

## DIBLOCK COPOLYMER THIN FILMS – PHYSICS AND APPLICATIONS

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**abstract:** Block copolymers have seen a significant increase in interest over the past few years. The unique properties of such polymers make them an ideal candidate for a number of technological applications. Recent efforts aimed at combining the self-assembling nature of block copolymers with semiconductor thin-film processing techniques have proven extremely fertile, opening a novel field of block copolymer nanolithography. In the current paper an attempt is made to review some of the more important techniques and results (developed in our group and elsewhere) in the field of diblock copolymer thin films, with emphasis on technological applications and physical properties. In particular we report the experimental observation of a two dimensional order-disorder transition in a thin film of diblock copolymer.

### Introduction

Diblock copolymer molecules are composed of two covalently bonded blocks of polymers that are immiscible in bulk. Due to the constraints imposed by molecular connectivity, macroscopic phase separation is not possible; instead the polymer exhibits microphase separation on a molecular scale, where micelles (or microdomains) of the minority polymer block form within a matrix of the majority polymer block. By tailoring the ratio of the block lengths within the copolymer molecule one can produce microdomains shaped like spheres (in a body centered cubic lattice), cylinders, gyroids or lamellae for bulk samples. In terms of thin film morphology, one can obtain triangular lattices of spheres (for highly asymmetric blocks) or in-plane arrays of cylinders (if more-symmetric, cylinder-forming blocks are used); the gyroidal morphology has not been reported in thin film samples. The lamellar morphology has not seen much interest in terms of thin films.

### Experimental

Very thin polymer films can be obtained by a variety of techniques, the most commonly used being spin coating from a dilute solution (a method borrowed from the semiconductor industry). Film thicknesses that range from few nanometers to tens of micrometers can be obtained by this method. For a diblock copolymer film, the thickness corresponding to a single layer of microdomains (monolayer) is usually on the order of a few tens of

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nanometers and scales with the molecular weight of the polymer. Other methods used for obtaining such thin polymer films include dip coating and flow coating.

Thin films of diblock copolymer require specific techniques for characterization. Methods commonly used in bulk samples (such as small angle x-ray scattering) are inapplicable for thin films, due to the insufficient amount of polymer present. For thin films, therefore, the in-plane structure must be determined by direct imaging techniques. These methods, developed partly by our group, include FE-SEM (field emission scanning electron microscopy – in order to use this technique, the samples must be previously prepared, either by preferential removal of the minority block followed by etching, resulting in topographic contrast [1,2], or by staining one of the blocks, resulting in chemical contrast [3]) and TM-AFM (tapping mode atomic force microscopy, which relies on the existence of a mechanical contrast between the two blocks, such as a different elastic constant. This is the case if the minority block is glassy while the majority block is rubbery at the imaging temperature [3]). Besides its simplicity, the latter method has the advantage of being non-destructive, which allows dynamical studies. It has therefore become our method of choice. A micrograph obtained by TM-AFM is presented in Fig. 1. The out-of-plane structure can be determined by TEM (transmission electron microscopy) or by DSIMS (dynamic secondary ion mass spectroscopy [4]).

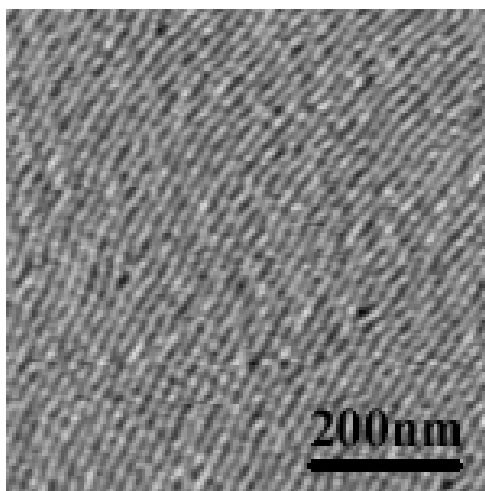


Fig. 1: TM-AFM micrographs of a polystyrene-*b*-poly(ethylene-*alt*-propylene) (PS-PEP) copolymer, forming glassy PS cylinders embedded in a rubbery matrix of PEP.

## Results and Discussion

### Applications

Technological interest in thin films of diblock copolymer has seen a significant increase after their use as self-assembled lithographic templates for nanometer-scale lithography was demonstrated by several groups [1,5,6]. The most common method used today for fabricating feature sizes on the order of several nanometers is electron beam lithography, a very expensive and slow process. Imprint stamping has seen recent interest as an

economical alternative to electron beam lithography. When simple periodic features are desired, diblock copolymer lithography seems to be the method of choice for nanometer-scale fabrication. This technique allows the transfer of nanometer-scale patterns that self-assemble in the polymer film to arbitrary substrates. Arrays of metal dots (if a sphere-forming polymer is used as the template) or metal lines (if a cylinder-forming polymer is used instead) can be obtained. A periodic array of metal dots can be used for magnetic information storage, leading to a significant increase in data density. Prototype hard disks have already been manufactured by this technique [7,8], and commercial products are on the way.

Most practical applications of this lithography technique, however, are strongly dependent upon the degree of order preexisting in the polymer film. For metal dot arrays, for example, one should be able to address each metal dot independently, while for metal wires one would like to have long, straight, continuous wires running across the sample. It is essential therefore to develop methods for aligning polymer microdomains in thin films. While for bulk samples, various degrees of alignment have been achieved (by means of shear, flow or sweeping temperature gradients), in thin films long range order has been notoriously difficult to attain. For sphere-forming diblock copolymers, alignment with straight substrate features has recently been shown to work [4,9]. For cylinder-forming diblock copolymers, alignment with strong electric fields has been achieved [10]. Unfortunately, the electric fields required are so strong that they can only be extended to very small areas of a sample (few square microns). A lot of recent work has been reported in this area, and the problem of alignment over large areas seems to be tractable, at least for thin films of cylinder-forming diblock copolymers [11].

### **Scientific Importance**

Besides their commercial uses, thin copolymer films are of scientific interest due to their two-dimensional crystalline nature, which suggests an obvious application as model systems for real two-dimensional atomic crystals (in the case of sphere-forming polymers) or smectic liquid crystals (in the case of cylinder-forming polymers). Several investigations have been carried out regarding the mechanisms responsible for pattern coarsening and alignment occurring during the annealing phase [3,4,9], leading to novel ideas in the field of pattern formation.

A recent experiment carried out by our group employed a sphere-forming diblock copolymer film for studying the melting phase transition (or, for our system, the order-disorder transition) in two-dimensional crystalline systems. It is interesting to note that two dimensional phase transitions of the sort observed here are rare, and most of the previous experimental realizations were achieved in suspended colloidal systems, which suffer from limited resolution and finite sample effects. In contrast, our approach of using a thin diblock copolymer film provides a practically infinite two-dimensional specimen. Our sample consisted of a sphere-forming polystyrene-*b*-poly(ethylene-*alt*-propylene) (PS-PEP) diblock copolymer layer, where the molecular weights of the two blocks were 3300 g/mole (PS) and 23100 g/mole (PEP) [12]. PS formed spherical microdomains embedded in a PEP matrix. The resulting triangular lattice had a lattice spacing of approximately 25 nm. After an annealing step above the glass transition temperature of both blocks but below the order-disorder temperature (ODT), the sphere pattern coarsened and developed well-defined

grains, with the grain size dependent on annealing conditions. For a typical annealing time of 1 hour at 70°C, the grain size was on the order of 1 micron, or 40 lattice spacings.

The experimental setup (shown schematically in Fig. 2) involved a temperature gradient stage onto which the polymer sample was annealed in an inert atmosphere. Temperature stability of  $\pm 0.1^\circ\text{C}$  with absolute temperature accuracy of  $2.0^\circ$  was obtained on the gradient stage by using dedicated temperature controllers in conjunction with low thermal mass Peltier heaters. The sample was placed across the gradient and annealed for a specified time (on the order of a few hours), such that each point along the sample corresponded to a different annealing temperature. In particular, the hot end of the sample was annealed above, while the cold end was annealed below the bulk ODT. Subsequently the sample was rapidly quenched by a brief immersion in liquid nitrogen, and allowed to equilibrate with room temperature. TM-AFM micrographs were acquired at various positions across the sample (corresponding to various annealing temperatures).

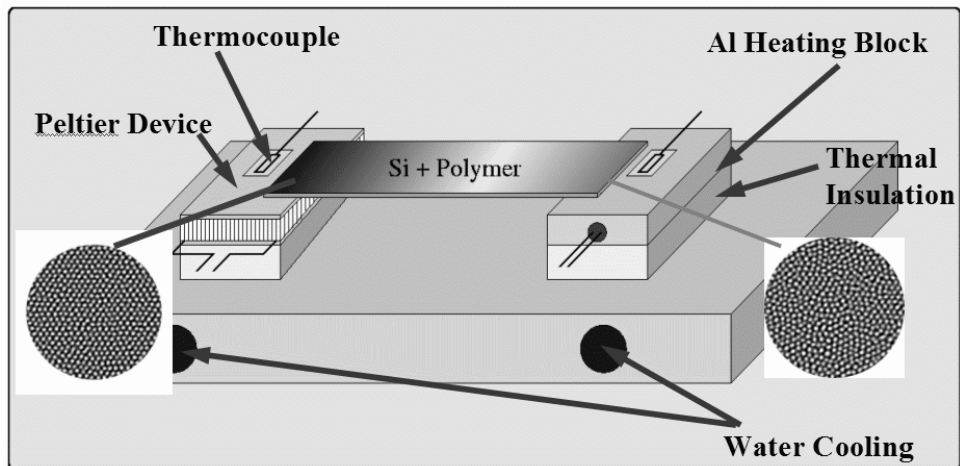


Fig. 2: *The gradient stage setup.* The temperatures at the two ends of the sample (silicon wafer covered with the polymer layer) are controlled within  $0.1^\circ\text{C}$ , the temperature gradient being constant through the rest of the sample. Each point along the sample corresponds to a different annealing temperature. The hot end is annealed above ODT (disordered lattice - inset right) while the cold end is annealed below ODT (ordered lattice - inset left). The gradient stage is placed in an inert nitrogen atmosphere during the annealing.

From the resulting micrographs, translation and orientation correlation functions were determined and the corresponding correlation lengths calculated as a function of the annealing temperature (it is important to note here that the orientation correlation length is a robust measure of grain size). At the same time, the number of topological defects (dislocations and disclinations) in the lattice was calculated. Orientation correlation lengths (and, corresponding, grain sizes) were seen to abruptly collapse as temperature was increased past a certain value ( $127^\circ\text{C}$ ), corresponding to the thin film ODT. At the same value of the temperature, the density of topological defects increased dramatically, proving that the observed phase transition was defect-mediated. Fig. 3 shows the dependence of the correlation lengths, and of the density of disclinations, on temperature.

It is interesting to note that the thin-film ODT and the bulk ODT were extremely close to each other (within the experimental uncertainty). One would be tempted to expect that the

crystallographic differences between the body-centered-cubic bulk configuration and the triangular plane lattice, in conjunction with the substrate interactions, would induce a shift in the ODT as the film thickness approaches that of a monolayer. We currently have no convincing explanation for this phenomenon.

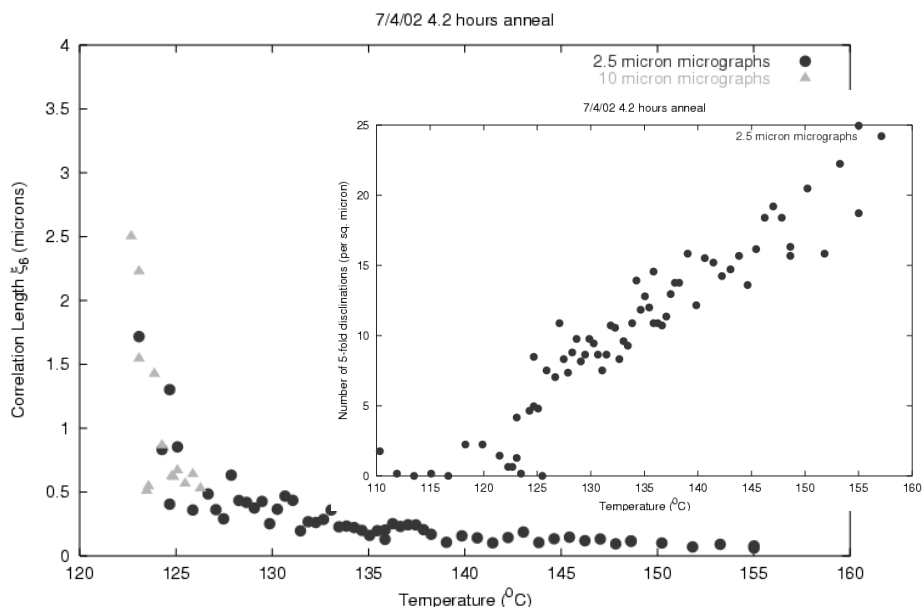


Fig. 3: The temperature dependence of the orientation correlation length (and correspondingly, of the grain size).

The collapse of the correlation length above 127°C corresponds to the thin film order-disorder transition. Data points were obtained by two different techniques [13], hence the different symbols on the graph. Around the same temperature the density of topological defects shows a dramatic increase (inset: the density of disclinations).

## Conclusions

We presented a review of some of the important applications of diblock copolymer thin films. We described, as well, an experimental setup which allowed us to capture and image a whole phase transition on a single diblock copolymer sample. The order-disorder transition we observed is rare in two dimensions, and our setup provides a new system for studying such phase transitions.

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