

Atomic force microscopy investigation of asymmetric diblock copolymer morphologies in thin films

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Received 4 December 2003; received in revised form 11 February 2004; accepted 19 February 2004

Available online 27 March 2004

Abstract

Microphase separation and the resulting morphology of asymmetric diblock copolymers of poly(ϵ -caprolactone) (PCL) in thin films have been investigated by atomic force microscopy. Copolymers consisted of a short block of PCL ($M_n \sim 2500$ – 4500 g/mole) and a longer second block of poly(methyl methacrylate) (PMMA), poly(styrene) (PS) or poly(cyclohexene oxide) (PCHO). Tendency for microphase separation above the glass transition temperature of the second block (PMMA, PS or PCHO) resulted in a pitted morphology on the surface of the thin films. This tendency was strongest for PMMA and weakest for PCHO. The presence of up to 54% PMMA homopolymer in PCL-PMMA block copolymer did not prevent the formation of such pitted morphology on the surface. The effect of the chemical structure of the second block and the possible orientations of the block copolymer molecules in thin films are discussed.

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Keywords: Asymmetric diblock copolymer; Atomic force microscopy; Morphology; Microphase separation

1. Introduction

A significant amount of work have been devoted to the biodegradable polyester blends to modify their mechanical and thermal properties and degradation rates [1]. Most polymer pairs are mutually immiscible and result in macroscopically phase separated structures. Block copolymers of these immiscible pairs show microphase separation because the two incompatible polymers are chemically bonded to each other and thus act as interfacial agents in blends of immiscible polymers towards enhancing miscibility. The microphase separation of the different blocks leads to diverse morphologies, especially in thin films [2].

Poly(ϵ -caprolactone) (PCL) is a non-polar aliphatic polyester having a melting temperature T_m of 63 °C and

a glass transition temperature T_g of -70 °C. PCL is highly crystallizable and can form useful polymer blends with other polymers to be used in a variety of applications [1]. PCL is immiscible with high molecular weight poly(styrene) (PS) [3]. Miscibility of PS and PCL oligomers at low T and the existence of upper critical solution temperature (UCST) behaviour were predicted [4] in accordance with experiments [5,6]. Poly(methyl methacrylate) (PMMA, $T_g = 105$ °C) is less hydrophobic compared to PS ($T_g = 100$ °C) due to the presence of methyl acrylate side groups. PCL is also immiscible with PMMA. Poly(cyclohexene oxide) (PCHO) has been much less studied compared to PS or PMMA. T_g of PCHO was determined to be 71 °C [7]. To our knowledge, no study has been known on either blends or copolymers of PCL and PCHO.

Microphase separation in asymmetric diblock copolymers of thermodynamically incompatible blocks results in a morphology where spheres or cylinders of the smaller block are dispersed in the matrix of the longer block. PS-PMMA diblock copolymers having 30

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volume% PMMA showed cylindrical PMMA domains that were oriented normal to the surface of PS-PMMA random copolymer brush. Addition of PMMA homopolymer into PS-PMMA diblock copolymers increased both the diameter and the spacing of the cylindrical microdomains [8].

Asymmetric diblock copolymers of PB-PEO having the crystallizable PEO block as the minority phase showed spherical PEO domains in the matrix of PB. Extreme confinement of the PEO block in spheres of ~12 nm diameter prevented crystallization at room temperature. Crystallization was only observed at temperatures below -20 °C [9–11].

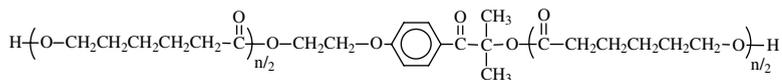
In this study, we investigated the effect of a very small (20–37 repeating units (n), $M_n \sim 2500$ –4500 g/mole) PCL block on the microphase separation and thin film surface morphology of diblock copolymers having PMMA, PS or PCHO as the second larger block. Our results indicate that the observation of micro phase separated morphology with such short PCL blocks depends significantly on the chemical structure of the second block.

2. Experimental

2.1. Synthesis of block copolymers

2.1.1. Preparation of PCL-PMMA block copolymers

Appropriate solutions of prepolymers (PCL) [12] containing photoactive group in the mid-chain or side-chain and MMA were placed in pyrex tubes and degassed with nitrogen prior to irradiation by a merry go round type photoreactor equipped with 15 Philips 8 W/06 lamps emitting light nominally at $\lambda > 300$ nm and a cooling system. Photopolymerizations were carried out in bulk. At the end of given time, polymers were poured into methanol, filtered, dried and weighted. It should be pointed out that mid-chain functional PCL of the following structure yields only block copolymers since it does not form low molecular weight radicals upon irradiation.



2.1.2. Preparation of PCL-PCHO block copolymers

Appropriate solutions of prepolymers (PCL) [12] containing given amounts of benzoin end-chain prepolymer and onium salt ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) were placed in pyrex tubes and degassed with nitrogen prior to irradiation by a merry go round type photoreactor equipped

with 15 Philips 8 W/06 lamps emitting light nominally at $\lambda > 300$ nm and a cooling system. Photopolymerizations were carried out in bulk. At the end of given time, polymers were poured into methanol, filtered, dried and weighted.

In the following scheme synthesis of PCL-PMMA and PCL-PCHO block copolymers using benzoin end-chain PCLs as prepolymers are given (Scheme 1).

2.1.3. Preparation of PCL-PSt block copolymers

Appropriate solutions of 4-hydroxy TEMPO containing prepolymer (PCL-HTM) and St were freed from oxygen by purging with dry nitrogen and then heated at to 125 °C for given times. At the end of reaction, the copolymers were precipitated into cold methanol and dried in vacuo.

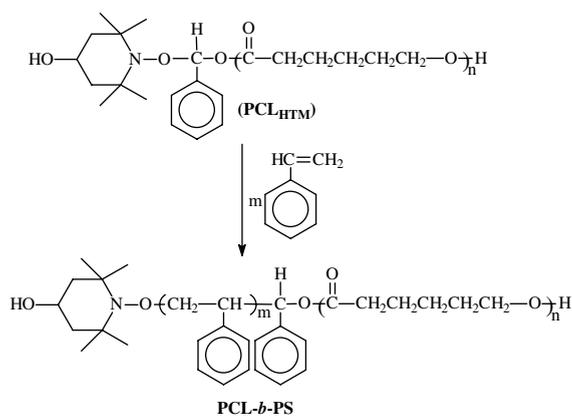
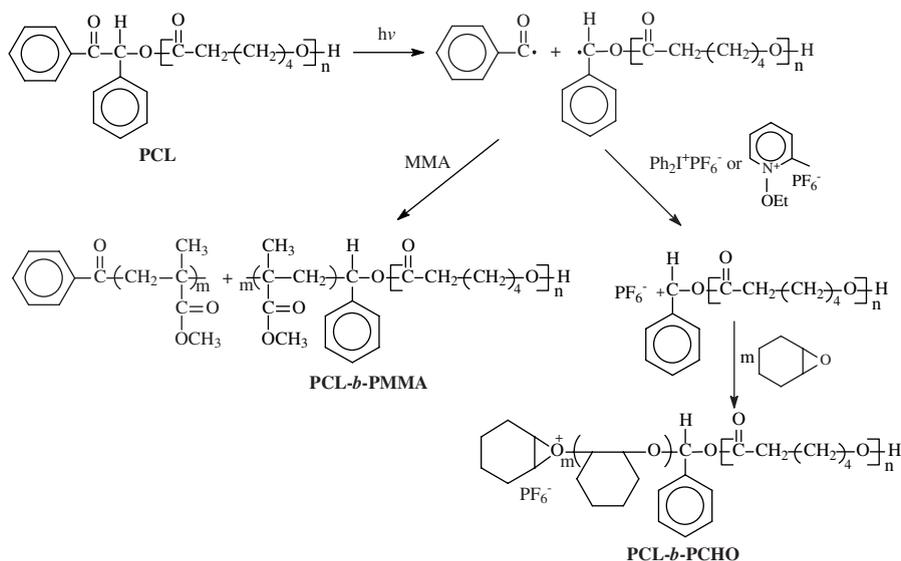
In Scheme 2, synthesis of PCL-PSt block copolymers by stable free radical mediated polymerization (SFRP) using TEMPO end-chain functionalized PCL is given. In this case no homopolymer is formed.

The molecular weights and the percentages of the investigated diblock copolymers are tabulated in Table 1. When indicated block copolymers contained also homopolymers. The detailed separation and characterization processes were given in previous articles [12,13].

Thin film preparation: Block copolymers were dissolved in chloroform at a concentration of 16–20 mg/ml. The films were prepared by spin-coating from solutions onto glass or oxidized silicon substrates at 2000 rpm for 1 min. Silicon substrates were made hydrophilic prior to spin-coating by keeping them in UV-ozone cleaner for 20 min. A water drop completely wetted such hydrophilic surfaces. Spin-coated films were initially kept at 80 °C for 1 h for solvent evaporation. The temperature was then increased to 110 °C (~10 °C above the glass transition temperature of PMMA and PS, ~40 °C above the glass transition temperature of PCHO) and the films were annealed for 5 h for equilibration of the microphase separated surface morphology. After annealing the films were quenched to room temperature of 25 °C.

AFM measurements: NT-MDT Solver P47 AFM was used in the tapping mode to measure the film thicknesses

and to characterize the resulting morphology. Film thicknesses were determined by scraping the polymer film in an area of $2 \mu\text{m} \times 2 \mu\text{m}$ by the AFM tip in contact mode and then taking the height image of the scraped area in tapping mode. Ultrasharp Si cantilevers having force constants of 3 N/m or 48 N/m were used.



3. Results

AFM height pictures of the surface morphology of PCL-PMMA, PCL-PS and PCL-PCHO block copolymer (polymer #3, #4 and #5, respectively in Table 1, chemical structures are seen in Schemes 1 and 2) thin films in $10\ \mu\text{m} \times 10\ \mu\text{m}$ area are seen in Fig. 1. Fig. 2 shows the AFM phase pictures of the same scans of Fig. 1. All films were approximately 60 nm thick and were annealed at $110\ ^\circ\text{C}$ for 5 h in vacuum. A pitted surface morphology was observed in PCL-PMMA (Fig. 1a) and PCL-PS (Fig. 1b) thin films. The average depth of the pits was ~ 25 nm in Fig. 1a and ~ 12 nm in Fig. 1b. The size of the pits varied from 50 to 200 nm. In addition to the pits, some ~ 10 nm height islands are also seen in Fig. 1a. Fig. 1b also have similar islands having heights

Table 1
The characteristics of the investigated diblock copolymers

#	Prepolymer ^a (M_n) ^b	Copolymers	Yield ^b (%)	Homopolymer ^c (%)	Block copolymer	
					(M_n) ^d	(M_w/M_n) ^d
1	2600	PCL-PMMA	9	54 (PMMA)	130,000	1.12
2	3300	PCL-PMMA	14	28 (PMMA)	93,000	1.09
3	4400	PCL-PMMA	21	0 (PMMA)	79,000	1.08
4	2500	PCL-PS	26	0 (PS)	102,000	1.89
5	2500	PCL-PCHO	58	7 (PCHO)	7600	1.79

^a PCL.

^b Conversion of second monomer used.

^c Determined independently by selective solvent extraction and H-NMR (see Refs. [12,13] for the details of the procedure) and AFM measurements were performed with the samples containing indicated amount of the homopolymers.

^d Determined by GPC according to PS standards.

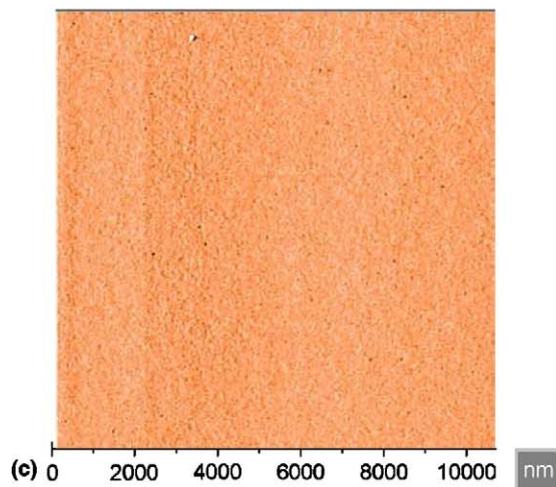
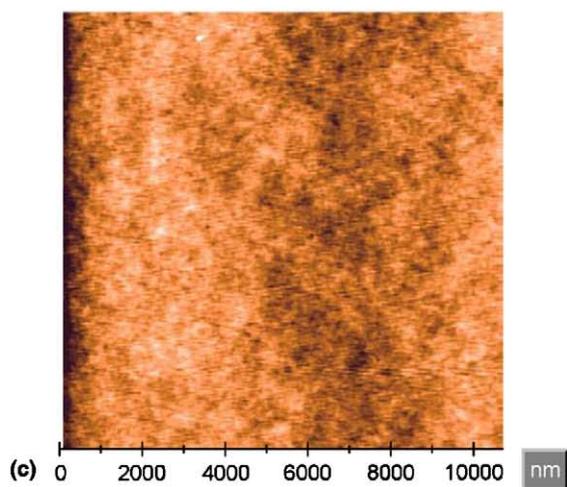
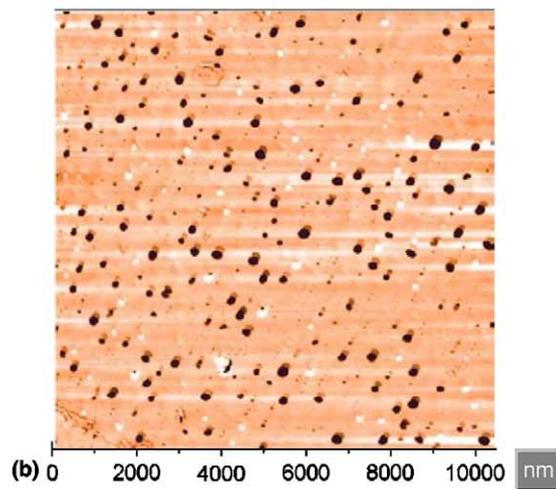
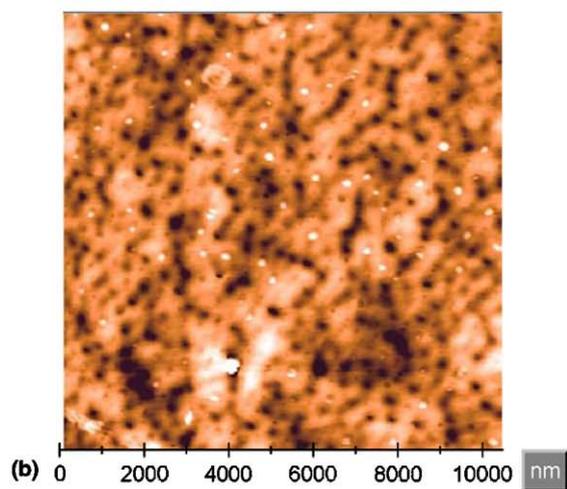
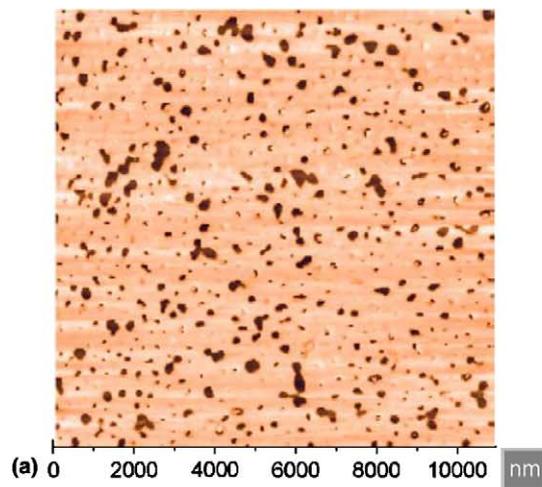
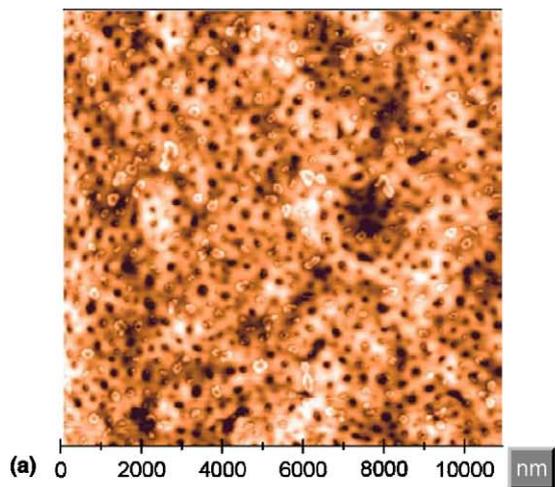


Fig. 1. AFM height pictures of PCL copolymers with different chemical blocks after annealing at 110 °C for 5 h: (a) PCL-PMMA, (b) PCL-PS, (c) PCL-PCHO.

Fig. 2. AFM phase pictures of PCL copolymers with different chemical blocks after annealing at 110 °C for 5 h: (a) PCL-PMMA, (b) PCL-PS, (c) PCL-PCHO.

of 6–10 nm. The size of these islands varied between 100 and 200 nm. These islands correspond to the dark areas in the phase picture of Fig. 2a and b and are mostly accumulated around or on top of the underlying pits. Phase pictures show much better contrast in detecting such regions and the smallest size observed in phase pictures goes down to 40 nm. The height and phase image of PCL-PCHO block copolymer thin film (Figs. 1c and 2c, respectively) were both smooth and uniform without any surface features. The root-mean-squared roughness of the height image was only 0.5 nm.

The presence of upto 54% PMMA homopolymer in PCL-PMMA block copolymers did not prevent the observation of pitted surface morphology in thin films after annealing above the glass transition temperature of PMMA. Fig. 3 shows the height image and Fig. 4 shows the phase image of the surface of thin films prepared by blends of PCL-PMMA block copolymer and PMMA homopolymer. The volume fraction of PMMA was 54% in (a), 28% in (b) and 0% in (c). Note that Fig. 3c is the same as Figs. 1a, and 4c is the same as Fig. 2a. As the amount of PMMA homopolymer increased, the distance between the surface pits decreased. The average distance between the pits was determined by Fourier transforming the phase pictures. A broad circle was obtained in Fourier transform of Fig. 4a and b. The average diameter of the circle gave the average distance between the pits as ~ 240 nm for 54% PMMA and ~ 290 nm for 28% PMMA. These values were also checked by direct distance measurements and averaging. For Fig. 4c without any PMMA homopolymer, FFT gave a bright circular area having a diameter of 400–500 nm. Direct distance measurements between nearest neighbour pits also confirmed this average spacing.

In order to have a better idea on the molecular length scales of the morphology of PCL-PMMA/PMMA blends, thinner films (thickness ~ 20 nm) of polymer #1, #2 and #3 in Table 1 were prepared on hydrophilic silicon oxide substrates. The resulting morphologies are seen in Fig. 5 after annealing at 130 °C for 5 h. All films showed layered structures parallel to the substrate. Fig. 5a and b have a very thin smooth layer (thickness ~ 5 –10 nm) covering the substrate surface and a second layer with large holes (diameter ~ 0.5 –4.0 μm) are seen on top of the first layer. The evidence for the smooth first layer comes from scratch tests by AFM tip and also from surface features that appear in the holes after annealing, as seen in the phase picture Fig. 5d corresponding to the same sample and same scan area as that of Fig. 5a. No evidence for the existence of a smooth layer on the substrate was obtained for pure PCL-PMMA block copolymer in Fig. 5c. The depth of the holes are ~ 10 –12 nm in Fig. 5a, 8–10 nm in Fig. 5b and ~ 10 nm in Fig. 5c. In Fig. 5a–c, there exists ~ 2 –3 nm thick intermediate layer circling the inner side of the

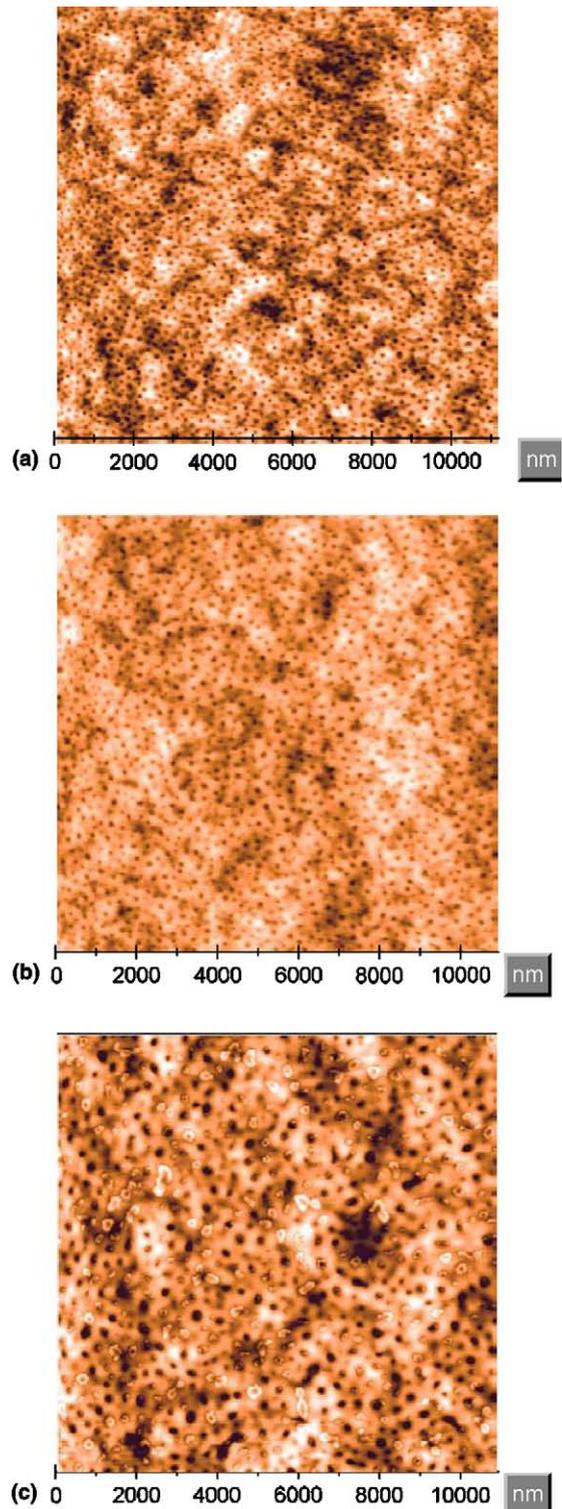


Fig. 3. AFM height pictures of PCL-PMMA block copolymers with different amounts of PMMA homopolymers after annealing at 110 °C for 5 h. The percentage of block copolymer: (a) 46%, (b) 72%, (c) 100%.

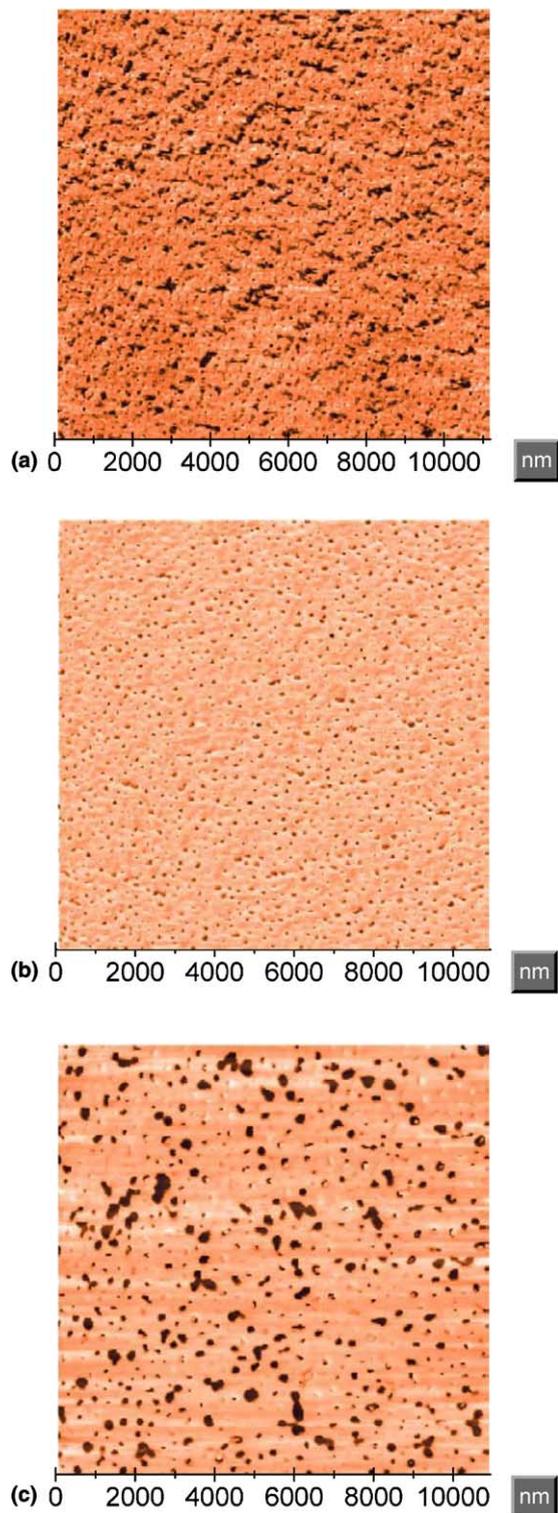


Fig. 4. AFM phase pictures of PCL-PMMA block copolymers with different amounts of PMMA homopolymers after annealing at 110 °C for 5 h. The percentage of block copolymer: (a) 46%, (b) 72%, (c) 100%.

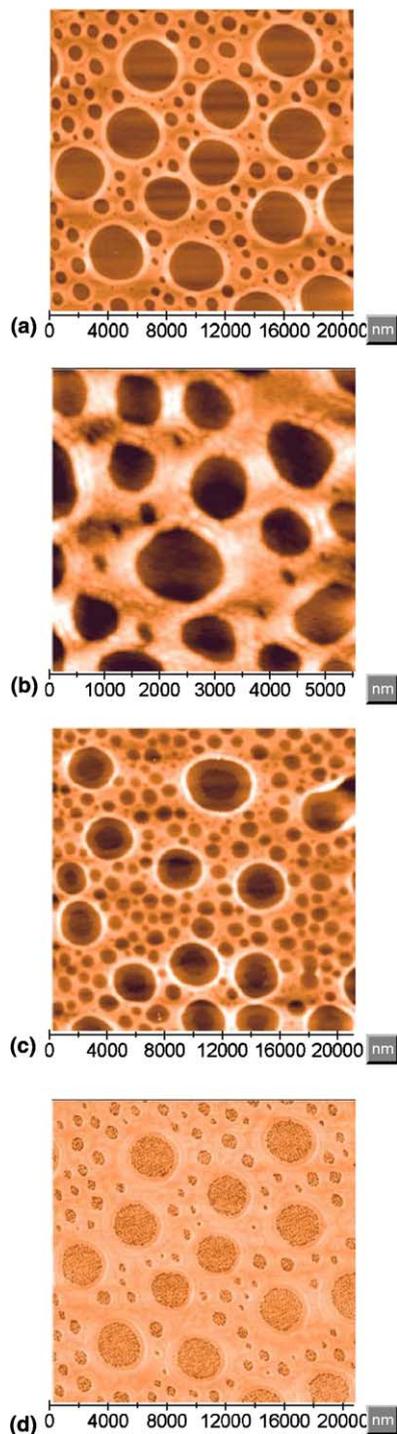


Fig. 5. AFM height pictures of very thin (~ 20 nm) PCL-PMMA block copolymer films on hydrophilic Si substrates after annealing at 130 °C for 5 h. The percentage of the block copolymer was: (a) 46%, (b) 72%, (c) 100%. (d) AFM phase picture of the scan in (a). Features due to thickness undulations are seen in the holes.

large holes. The width of this layer is ~ 300 nm in Fig. 5a, and ~ 800 nm in Fig. 5c.

4. Discussion

The observation of the pitted surface morphology in thin films of PCL-PMMA and PCL-PS diblock copolymers is due to the microphase separation between PCL and the second block (PMMA or PS). The difficulty of observing more ordered microphase separated morphology (lattice of PCL spheres in PMMA (or PS) matrix) is not surprising considering the small size of PCL blocks compared to the second block (see Table 1). The mass fraction of PCL in the copolymer was only 2–6% for PCL-PMMA and 2.4% in PCL-PS. To our knowledge, such strongly asymmetric diblock copolymers have so far not been investigated. Such low molecular weight PCL ($M_n \sim 2500$ – 4400 g/mole) in the copolymers will be confined to spherical regions of diameter approximately 10 nm in the matrix of the amorphous second block. Extreme confinement also hinders crystallization of polymers [9,14]. Thus, the small size scale of PCL spheres together with lack of crystallization at room temperatures prevented the observation of more ordered structures.

The surface patterns observed by AFM (Figs. 1 and 2) reflect the tendency of microphase separation and the resulting structure formation. The contact angle of a water drop on PMMA ($\sim 50^\circ$) is much smaller than that on PCL ($\sim 95^\circ$) indicating the relatively lower surface energy of PCL compared to PMMA. On a hydrophilic substrate with $-\text{OH}$ groups, PMMA would prefer to be on the substrate and PCL on the free surface. A large fraction of PMMA ($\sim 95\%$ by mass) prevents layer formation for 60 nm thick films. But the tendency of PCL to be at the top surface creates a pitted surface morphology as PMMA on top of PCL spheres is removed. Islands or holes at the free surface of thin films of asymmetric diblock copolymers having a layered spherical domain structure were previously observed when the film thickness was not equal to an integral number of layer thickness [15]. The pitted surface morphology we observe is different than the holes observed in the thermodynamical equilibrium state. The slow diffusion of PMMA at 110 $^\circ\text{C}$, only 10 $^\circ\text{C}$ above the glass transition temperature, must be the limiting kinetic factor in reaching thermodynamic equilibrium.

Spherical regions of size ~ 40 nm in the surface pits correspond to microphase separated PCL. Such regions are clearly seen in Fig. 6 for polymer #1 (PCL-PMMA copolymer with 54% PMMA homopolymer) in an area of $2 \mu\text{m} \times 2 \mu\text{m}$. The observed lateral length scale in our AFM measurements are larger than the diameter of the spherical regions expected, mainly due

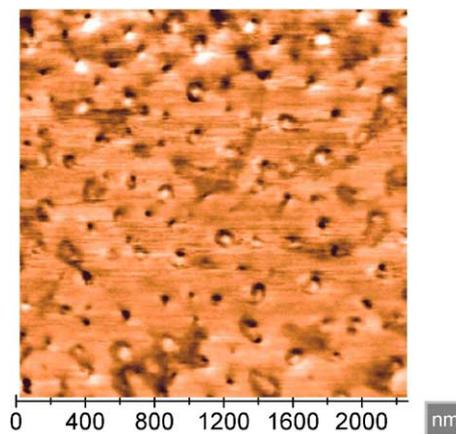


Fig. 6. AFM phase picture of polymer #1 (PCL-PMMA copolymer with 54% PMMA homopolymer) showing the existence of spherical PCL domains in the matrix of PMMA block.

to three contributions: (i) the finite size of the AFM tip (radius of curvature ~ 10 nm) results in a convoluted AFM image of the tip and the object. For a measured lateral length scale of 40 nm and a tip radius of 10 nm, the corrected length scale turns out to be 31 nm, 22% less than the measured value [16]. This percentage increases with decreasing lateral length. (ii) Due to the lack of a selective solvent for separation of PCL homopolymer after the synthesis, some PCL homopolymer might have left in the samples. In that case, PCL homopolymer would prefer to be on the free surface due to its lower surface energy compared to PMMA and would like to be in touch with the PCL block of the copolymers. We think the islands of height ~ 10 nm that are seen in Fig. 1a and b (darker regions in Fig. 2a and b) is due to the accumulation of PCL homopolymers on top of the PCL blocks of the copolymers. Such accumulation of PCL homopolymers prevent the observation of underlying PCL blocks of the copolymers and also increases the observed lateral length scales. The different phase contrast of these regions than that of the pits is due to the difference in the viscoelasticity of PCL homopolymer having a large photoactive group at one end and the PCL domains of the block copolymer. The darker regions in the phase picture of Fig. 2a and b indicate that PCL homopolymer is softer which is expected as the bulky photoactive groups may prevent the crystalline order. Note that the phase picture is more sensitive to these soft regions than the height picture: some dark regions are seen in the phase picture while any islands can hardly be seen in the height picture. (iii) Above the glass transition temperature of the second block, the films are not stable and a slow dewetting process takes place together with microphase separation. The size of the

surface pits increase with annealing time resulting in a less ordered microphase separated morphology.

The lack of pitted surface morphology in thin films of PCL-PCHO copolymers (even with samples containing 25% PCL by mass) indicate a better miscibility of PCL with PCHO. No signs of microphase separation that is measurable by AFM could be observed as PCL and PCHO segments exhibit structural similarities i.e., both are main chain polymers and contain oxygen and 6 carbon atoms. These films also remained stable against dewetting at 130 °C (~ 60 °C above T_g) up to 5 h indicating a stronger interaction of PCHO molecules with the underlying glass substrate. This interaction may be due to the hydrogen bonding of oxygen atoms present in the polyether structure.

The presence of PMMA homopolymer in the copolymer increases the order of pits on the top surface while decreasing the distance between the pits. It is expected that the added PMMA homopolymer will accumulate in the matrix formed by the PMMA block and will increase the average distance between the PCL blocks. The observed decrease of the average distance between the pits with increasing amount of PMMA homopolymer can only be explained by surface segregation, rather than homopolymer taking place in the matrix of copolymer. The interaction of PMMA is known to be strong with the hydroxylated oxidized silicon substrates [17,18] due to hydrogen bonding between the surface —OH groups and the —C=O group in PMMA. Thus PMMA homopolymer is expected to form a smooth layer on the substrate on top of which the copolymer forms the microphase separated structure.

Proof that PMMA prefers the underlying substrate also comes from structures obtained by thinner films on hydrophilic silicon oxide surfaces. In Fig. 5a and b corresponding to blends of homopolymer and copolymer, a smooth film was observed in the holes, while in Fig. 5c corresponding to pure copolymer film did not show any. When the films were annealed at 130 °C for 5 h, this smooth film showed thickness undulations in the holes as seen clearly in Fig. 5d (phase picture of Fig. 5a). We have been investigating whether such undulations are due to dewetting of the PMMA film or due to surface micelle formation by the diblock copolymers that may be present in this smooth surface layer. On top of a PMMA film, a thin PCL-PMMA block copolymer layer minimizes its interfacial energy by orienting in such a way that PMMA block is in touch with the underlying PMMA film, and the lower surface energy PCL block is at the free surface. The 2–3 nm high intermediate layer circling the inner part of the large holes which is clearly seen in Fig. 5c must be the PMMA block of the copolymers. Though stretching of PMMA block lowers the entropy, the enthalpic gain due to increased interfacial area dominates.

In conclusion, our results show that even for extremely asymmetric diblock copolymers of a short crystallizable block and much longer amorphous block microphase separated structures can be observed. For such asymmetric copolymers, miscibility becomes more critical. While signs of microphase separation were observed in PCL-PMMA and PCL-PS copolymers, no indications of phase separation was found by AFM in PCL-PCHO copolymers. Addition of PMMA homopolymer resulted in more ordered structures on the top surface due to segregation of PMMA to the substrate. It is not yet clear how the underlying PMMA layer on the substrate progressively changes the microphase separated structure from a layered structure in thin films to more ordered spheres of PCL in thicker films. Our investigations of the effect of surface chemistry on the structure have been continuing.

Acknowledgements

A.L.D. acknowledges the financial support of Turkish Academy of Sciences in the framework of the Young Scientist Award program (grant EA/TÜBA-GEBİP/2001-1-1).

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