The block length effect of polymethyl methacrylate on surface morphology of polystyrene block polymethyl methacrylate copolymers

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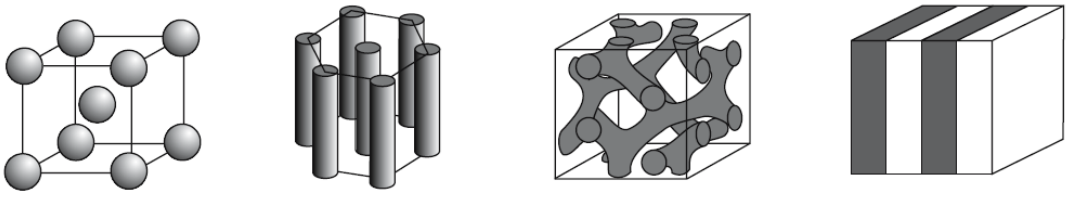
Abstract— *The effect of polymethyl methacrylate (PMMA) block length on the surface morphology of the two block copolymers (BCPs) was investigated by AFM using tapping mode. Two asymmetric polystyrene block polymethyl methacrylate (PS-b-PMMA) copolymers with different PMMA block lengths were synthesized by a novel combination technique; living anionic polymerization and hydroboration autoxidtion reactions. The molar mass of PS block was ($M_{W\,PS}$ = 90000 g/mol) and the molar mass of PMMA blocks were ($M_{W\,PMMA}$ =130000 and $M_{W\,PMMA}$ =180000 g/mol). Thin films of two asymmetric copolymers were prepared by solvent casting (10 mg/5 ml THF) on freshly cleaved mica. The results showed that phase separation do occur and equilibrium morphologies were observed. It was found that BCP with PMMA molar mass ($M_{W\,PMMA}$ =130000 g/mol) form parallel cylinders (stripes) oriented horizontally to the substrate. While BCP with PMMA molar mass ($M_{W\,PMMA}$ =180000 g/mol) form hexagonal ordered cylindrical oriented perpendicular and parallel to the substrate.*

Keywords— ***AFM, block copolymer, phase separation, polystyrene block polymethyl methacrylate, surface morphology.***

I. INTRODUCTION

Multiphase polymer system include a wide range of materials such as composites, block copolymers (BCPs), blends, alloys, and gels, have gained much interest due to their unique properties. Accordingly, characterization of the inter-phase and other properties are crucial for understanding the behavior of these materials.[1] BCPs are material in which dissimilar blocks are covalently bonded. Because of this dissimilarity between the copolymer blocks, phase separation and segregation would occur at different molecular aspects. Only BCPs can be defined as multiphase system having stable microstructures, even after many processing cycles.[2]

An important property of BCPs is their ability to self-assemble into periodic nanostructure.[3] Self-assembly of BCPs domains have several technological applications and is of great scientific interest. It is a phenomenon where the components of a system assemble itself spontaneously via an interaction to form a larger functional unit. This spontaneous organization can be due to direct specific interaction and/or indirectly through their environment. BCPs self-assembly have attracted considerable attention for many decades, because it can yield ordered structures in wide range of morphologies, including spheres, cylinders, lamellae and many other complex structures,[4] as shown in Scheme 1.



SCHEME 1: THE CLASSICAL BCPS MORPHOLOGIES, CUBIC PACKED SPHERES, HEXAGONAL PACKED CYLINDERS, DOUBLE GYROID, AND LAMELLAE[5]

Such structures are promising for applications in many fields of nanotechnology, such as surface pattering, lithography, templating for the fabrication of quantum dots, nanowires, magnetic storage media, nanopores, and silicon capacitors.[6] The self-assembly of BCPs is driven by a competition between the positive enthalpy of mixing of the respective block and the tendency of polymers to desire a random coil configuration. Under certain condition of the BCPs microphase separation into well defined domain structures occurs on the length scale of the respective blocks.[7]

BCP of polystyrene (PS) and polymethyl methacrylate (PMMA) (PS-b-PMMA) is one of the most studied system.[8-13] PS-b-PMMA copolymers have been used extensively to make templates for fabrication of nanostructured materials. PS and PMMA are frequently used as binary model systems to study thin film polymer structure formation, polymer-polymer and polymer-substrate interactions, and pattern formation and phase separation dynamic in polymer thin films.[14] PS and PMMA are immiscible components, hence they have a tendency of phase separation and on phase separation they form well defined domains. The total molar mass of the polymer and the fraction of each block determine the shape and the size of the phase separation domains.[15,16] Many studies[17-21] and reviews[22-25] on BCPs thin films have showed the effect of; annealing conditions, the role of substrate, film thickness, interfacial interaction, molar mass, block length of two blocks. To our knowledge, the effect of molar mass of PMMA on BCPs thin film has not been paid enough attention.

Living polymerization the most used methods to synthesize multiphase copolymers that due to the ability of sequence monomer addition to the living end of the polymer chain. Living anionic polymerization one of these methods used to produce block and other copolymer structures.[26,27] As result of the limitations of this method such as inclusive selection of the monomer as well as solvent no many polymers can be polymerized using this process.[7] To overcome these limitations, a combination of different polymerization techniques such as living anionic and hydroboration autoxidtion reactions gives the opportunity to synthesis multiphase copolymers with its dissimilarity. Hydroboration autoxidtion reactions were introduced by Chang and coworkers, they synthesis several blocks and graft copolymers based on polyolefin.[5,28,29]

Atomic forces microscopy (AFM) is one of the most effective techniques can be used to characterize BCP morphology. It is well known the importance of AFM as an analytical tool able to characterize surface morphology and heterogeneous systems.[30] AFM gives direct images of the structure from a small piece of a sample. Furthermore, AFM images depict the contrast of hard and soft domain of the sample. AFM in tapping mode has been used successfully in the interpretation of the morphology of polymer blends and BCPs.[31,32]

The aim has been to study the surface morphology of thin films of PS-b-PMMA copolymers with different PMMA molar masses using AFM. The technique used to synthesize these BCPs is a novel combination between living anionic polymerization and hydroboration autoxidation reactions. These BCPs were fully characterized in previous work using chromatographic analysis namely Liquid Chromatography at Critical Condition (LCCC) and Nuclear Magnetic Resonance (NMR).[15] The investigation whether the morphology of the BCPs adopt similar display to other systems synthesized with other techniques.

II. EXPERIMENTAL

2.1 Materials

The following solvents were used as received: cyclohexane (Sigma-Aldrich, HPLC grade), heptane (Sigma-Aldrich, HPLC grade), methanol (Acros, 99.85%), n-butyllithium (Aldrich, 15% in hexane), 0.5 M 9-BBN (Sigma-Aldrich in THF), allylchlorodimethylsilane (Sigma-Aldrich), PS and PMMA standards (Polymer Laboratories), oxygen gas (Afrox), styrene (Plascon Research), toluene (Analytical Reagent, 99.9%), and THF (Sigma-Aldrich, 99.9%).

2.2 Polymer synthesis

BCPs were synthesized using combination of two polymerization techniques; living anionic polymerization and hydroboration autoxidtion reactions. First block PS terminated with allylchlorodimethylsilane was prepared using living anionic polymerization (styrene (40 mmol), butyllithium (0.69 mmol) in 10 mL toluene), The molar mass of the PS used was ($M_{W\ PS}$ = 9000 g/mol and had a PDI of 1.2). For the synthesis of second blocks PMMA were prepared using hydroboration autoxidation reactions of allyl functional PS. The molar mass of the PMMA blocks were ($M_{W\ PMMA1}$ = 130000 and $M_{W\ PMMA2}$ = 180000 g/mol). Full details of the synthesis and characterization of these blocks are described in reference.[15] Table 1 lists the two BCPs used in this study.

TABLE 1
CHARACTERISTICS OF BCPS USED IN THIS STUDY

BPCs	$M_{W\ PS}$ (g/mol)	$M_{W\ PMMA}$ (g/mol)
BPC1	90000	130000
BPC2	90000	180000

Size exclusion chromatography (SEC) instrument used in this study was a Waters (1515 isocratic HPLC pump; Water 717 plus auto sampler; Waters 2487 dual λ absorbance detector, and Waters 2414 refractive index (RI) detector at 30 ^{o}C).

2.3 Film preparation and AFM measurements

Thin films of BCPs for AFM measurements were prepared by solution casting method on mica chips (1 x 1 cm^{2}). One drop of (10 mg/5 mL) BCP in THF was placed on freshly cleaved mica chip and then covered with another mica chip to spread the solution between the two chips. The two mica chips were slid against each other in opposite direction to form an thin film. The thin films bock copolymers were annealed at 120 ^{o}C under vacuum for 24 h.

AFM images were obtained on a multimode AFM model no. MMAFMLN, with a Nanoscope IIIa controller from Veeco, operating in tapping mode, and using a low resonance frequency silicon cantilever with a resonance frequency of about 60 KHz and a spring constant of k=50 N/m. The scan rate was set in the range of 0.5 to 0.7 Hz. The substrate containing the polymer samples was attached to the sample holder with double sided adhesive tape. All experiments were carried out under ambient conditions.

III. RESULTS AND DISCUSSIONS

SEC result of the BCP1 is shown in Fig 1. SEC chromatograms of unpurified BCP1, the first peak is corresponding to PS block, which has low molar mass comparing to BCP1 in second peak, purification process was applied using solvent extraction to remove unreacted PS block. A mixture of (Heptane/Cyclohexane) was used as solvent for PS and nonsolvent for BCPs. The results were not conclusive due to co-precipitation of PS block, as shown in Fig 2 for the BCP1. A presence of shoulder at low molar mass in nonsoluble fraction is seen. This indicats the presence of traces of PS block that co-precipitated with the PS-b-PMMA copolymer. Similar result was obtained for the BCP2 (not shown here).

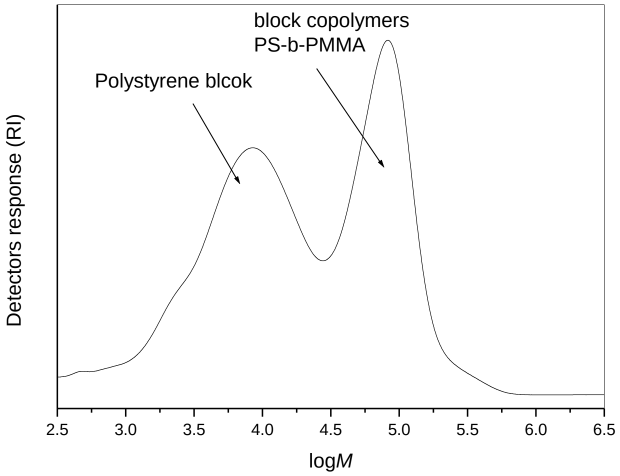


FIGURE 1. SEC OF BCP1, BEFORE SOLVENT EXTRACTION.

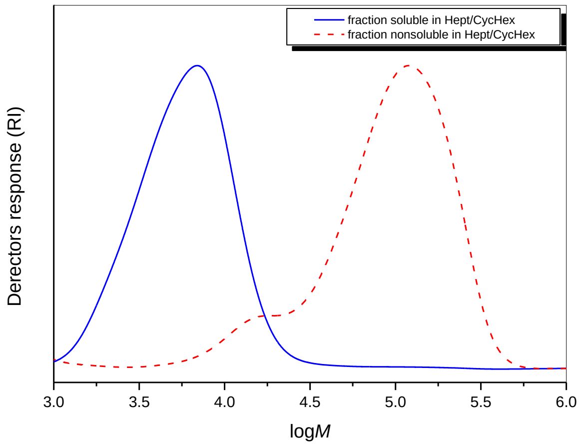


FIGURE 2. SEC OF BCP1, AFTER SOLVENT EXTRACTION (HEP/CYHEX).

3.1 Morphology study

Fig's 3 and 4 show topographic (height) and phase images of thin films of BCP1 and BCP2, respectively. In practice the height and phase images are recorded simultaneously. On homogeneous materials, phase imaging provides higher contrast for morphological features. Phase images for heterogeneous materials often reflect differences in the properties of individual components, and are extremely useful for compositional mapping in blends, copolymers, composites, etc. The AFM phase images fig's (3b,3d), and (4b,4d) reveal a characteristic microphase separation morphology of PS and PMMA domains. This is due to the low entropy gain upon mixing.[21] However, upon microphase separation a rich variety of microstructure developed in system of BCP depending on the relative lengths of each block, and several morphologies can be obtained.

Bright and dark domains are observed in all AFM images, the difference in contrast in phase images are due to the difference in the elastic modulus, the brighter domain represent higher elastic modulus of the block segment. PMMA at room temperature has higher modulus than PS as Peng et al.[33] described. This in agreement with result obtained by Hoffman et al.[34] where they determine the elastic modulus of various polymers including PS and PMMA using AFM.

Fig 3 shows highly oriented domains where PMMA form stripes oriented parallel to the substrate. This could also arise from cylinders aligned parallel to the substrate as reported by Khaydarov et al.[32] when they investigated the surface structure of thin films (dissolved in toluene at 160 ^{o}C for 24 h) of asymmetric PS-b-PMMA copolymer prepared via Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization. Similar observation was made by Edwards et al.[35] Also, highly ordered striped morphologies were obtained when the surface morphology of symmetric PS-b-PMMA copolymer thin films (dissolved in toluene for 24 h) were studied, after an extended duration of the treatment for 48 h, a mixed morphology containing striped and hexagonal structured were appeared.[6]

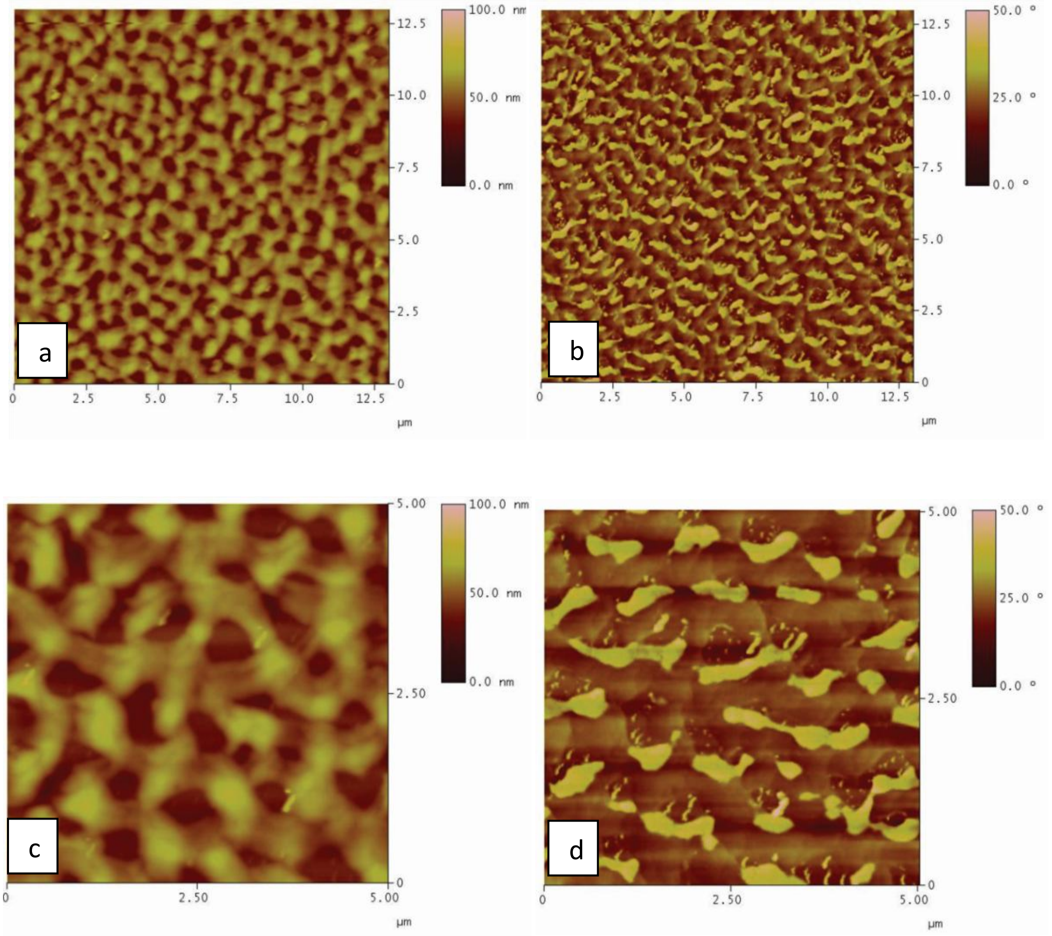


FIGURE 3: AFM IMAGES OF BCP1, A) HEIGHT IMAGE, B) PHASE IMAGE AT SCAN SIZE 13 X 13 MM, C) HEIGHT IMAGE, AND D) PHASE IMAGE AT HIGH MAGNIFICATION AT SCAN SIZE 5 X 5 MM.

The width of the cylindrical PMMA domains was measured to be in average about 230 nm and the length was average about 600 nm. Longer domains were also observed to be with average length of 1700 nm, this could be an indication of two or three combined PMMA domains.

AFM images of BCP2 in Fig 4 exhibit rather different morphology in comparison to BCP1 in Fig 3. This could be expected because the size of the microstructure and its type of ordering can be controlled by changing molar mass, chemical structure, molecular architectures and composition of the block copolymers through careful chemical synthesis.[24] By varying the molar mass and relative composition of a diblock, it is possible to obtain range of morphologies.[24,36]

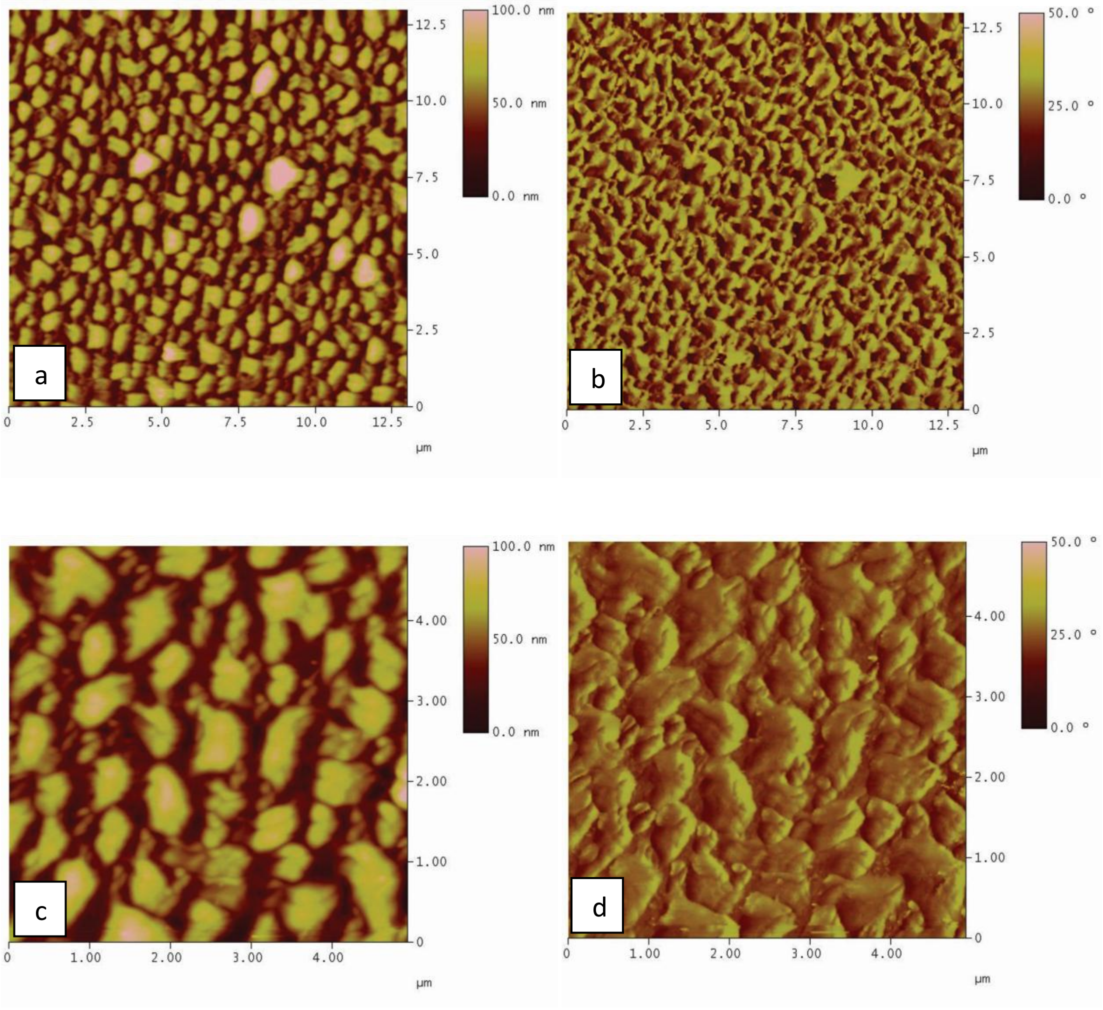


Figure 4: AFM images of BCP2, a) height image, b) phase image at scan size 13 x 13 mm, c) height image, and d) phase image at high magnification at scan size 5 x 5 mm.

The AFM images in Fig 4 the hexagonal ordered cylindrical of PMMA domains oriented perpendicular to the substrate were observed. This observation has been reported in many studies.[37-40] However, to achieve the perpendicular orientation of the PMMA cylinders to the film plane, external energy is required to overcome the surface energy of the substrate. Sophisticated modifications of the surface including chemical prepatterning and graphoepitaxy or utilization of directional fields such as an electric field and evaporation of solvents have been used for the perpendicular orientation of block copolymer domains to the substrate.[39] The dimensions of the domains were measured to be in average about 230 nm and the length was average about 600 nm, the merged domains were observed to be with average length of 1000 nm.

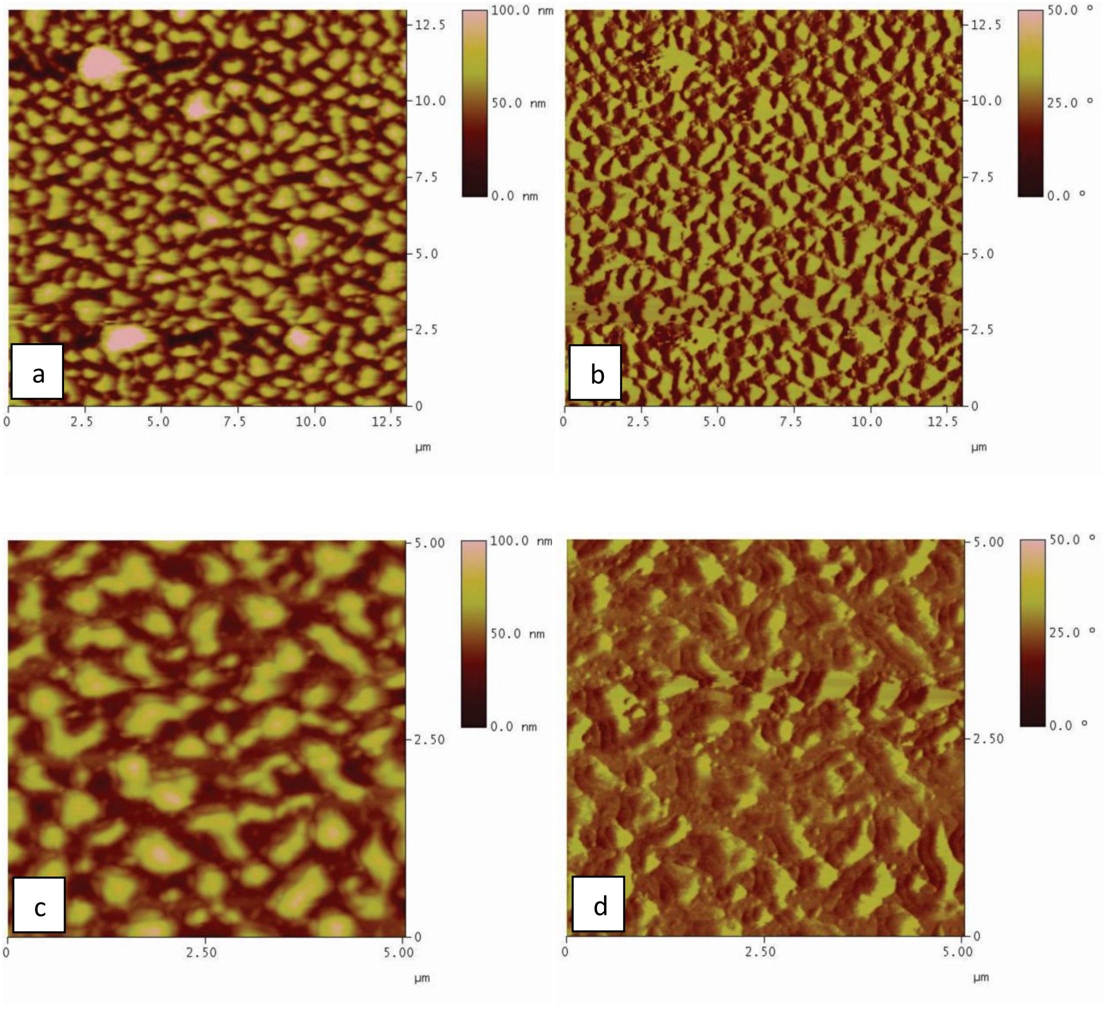


FIGURE 5: AFM IMAGES OF BCP2, A) HEIGHT IMAGE, B) PHASE IMAGE AT SCAN SIZE 13 X 13 MM, C) HEIGHT IMAGE, AND D) PHASE IMAGE AT HIGH MAGNIFICATION AT SCAN SIZE 5 X 5 MM.

AFM images were taken at different locations on the substrate for both BCP1 and BCP2. Unlike AFM images of BCP1 (not shown here), the AFM images of BCP2, show that the orientation of domains were not homogenous over the entire surface of the BCP2, as shown in Fig 5. A mixed morphology of cylindrical PMMA domains oriented perpendicular and parallel to the substrate were observed. The mixed morphology on thin films of PS-b-PMMA has been reported by Peng et al.[6]. The diameter of the cylindrical domains was measured to be in average about 250 nm and the length was average about 750 nm, longer domains were also observed to be with average length of 1100 nm.

IV. CONCLUSION

In summary, we have investigated the block length (molar mass) effect of PMMA on surface morphologies of PS-b-PMMA copolymer thin films. BCPs were synthesized by a novel combination techniques; living anionic polymerization and hydroboration autoxidation reactions. Our results showed that microphase separation do occur and equilibrium morphologies were observed. Moreover, it could be concluded that the BCP composition, in particular, affect the microphase morphology. It was found that BCP with PMMA $M_{W\ PMMA}$ =130000 g/mol form parallel cylinders (stripes) oriented horizontally to the substrate. On the other hand, BCP with PMMA $M_{W\ PMMA}$ =180000 g/mol form mixed morphology of cylindrical PMMA domains oriented perpendicular and parallel to the substrate.

Considering that some aspects of these thin film systems, in particular understanding their microstructure remains a worthwhile pursuit. Indeed, it is useful to understand all these details of morphology changes in block copolymers under different conditions. In spite of many studies on the phase behavior of block copolymers, the attention paid to their structure property correlation seems to be insufficient, moreover, theoretical descriptions of forming these morphologies is still a significant research focus. Consequently, future work continue to research in this field to focus on these issues.

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