aligned samples with respect to the extension axis were investigated. In the first, the cylinders were normal to the shear axis and in the second they were parallel. In the perpendicular orientation, the domain spacing increased as the sample was stretched

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PII: S0032-3861(99)00424-3

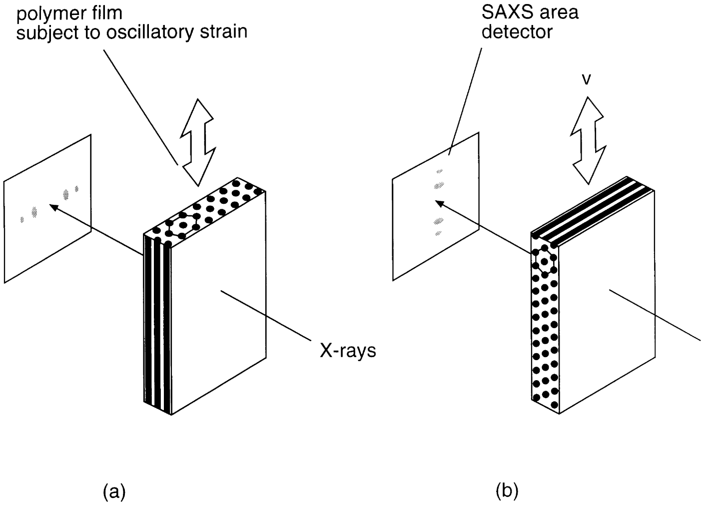

Fig. 1. Schematic of the conditions application of oscillatory shear to pre-sheared block copolymer forming a hexagonal phase, cut so that the cylinders are (a) parallel and (b) perpendicular to the shear direction.

and the deformation was affine at low strains. At about 170% strain, however, a second set of reflections indicated that some domains had relaxed into their original unstretched spacing. In the parallel orientation, the deformation was affine even above the yield point (110% strain). For both orientations, a four-point pattern was observed at large strains (400%) [6]. This results from a buckling of the rods. This buckling instability has been analysed theoretically for the case where both blocks are molten [8]. In the case that one component is stiff (i.e. glassy), which is appropriate to the experiments described herein, the theory is modified because one component is much less susceptible to deformation. Similar evidence for buckling instabilities at large strains has been obtained for poly(styrene)–poly(isoprene)–poly(styrene) triblocks using SAXS [5,9]. Tarasov et al. [9] also investigated the effect of large tensile strains ($>100\%$) on the hexagonal-packed cylinder of a PS–PB–PS triblock copolymer using SAXS and observed four-point patterns at large strains.

Here we report results of a time-resolved study of the deformation of a triblock copolymer forming a hexagonal-packed cylinder phase. The sample was only subjected to small strains, since we focus here on the affine or non-affine deformation of the lattice, not on buckling instabilities. The Kraton copolymer was pre-aligned by compression molding above the glass transition temperature. Samples were then subjected to oscillatory tensile deformation at room temperature and SAXS data was obtained synchronously with the deformation. In one sample, strain was applied parallel to the cylinders and in another sample, the strain was perpendicular to the rods. It was thus possible to correlate changes in the microscopic domain spacing (obtained via SAXS) to macroscopic changes in sample dimensions, and to probe whether the deformation is affine or not. It proved possible using synchrotron SAXS to obtain diffraction patterns at a time resolution of 2 ms for a deformation at 10 Hz. Furthermore, dynamic elongational moduli were obtained simultaneously with the SAXS data, thus probing the mechanical relaxation process.

## 2. Experimental

### 2.1. Sample preparation and characterisation

The PS–PEB–PS copolymer was obtained as a gift from Shell Chemicals. Sample Kraton G1652 is stated by the manufacturer to contain approximately 30% PS by volume, and is thus expected to form a hexagonal-packed cylinder phase, as verified by SAXS. The mass average molar mass was determined from GPC to be $M_w = 75\,100\ \mathrm{g\ mol^{-1}}$, with a polydispersity index $M_w/M_n = 1.09$.

The polymer was processed into a 2 mm thick film by compression moulding. The window-pane mould ($125 \times 250 \times 2\ \mathrm{mm^3}$ dimensions) was placed in a 50-tonne hydraulic press with electrically heated plates. The temperature of the plates was 170–180°C (i.e. well above the glass transition temperature of the copolymer). The polymer sample (150–200 g) was placed in the centre of the hot mould, which was then put in the press. The pressure was gradually increased until excess of the sample appeared on the edge of the mould. The mould was left in the press (under maximum pressure) for ~20 min and was then moved to another one for cooling. As a result of this processing, the cylinders of the microstructure were oriented radially in the film and the test samples were cut parallel and perpendicular to the cylinder axis at the edges of the sample. The orientation was checked by SAXS prior to deformation.

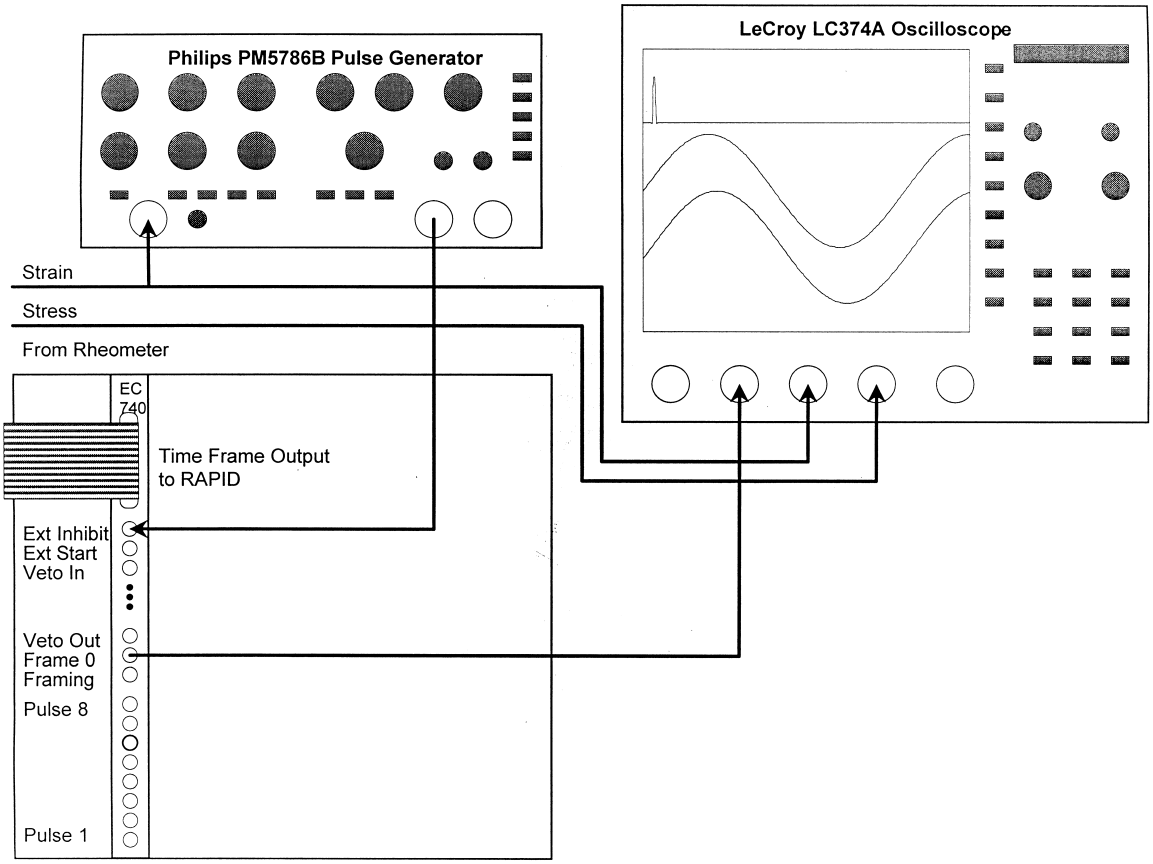

Fig. 2. Schematic of the data acquisition electronics.

### 2.2. Simultaneous small-angle X-ray scattering and rheology

SAXS experiments were conducted on station 16.1 of the Synchrotron Radiation Source, Daresbury Lab, UK. Details of the beamline and camera geometry have been provided elsewhere [10]. Scattered photons were collected on the RAPID multiwire gas-filled area detector [11]. A scattering pattern from an oriented specimen of wet collagen (rat-tail tendon) was used for calibration of the $q$ scale ($q = 4\pi \sin \theta/\lambda$, where the scattering angle is defined as $2\theta$ and $\lambda = 1.5$ Å is the wavelength). Measurements of dynamic mechanical properties were performed in tandem with the SAXS experiments, using a Rheometrics Solids Analyzer RSA II system with a film/fibre fixture. An extensional oscillatory strain was applied to the polymer film and the dynamic and loss shear moduli, respectively, $E'$ and $E''$, were measured during the deformation process. All experiments were conducted at room temperature, where PS is glassy and PEB is rubbery. With the rheometer in situ at the X-ray beamline the extension direction **v** was vertical, and the X-ray beam was incident normal to the film (Fig. 1). This rheometer has previously been exploited for simultaneous SAXS/rheology experiments on polymer melts and gels using a different tool, a modified shear sandwich fixture, as described elsewhere [12].

To synchronise the data, the data acquisition system was triggered from the rheometer strain output on every cycle, as schematised in Fig. 2. The rheometer produces two bipolar analogue signals, one for strain and one for stress. A Philips pulse generator (Fig. 2) was set in externally triggered mode. The strain signal from the rheometer was supplied to the trigger input and the trigger level adjusted to trigger at the required point in the cycle. The pulse generator was set to trigger the Time Frame Generator (TFG), via its external start input.

For a 10 Hz (100 ms) experiment, the TFG was set give 96-frame pairs. Each frame pair was set to give a 10 μs dead frame and a 990 μs live frame. This gave a total TFG cycle of 96 ms, slightly less than the rheometer cycle. To ensure synchronisation, the pause bit was set in the first dead frame. When the data acquisition software started the TFG, the TFG stepped to the first dead frame and waited because of the pause bit. When the rheometer strain cycle crossed the threshold, the pulse generator produced an output pulse. On the rising edge of this, the TFG was started and data was collected in 96 frames for 96 ms. The TFG then returned to frame 0 and waited for the next trigger pulse. In this way the TFG and rheometer were re-synchronised each cycle, so there was no risk of the timing drifting out of step. The TFG was programmed to run for up to 4095 complete cycles, to allow sufficient counting statistics to

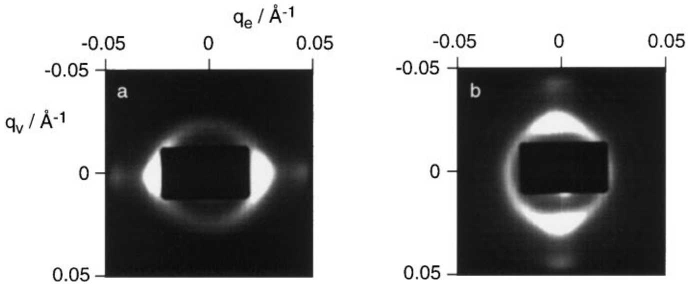

Fig. 3. SAXS patterns obtained for compression-molded samples, as mounted in the rheometer: (a) Cylinders parallel to flow direction; (b) cylinders perpendicular to flow direction.

be accumulated by binning the data from the cycles frame by frame.

The frame 0 pulse from the TFG (which controlled the data acquistion system) was recorded on the oscilloscope along with the stress and strain signals from the rheometer to allow accurate time correlation of the X-ray data with the rheometer data.

## 3. Results and discussion

The pre-oriented specimens were subjected to oscillatory shear in two orientations. In the first, the axis of the cylinders was parallel to the shear axis (Fig. 1(a)). In the second, the rod axis was normal to the shear direction (Fig. 1(b)). As schematically indicated in Fig. 1, SAXS patterns were collected on the area detector. For both orientations, reflections in the positional ratio $1 : \sqrt{3}$ were observed along a direction normal to the cylinders, as illustrated for the SAXS patterns for samples as mounted shown in Fig. 3. The existence of both these reflections in the two orientations indicates that the sample was not a single crystal, rather a two-dimensional powder, in which the hexagonal lattice is rotated around the cylinder axis [13,14]. The high degree of anisotropy observed in the SAXS patterns, as shown in Fig. 3 demonstrates that the rod axes possess a high degree of mutual orientation.

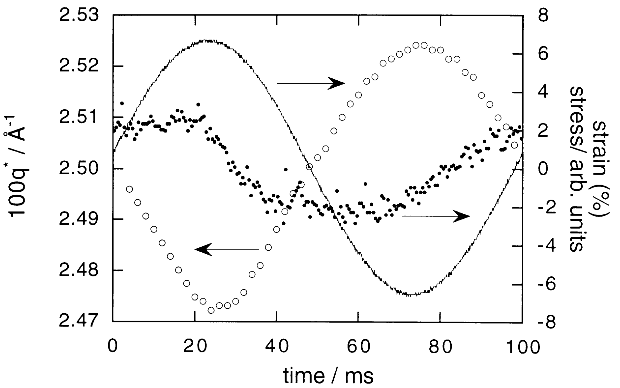

Fig. 4. Variation of first order peak position ($q^*$) and stress (●) with strain (—) for the sample with rods parallel to the shear direction. Data is presented for one cycle of shear (averaged over 500 cycles) at 10 Hz and 6.7%.

To facilitate quantitative analysis of the SAXS data, the two-dimensional patterns were reduced by integration to one-dimensional profiles of intensity along a particular direction. Where the reflections were horizontal (Fig. 3(a)), the intensity was integrated in a horizontal slice, and for the orthogonal orientation (Fig. 3(b)), integration was performed in a vertical slice. We consider first a sample oriented with rods parallel to the shear direction and subjected to oscillatory strain at 10 Hz and 6.7% strain. SAXS data were collected in 50 frames of 2 ms duration, averaged over 500 cycles of shear. This strain amplitude is outside the linear viscoelastic regime, and as such is expected to lead to deformation of the hexagonal lattice. The position of the first order reflection, $q^*$, was obtained as a function of time during the cycle by fitting the location of the first order reflections to a Gaussian function. The result is shown in Fig. 4 for a sample with rods parallel to the shear direction, in which the strain and force (proportional to stress) output voltages from the rheometer are also plotted. It is clear that the domain spacing increases as the sample is extended, and decreases as the sample contracts. Furthermore, the microscopic domain spacing change is in phase with the macroscopic deformation. However, whereas the strain varies by ±6.7%, the domain spacing only changes by ±1.1%, i.e. the deformation is not affine. For an affine (volume conserving) deformation, if the extension is 6.7%, then assuming a cylindrically symmetric contraction, a reduction of dimensions normal to the extension axis of $(1 + 0.0067)^{1/2} = 3.3\%$ is expected. However, it has to be borne in mind that an aligned hexagonal phase is not cylindrically symmetric, and there is a difference in packing of (10) and (11) planes which will lead to anisotropic mechanical properties in the hexagonal plane, if these planes are macroscopically oriented. This could cause a larger contraction of the sample normal to the (10) planes compared to the (11) ones. An alternative explanation for the non-affine deformation is that most of the macroscopic strain is taken up by domains which are misorientated with respect to the shear direction, and which are rotated when strain is applied. It is also apparent from Fig. 4 that the stress is out-of-phase with the strain (it is also somewhat noisy).

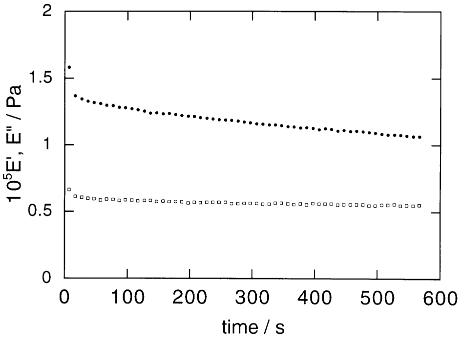

Fig. 5. Relaxation of dynamic extensional moduli during strain under the conditions indicated for Fig. 4. Data obtained concurrently with the SAXS data of Fig. 4. (●) $E'$, (□) $E''$.

But it is clear that the deformation of the microscopic domains follows the applied strain. Both peak position and intensity varied sinusoidally, and in phase with the strain.

The dynamic extensional moduli were monitored simultaneously with the SAXS data. Typical results are shown in Fig. 5, where $E'$ and $E''$ are plotted as a function of time, during a steady shear experiment at 10 Hz and 6.7% strain (this data was obtained concurrently with the SAXS data in Fig. 4). This shows a two-step process of deformation of the lattice, an initial fast process followed by a much slower one. Quantitative analysis of this data is hampered by the lack of data points during the initial rapid process. Nevertheless, we speculate that these processes can be assigned as follows. The fast initial process might correspond to the rotation of misaligned grains with respect to the shear direction. The slow process would then be due to a steady slight increase in the perfection of lattice order *within* grains as time progresses. This is possible because the strain is high enough to produce non-linear viscoelastic flows.

The microscopic deformation of a sample with the rods oriented normal to the shear axis was also correlated to the macroscopic strain. Representative data from a strain experiment at 1 Hz and 6.7% strain is shown in Fig. 6. The data is presented as a contour plot from a stack of one-dimensional intensity profiles as a function of time, increasing from top to bottom. Intensity profiles were recorded in 100 frames of 10 ms duration, averaged over 100 cycles. Here the acqusition of SAXS data was not triggered with respect to the applied strain waveform. Nevertheless, Fig. 6 shows a sinusoidal variation of peak position with strain. Both first and second order reflections move out with increasing time during the first half of the cycle, and then recover to their initial value at the end of the cycle. In this case, $q^*$ varies by $\pm 4.8\%$ with respect to its mean value. This is not as large as the applied strain. Since we are deforming the lattice parallel to its repeat direction, this directly indicates a non-affine deformation. We suggest that this is due to the take-up of strain by misaligned grains, i.e. those in which the cylinders are misaligned with respect to the shear direction.

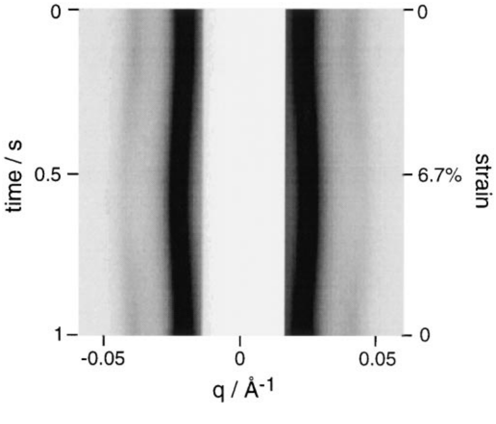

Fig. 6. Contour plot of SAXS profiles for the sample with rods normal to the shear direction, for one cycle of shear at 1 Hz (6.7% strain) (data shown are an average over 100 cycles).

Our results are not in accord with those of Odell and Keller [6]. For a deformation perpendicular to the cylinders, they found an affine deformation up to 20% strain, whereas we find non-affine behaviour at 6.7% strain. They reported affine behaviour up to 3% strain for extensions parallel to the cylinders and we observe non-affine behaviour at 6.7% strain. However, there are important differences in the samples and deformation procedures. First, the experiments of Odell and Keller were performed in uniaxial extension, whereas we apply oscillatory tensile deformation. It is possible that if the frequency of oscillatory deformation is faster than the microscopic relaxation time, the polymer cannot respond in an affine manner. In contrast, drawing can be a slow process, enabling the polymer chains to respond to the strain and for the sample to deform affinely. Second, there is a difference in microstructure between our copolymers and those studied by Odell and Keller. Their triblock copolymers contained a PB mid-block whereas in our Kratons, the midblock is hydrogenated polybutadiene with a random distribution of 1,4- and 1,2-units giving poly(ethylene-*co*-butylene) which is less rubbery than poly(butadiene) (based on comparison of elongation at break) [15], and consequently appears to be less able to undergo affine deformation.

## 4. Summary

A triblock copolymer forming a hexagonal-packed cylinder structure has been subjected to oscillatory elongational shear, and simultaneous SAXS/rheology experiments enabled the deformation of the lattice to be correlated to the macroscopic applied strain, to a time resolution of 2 ms. Samples in which the cylinders were parallel or perpendicular to the strain direction were investigated. In both cases, for the small strains investigated (7%), the lattice was found to deform in phase with the applied strain, although the stress was out-of-phase. However, the deformation was highly non-affine as the relative change in lattice spacing was significantly smaller than the applied strain. This non-affine behaviour is ascribed to the reorientation of misaligned grains. Rheology data obtained concurrently with the SAXS experiments indicate a two-step relaxation process, consistent with this picture, i.e. an initial fast process of grain reorientation followed by a slower process due to the increase in lattice order within grains.

## Acknowledgements

I.W.H. and A.J.R. are grateful to EPSRC for support via grant GR/K56117 for the rheometer. C.S. was supported by a Case award with Akzo-Nobel Chemicals. We thank Shell Chemicals for the gift of the Kraton copolymer.

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