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STUDY THE ORDER OF MORPHOLOGY SELF-ASSEMBLED TRIBLOCK COPOLYMER THIN FILMS BY FFT OF THE AFM IMAGES

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ABSTRACT

A variety of block copolymer thin films with well-ordered nanostructures, which can be employed as templates for nanotechnologies including nanostructure membranes, nanoparticle synthesis, photonic crystal, and high-density information storage media, can be realized simply and at low cost by self-assembly. Long range ordering of morphology is paramount to realize applications of self-assembled block copolymer thin films in nanotechnologies. A better understanding of what parameters affect the ordering process can lead to the production of highly ordered arrays of nanostructures.

In this paper, in order to effectively analyze the improvement in ordering, the Fast Fourier transform (FFT) analysis of the AFM images is used. Fast Fourier transform provide a mathematical analysis of the image that is similar to producing a diffraction pattern. From this “diffraction pattern” information on the order in the system can be obtained. Moreover, calculating an ordering parameter from the FFT provides a quantitative measure of the order present in the polymer template. The order parameter is calculated using equations which were tested against a manufactured perfect system and imperfect system to ensure that a perfect system would provide an order parameter of 1 and an imperfect system would create an order parameter of 0. The results show that the method is reasonable and effective to analyze the improvement in ordering that is achieved by using solvent annealing. Furthermore, the method can be used to understand the parameters in triblock copolymer thin film self-assembly process that create the most well ordered system.

Keywords: order parameter, nanostructure, self-assembled, block copolymer

1. INTRODUCTION

Block copolymers used in industrial applications were traditionally used as adhesives or for their mechanical properties. More recently triblock copolymers have shown promise for a wide range of applications in nanotechnology, because triblock copolymers can spontaneously form microphases on the length scale of 10 to 100nm. One possible application for triblock copolymers that exhibit nanoscale features is to use them to create highly ordered templates. A variety of self-assembled block copolymer thin films can be employed as templates for many nanotechnologies, such as nanostructure membranes [1], nanoparticle synthesis [2], photonic crystal [3, 4], and high-density information storage media [5] and so on. A major limitation of moving this technology from the laboratory to a commercial application is the inability to achieve long range ordering in the template [6-8]. To make full use of this technology, controlling the orientation of the microphases is imperative. However, controlling how the microdomains are oriented is key to utilizing triblock copolymers to pattern nanoscale features. So a better understanding of what parameters affect the ordering process can lead to the production of highly ordered arrays of nanostructures.

Ordering of the microphases can be determined by examination with atomic force microscopy (AFM) in tapping mode. In tapping mode the lateral forces exhibited on the tip are dramatically reduced compared to the forces encountered when in contact mode. Therefore, tapping mode is ideal for imaging soft samples such as polymers [9]. Data collected from the instrument can be analyzed using a freeware AFM analysis program. This program provided a method for image resizing, zooming, and fast Fourier transform analysis [10].

The Fast Fourier Transform (FFT) analysis of the AFM images of the template provides a view of how well ordered the

polymer templates are. Fast Fourier transforms provide a mathematical analysis of the image that is similar to producing a diffraction pattern. The doughnut shape of the FFT represents only local ordering, where all the cylinders are a fixed distance apart but are oriented randomly. With the increasing of ordering, the doughnut will change into arc. The more well-ordered system, the shorter the length of arc is. At last, the arc will change into diffraction dot. However, a more quantitative method for describing the order is needed to quantify the effectiveness of solvent annealing to induce long range order in the triblock copolymer thin film templates.

The present paper shows that calculating an ordering parameter from the FFT provides a quantitative measure of the order present in the polymer template. The order parameter is calculated by comparing experimental results with a model of a perfect system. A completely unordered system has an order parameter of 0 while a perfectly ordered system has an order parameter equal to 1. Using the quantitative method, we effectively analyze the improvement in ordering induced by solvent annealing.

2. EXPERIMENTAL

2-1. Materials

The poly (styrene-ethylene/butylene-styrene) (SEBS) triblock copolymer coded as Kroton G-1650 was a commercial product of Shell Company. Its molecular weight, polydispersity and styrene content are 7.5×10^4, 1.36 and 27% respectively. Two solvents, xylene, a good solvent for both polystyrene (PS) and poly (ethylene/butylene) (PEB) blocks, and cyclohexane, a selective solvent for PEB blocks, are used in this work.

2-2. Preparation of samples

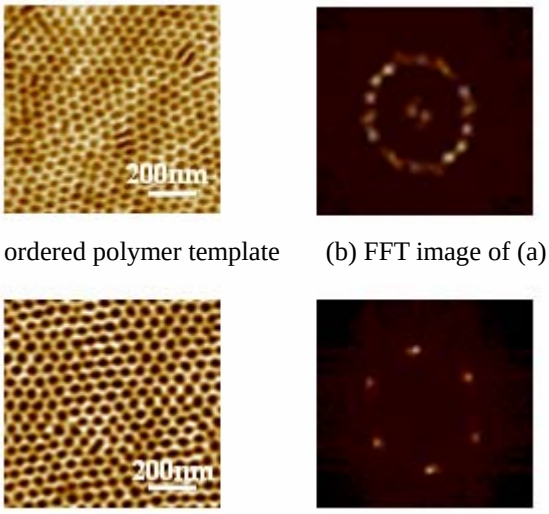
The SEBS powders were first dissolved into xylene to prepare 0.3wt% solution. Film was cast from 0.3wt% solution onto a freshly cleaved mica substrate and then dried under ambient conditions. A piece of filter paper was put into the Petri dish to cover its bottom. The sample was put on the filter paper. After adding 500 μl pure solvent xylene on the filter paper (not on the substrate), the dish was sealed in a closed vessel and kept at room temperature. The sample was taken out at intervals of 0.25h and measured after drying for few minutes in ambient air. In order to make up for loss of solvent, 200 μl pure solvent xylene was added on the filter paper each time before the sample was put inside the Petri dish for fumigating again.

2-3. Characterization

Digital Instrument multimode SPM III atomic force microscopy (AFM) was performed in Tapping-Mode. The height and phase images were recorded simultaneously under a moderate tapping conditions (set-point ratio $r_{sp}\approx0.70$) with a free amplitude of 80±10 nm and scan speed of 1.0 Hz. The operating frequency was readjusted after engaging the tip on the surface such that the operating frequency was kept on the low-frequency side of the resonance during the imaging. Commercial silicon cantilevers with spring constant of about $50Nm^{-1}$ were used.

3. RESULTS AND DISCUSSIONS

Figure 1(a) shows the AFM image of a non ordering polymer template. Figure 1(b) is a FFT of Figure 1(a). The toroidal shape of the FFT indicates only local ordering, as there is no net confinement of the reciprocal space vectors associated with the real space structure and all the cylinders are a fixed distance apart but are oriented randomly. Figure 1(c) and Figure 1(d), represent a more well-ordered system where the cylinders are all a fixed distance apart, and are positioned at exact points relative to each other.



(a) non ordered polymer template (b) FFT image of (a)

(c) well-ordered polymer template (d) FFT image of (c)

Fig.1. AFM images of self-assembled triblock copolymer thin film

A computer program was written that converts the FFT image (Figure 2 and Figure 3) into a plot of the radial average as arbitrary intensity vs. distance from the center in pixels. This provides an average intensity of all points at x distance from the center. This type of plot is often seen from small angle x-ray scattering. From the radial average plot, the distance with the maximum intensity peak is identified. At the maximum intensity distance the azimuthal average of the distance ± 5 pixels is calculated and plotted as a function of intensity vs. azimuthal angle. From this plot the order parameter is calculated using equation 1 where $I(q,\phi)$ is the arbitrary intensity at a distance q and angle ϕ from the center, and $P_2(\cos\phi)$ is

defined in equation 2. These calculations were tested against a manufactured perfect system and imperfect system to ensure that a perfect system would provide an order parameter of one and an imperfect system would create an order parameter of 0.

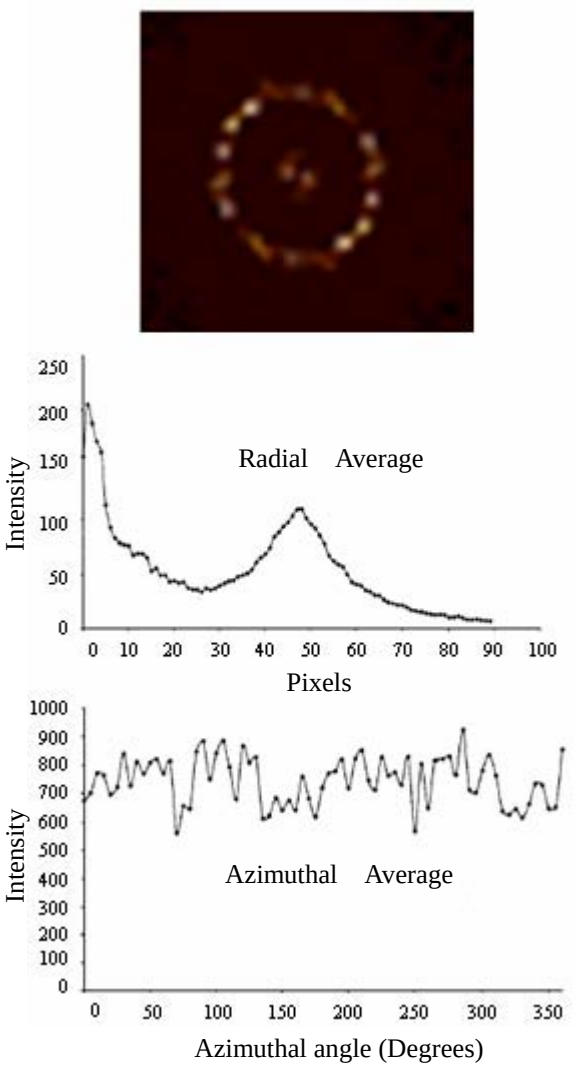


Fig.2. FFT of an unordered polymer template and its corresponding radial and azimuthal averages

$$< P_2(\cos\phi) >= \frac{\int I(q,\phi) P_2(\cos\phi) \sin 3\phi d\phi}{\int I(q,\phi) \sin 3\phi d\phi} \qquad (1)$$

$$P_2(\cos\phi) = \frac{1}{2}(3\cos^2 3\phi - 1) \qquad (2)$$

Using these equations the order parameter, the calculated order parameter fro the unordered polymer template in Figure 1(a), is 0.332. The calculated order parameter for the highly ordered polymer template in Figure 1(c) is 0.913. It is noted that this functional form for the distribution of reciprocal space vectors is preliminary; further analysis which expands the reciprocal space structure in terms of cylindrical harmonics would provide an alternative method.

The error for the order parameter calculation is determined by calculating the order parameter for the 6 section of 60 degrees each centered at each peak and averaging the order parameters from each section to determine the overall order parameter.

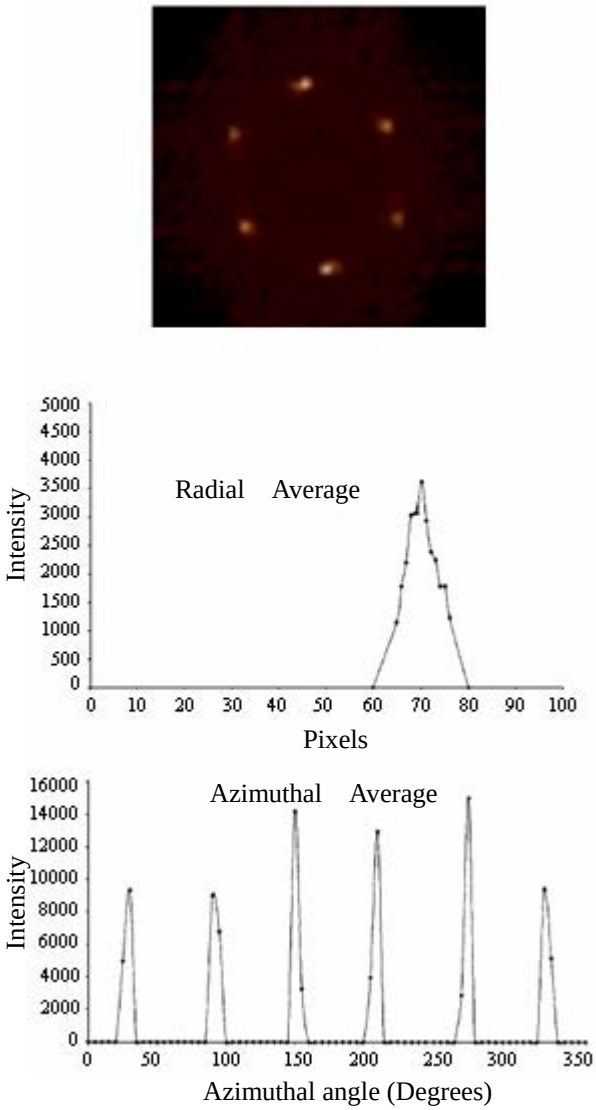


Fig.3. FFT of the ordered polymer template and its corresponding radial and azimuthal averages

Figure 4 shows that the evolution of the order parameter at different annealing times in the templates. This evolution of long range order induced by solvent annealing is compared to the long range order induced by temperature annealing. Figure 4

shows that the order that is achieved when the templates are prepared by high temperature annealing on a flat surface as well as templates prepared by solvent annealing are able to achieve an improvement in order parameter. During 120 minutes annealing time, templates that are prepared by high temperature annealing were able to create templates with order parameters approaching 0.41 and templates that are prepared by solvent annealing were able to create templates with order parameters approaching 0.95. The result shows that solvent annealing is more efficiently in improvement of ordering than high temperature annealing.

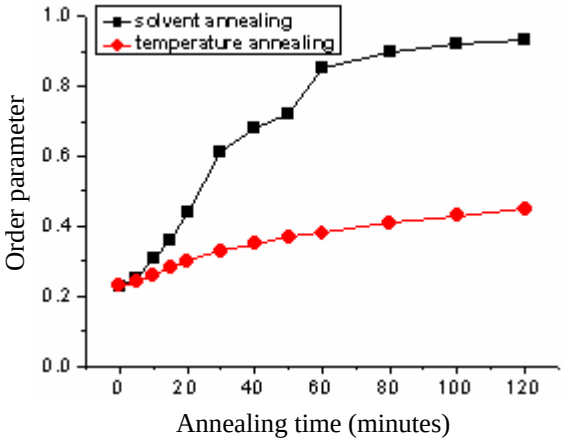


Fig.4. Diagram depicting the order parameter of triblock copolymer template that has been ordered by solvent annealing and temperature annealing

With this data demonstrates that solvent annealing improves the long range order, it is beneficial to provide further insight into the solvent annealing process and its impact on the diffusivity of the polymers in the triblock copolymer thin film. The development of long rang order involves the diffusion of polymer chains, either individually or collectively through the polymer matrix. As a result the development of long range order, an understanding of the diffusion of the polymer under different annealing conditions can be obtained.

4. CONCLUSIONS

It is important from an application driven stand point to improve the long range order of the triblock copolymer templates. However, the level of improvement that is required is dependant on the application. A balance must be achieved between the maximum order and cost effective processing. Therefore, it is important to understand the parameters that allows for the tuning of the order parameter to create a system with the required long range order. Calculating an ordering parameter from the FFT of AFM images has been achieved in this paper, and it provides a quantitative measure of the order present in the polymer template. Furthermore, using the method, we have studied that the evolution of long range order induced by solvent annealing is compared to the long range order induced by temperature annealing. Compared with the improvement of ordering induced by high temperature annealing, this order parameter induced by solvent annealing is a significant improvement.

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