

## On the Creation and Characterization of Super-Tailor Made Materials: Superlamella

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**Abstract:** Diblock Copolymers, with their ability to form nanoscale microphase separated structures have great potential to show interesting optical and transport properties. However, the obtained structures of these materials are usually polygrain in nature. That is, the microstructure orientation does not usually persist over appreciable distances, but instead changes in direction. Here, we present a technique for extending a single grain over macroscopic distances.

### Introduction

Block copolymers are known to form nanoscale microphase structured materials at temperatures below the order-disorder transition (ODT). These copolymer structures can be tailor made by controlling the block lengths and chemical composition. Like in crystalline materials (e.g., metals), such structures form “grains,” within which the ordered structure has the same orientation, but outside of which the material has the same structure, but different orientation. Therefore, the bulk material is isotropic in spite of the anisotropic microstructure. Typical grain sizes in low molecular weight diblock copolymers are on the order of 0.5 microns<sup>1</sup>. However, to achieve the full potential of these materials, e.g., as optical materials<sup>2</sup>, highly aligned or single grain materials (superlamella) may be advantageous. Shear and flow have been used to align diblock copolymers<sup>3,4</sup>. In this work, we introduce a new method to create highly aligned, single grain lamellar diblock materials called “superlamella.”

Superlamella are created by a process for block copolymers called “zone heating.” In this process, we manipulate the ordering process of a lamellar diblock copolymer using a surface and a temperature gradient. By doing so, we are able to create single grain materials of large size, “super-tailor-made” materials. In addition, we improve our understanding of how to manipulate nanoscale structures.

## Experimental Methods

A block copolymer polystyrene-*block*-polyisoprene (SI) was prepared by living anionic polymerization with *sec*-butyllithium as an initiator and cyclohexane as a solvent. By GPC, the resulting diblock copolymer was measured to have a polystyrene (PS) block molecular weight of  $1.12 \times 10^4$  and a polyisoprene (PI) block molecular weight of  $1.46 \times 10^4$ . In both cases, the polydispersity was ( $M_w/M_n$ ) is less than 1.05. By X-ray scattering and TEM, this block copolymer is known to have a lamellar structure, consistent with its nearly 50/50 composition<sup>5</sup>. The polymer was dissolved in toluene (about 5 wt %) along with a small amount of BHT (less than 1% of the polymer weight) as an antioxidant. Films were prepared from the filtered solution by casting, followed by annealing at high temperature under vacuum to remove residual solvent.

Polystyrene coated glass was prepared according to the procedure described by Philipse and Vrij<sup>6</sup>. Quartz glass blocks were first reacted with 3-methacryloxypropyltrimethoxysilane (TPM) in a mixture of ammonia/water (25% ammonia) and ethanol, rinsed with ethanol, then dried. The glass blocks were then placed in toluene, and polystyrene was polymerized with AIBN as an initiator. Some of the growing polymer chains reacted with the C-C double bond in the TPM layer attached to the silica surface during

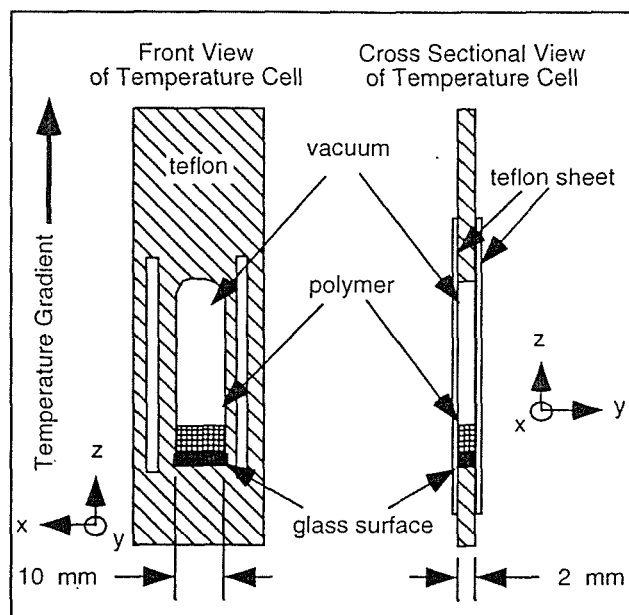


Figure 1 Schematic of the cell used to hold polymer sample. The surfaces on either side are exposed to thin sheets of Teflon.

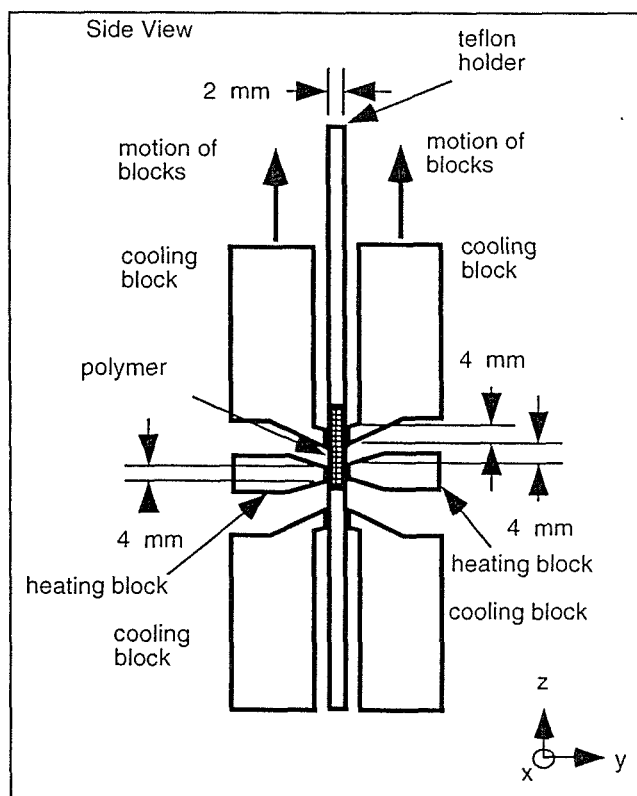


Figure 2 Schematic of zone heating device used for applying temperature gradient. Oz is parallel to the temperature gradient, Oy is parallel to the film norm, and Ox is parallel to the film surface.

polymerization, and in this way, a PS layer was formed on the glass surface.

Zone heating is described elsewhere<sup>7,8</sup>. The treated glass and the block copolymer were arranged in the sample cell as shown in Figure 1. Teflon sheets were placed on either side of the sample cell. After annealing the sample in the sample cell (to remove air), the sample was mounted between a sandwich consisting of a heating block surrounded by a cooling block on either side, as depicted in Figure 2. These blocks were then moved at a rate of 25 nm/sec from the point where the heating block was below the glass surface to the point where the cooling block was above the top of the polymer. The heating block was maintained at 210 °C by electric cartridge heaters and the cooling block at about 5 °C by circulating ethylene glycol/water. Using this device, we were able to apply a slowly moving temperature gradient of about 30 °C/mm.

SAXS was measured with a two dimensional imaging plate (IP) and a MAC science X-ray generator with point focus optics<sup>9</sup>. Scattering intensity is given as a function of the scattering vector  $\mathbf{q}$  where  $q=4\pi/\lambda \sin(\theta/2)$  where  $\lambda$  is the wavelength of the X-rays and  $\theta$  is the angle between the scattered X-rays and the incident beam. Background scattering intensity, in contrast to usual practice, was not subtracted. The incident beam had a diameter of about 0.5 mm in the sample.

## Results and Discussion

Figure 3 shows the X-ray scattering pattern from the block copolymer close to the glass surface. In this case, the beam is about 0.5 mm from the glass surface, and only irradiates the polymer sample. That is, the beam is not further narrowed by being blocked by the glass surface. Since the scattering from peaks of different order substantially differ in intensity, i.e., the first order peak was over 100 times stronger than the second order peak,

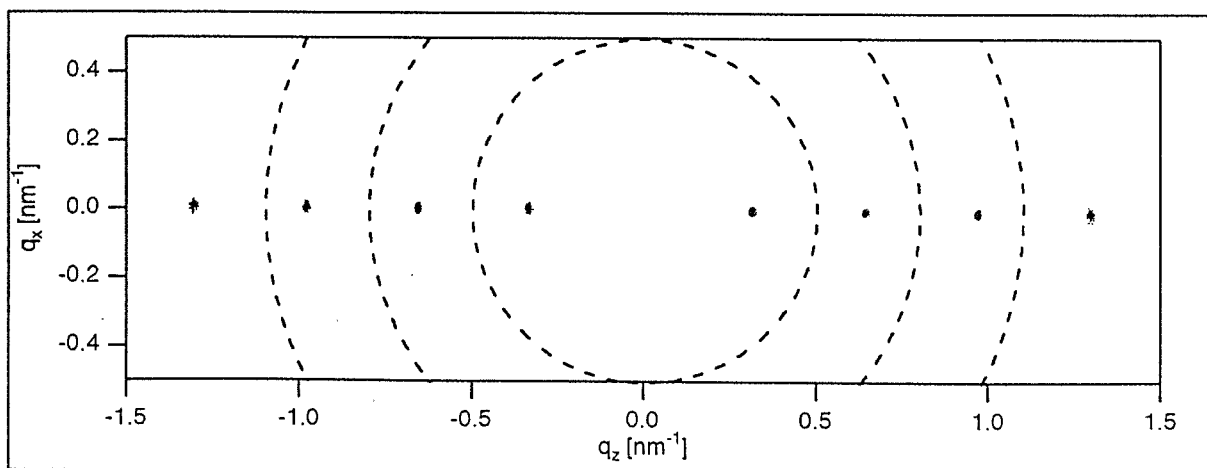


Figure 3. Two-dimensional (2-D) X-ray scattering pattern taken with the incident beam along the y-axis. Higher order intensities are enhanced via the procedure described in the text.

the data was treated in the following way. The scattering in the ring from  $0 < q < 0.5 \text{ nm}^{-1}$  is multiplied by one. The value  $q$  is the magnitude of the scattering vector  $\mathbf{q}$ , i.e.,  $q^2 = q_x^2 + q_z^2$  where  $q_x$  and  $q_z$  are the scattering vectors in the  $x$  and  $z$  directions respectively. The scattering in the ring from  $0.5 < q < 0.8 \text{ nm}^{-1}$  is multiplied by 200, and the scattering in the ring from  $0.8 < q < 1.1 \text{ nm}^{-1}$  is multiplied by 400. Scattering in the ring  $q > 1.1 \text{ nm}^{-1}$  is multiplied by 16000. In this way, one readily can observe higher order scattering peaks from the block copolymer. Circles drawn with dashed lines in the figure correspond to the limits described above. From Figure 3, we observe four orders of diffraction, an indication of large grain size. Furthermore, the scattering peaks are sharp and point-like, with nearly the same shape as the incident beam. Therefore, there seems to be no scattering from grains with different orientations. To within the resolution of the scattering instrument, the scattering corresponds to the ideal scattering from a single lamellar grain with its lamellar normal perpendicular to the glass surface and parallel to the applied temperature gradient. This single grain persists over a distance of at least 0.5 mm from the glass surface.

## Conclusions

Via the zone heating process, the nucleation and growth of block copolymer microstructure can be controlled and macroscopic grains can be formed.

Further results will be discussed at the meeting.

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