Precise Control of Nanopore Size in Thin Film Using Mixtures of Asymmetric Block Copolymer and Homopolymer

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Introduction

Block copolymers self-assemble into periodic morphologies with well-defined size and spacing having microdomains with characteristic length scales of a few to tens of nanometers and have been extensively studied due to their potential use as functional nanostructures.[1−6] The size and the type of the microdomains are dictated by molecular weight, volume fraction, segmental interactions, and molecular architecture of the blocks.[7,8] The lower limit of microdomain sizes is set by segmental interactions, whereas mobility limits the largest sizes achievable. The addition of a homopolymer affords an attractive route by which the size scale of the nanodomains achievable with neat block copolymers can be extended.[9]

Homopolymers with increasing molecular weight that are added to a block copolymer are more localized to the center of the microdomains, and if the molecular weight of the homopolymer is too large, macrophase separation occurs.[10−15] Recently, we showed that the extent of homopolymer localization in thin films was greater than that in bulk.[15] The extent of localization increased with increasing molecular weight of the homopolymer and saturated when the molecular weight ratio of the homopolymer to corresponding block chain was greater than 2.5.[15]

In a previous study,[16] a route to fabricate 6−10 nm nanoholes by selective removal of poly(methyl methacrylate) homopolymer (PMMA) in thin films of mixtures of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) and PMMA was demonstrated. However, the nanopores were not thermally stable. When the thin films were annealed at above glass transition temperatures (T_g) of PS and PMMA, the pores disappeared, and a surface topology with islands (or holes) was observed. Even at room temperature after several months, many of the nanopores disappeared. Precise control of the size of nanoholes was also difficult, since the films underwent a slight swelling during the selective removal of the homopolymer.

Here, a route to circumvent these limitations is shown by using ozone to cross-link PS matrix block without damaging the PMMA block.[17] By successively cross-linking the PS matrix, selectively removing the homopolymer, and annealing at elevated temperatures, the sizes of nanoholes could be precisely controlled, and good thermal stability of the nanopores is achieved.

Experimental Section

An asymmetric polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA), having a PS weight fraction of 0.70, a weight-average molecular weight (M_w) of 87 800, and a polydispersity of 1.03, was synthesized anionically. PMMA homopolymer with $M_w = 59\,600$ and a polydispersity of 1.06 (Polymer Laboratories Inc.) was used as received. A hydroxy-terminated random copolymer of styrene and methyl methacrylate, denoted PS-*ran*-PMMA,[18] having a PS weight fraction of 0.58, M_w of 11 000, and polydispersity of 1.13, was anchored to the substrate as described previously,[18] so as to orient the PMMA microdomains normal to the substrate.[18,19] Thin films (31−34 nm) of PS-*b*-PMMA/PMMA mixtures with different volume fractions of the PMMA homopolymer ($\phi_H = 0.015 \sim 0.22$) were prepared by spin-casting onto the random copolymer brush. ϕ_H is defined as the volume fraction of the homopolymer relative to the total PMMA phase (homopolymer plus the PMMA block in the PS-*b*-PMMA). The samples were annealed at 170 °C under vacuum for 2 days and then quenched to room temperature.

Thin films of the mixtures were exposed to ozone/air (20:80) with a very low flow rate of 0.6 cm^3/min at 17 °C for 30 min. Under these conditions, only the PS block was cross-linked, whereas the PMMA was not affected.[17] We found that, during this stage, holes were not formed because the polymer chains were frozen at 17 °C, much lower than the glass transition temperatures of PS and PMMA block. After cross-linking, the sample was dipped into acetic acid for ~4 h to remove the PMMA homopolymer completely. The sample was then annealed at 170 °C for 4 h to stabilize the pores formed.

The nanoporous structures were investigated by atomic force microscopy (AFM) in the tapping mode, and the sizes of nanopores were determined by Fourier transformation of the TEM images obtained with a TEM (Hitachi) operated at 100 kV. TEM samples were prepared as follows. First, homopolymer-extracted thin films were prepared on Si wafer, onto which a sacrificial SiO_x layer of 60−80 nm thickness was evaporated. These thin films were floated onto a 5 wt % aqueous hydrofluoric acid solution and then transferred to water.[16] The film was then retrieved with a carbon grid and overstained with RuO_4 for 4 h to obtain better contrast and avoid PMMA degradation even at high magnifications (×100 000). Under these conditions, only nanoholes were transparent to electrons, since PMMA was also stained. Also, we prepared large size nanoholes by etching out all the PMMA phase (PMMA block and PMMA homopolymer) by UV treatment. These nanoholes were also investigated by TEM after staining with RuO_4. The average diameter of pores was determined by calculating the surface area of each pore in TEM images having at least 100 pores with the aid of the commercially available software (Scion Images; Scion Co.).

Results and Discussion

Figure 1 shows a series of TEM images of thin films of neat PS-*b*-PMMA and PS-*b*-PMMA/PMMA mixtures that contained different amounts of PMMA homopolymer: (A−D) after removing PMMA homopolymer and (E, F) after removing all PMMA phases by UV exposure. As the amount of added PMMA homopolymer increased, the hole sizes after removing homopolymer increased

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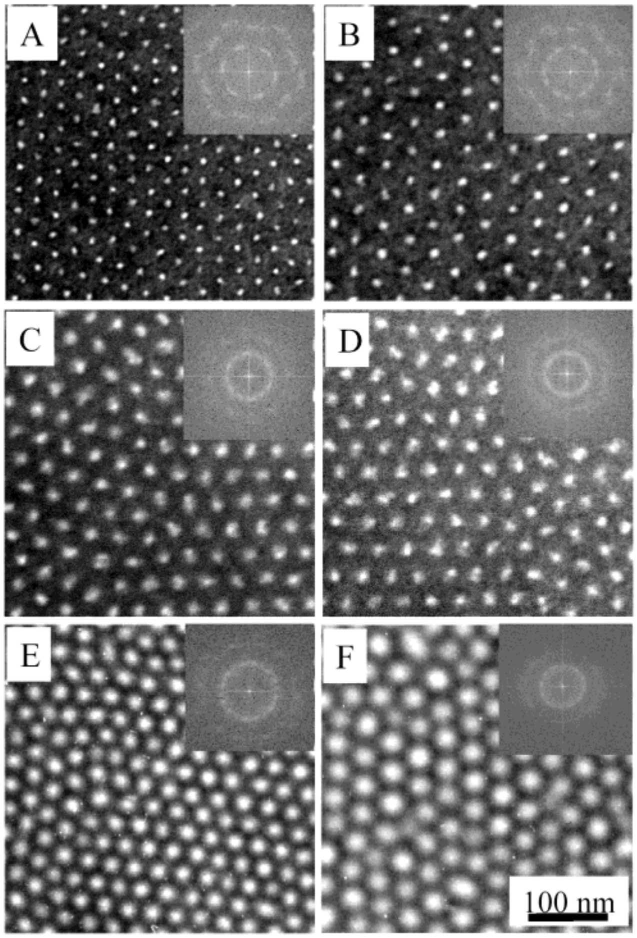

Figure 1. TEM images of thin films of PS-*b*-PMMA/PMMA mixtures with various amounts of PMMA homopolymer: (A−D) after selective removal of PMMA homopolymer and (E, F) after the removal of all PMMA phases by UV exposure. For (A−D), the PS and PMMA blocks were overstained with RuO_4 to obtain better contrast and to prevent possible degradation of PMMA block chain. Insets are Fourier transformed images of each TEM picture. The volume fractions (ϕ_H) of PMMA homopolymer in total PMMA phase are: (A, E) 0, (B) 0.015, (C) 0.09, (D, F) 22.

from ∼6 to ∼18 nm. Similarly, the diameter of the entire cylindrical nanodomains increased from ∼23 to ∼32 nm. No macrophase separation was observed up to $\phi_H \sim 0.3$, though the lateral hexagonal packing of cylindrical microdomains worsened with increasing ϕ_H in comparison to neat PS-*b*-PMMA.

Previously it was shown that the nanopores were produced from neat PS-*b*-PMMA when the film was exposed to ozone.[17] Though PS matrix undergoes cross-linking during exposure to ozone, it was not found to induce the volume contraction at 17 °C, which is far below the glass transition (T_g) of both PS and PMMA blocks. Once the film is heated to 170 °C, the cross-linked PS undergoes a volume contraction or shrinkage both laterally and in the thickness due to the relaxation of the PMMA chains.

The insets in Figure 1 are Fourier transforms (FT) of the TEM images. In all cases the FT images are full circles, indicating random orienting grains of hexagonally packed nanopores. The lattice spacing, which is inversely proportional to the peak position in the FT image, increases with increasing ϕ_H. These results show that the hexagonally packed cylindrical microdomains are preserved and that the center-to-center distance of microdomains increased with ϕ_H. The average diameter of the nanopores can be estimated as follows. Consider one hexagon of the cylindrical microdomains array as shown in Figure 2, composed of three different regions: PS matrix (I), PMMA block (II), and PMMA homopolymer (III). As reported previously,[15] the PMMA homopolymer with $M_w = 59\,600$ is highly localized to the center of cylindrical PMMA microdomains. It is also assumed that PMMA homopolymer is completely removed by acetic acid rinsing, and rearrangement of the chains occurs during annealing at 170 °C. The area of one hexagon (S) is the sum of the area of PS (S_{PS}) and that of the PMMA ($S_{PMMA,block} + S_{PMMA,homo}$). The volume fraction ($f_0$) of block PMMA in neat PS-*b*-PMMA is equal to $S_{PMMA,block}/(S_{PS} + S_{PMMA,block})$, and ϕ_H is given by $S_{PMMA,homo}/(S_{PMMA,block} + S_{PMMA,homo})$. There are two contributions to the final size of the pores produced. One is due to the removal of the PMMA homopolymer, and the other is from the volume contraction of the PS matrix that occurs during cross-linking.

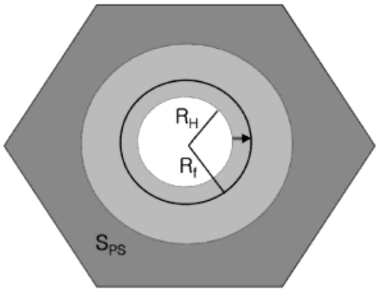

Figure 2. Schematic of one hexagonal unit area S. Three different regions are shown: PS block (I) (dark tone), PMMA block (II) (gray tone), and PMMA homopolymer (III) (white tone). Here, R_H represents the radius occupied by PMMA homopolymer only. The thick circle represents the final hole with radius of R_f, which is included by broadening of hole due to cross-linking of PS matrix in the arrow direction.

In Figure 2, R_H represents the radius of the holes due to the removal of the PMMA homopolymer only, and R_f denotes the final radius of produced holes. Thus, the area generated by cross-linking is $\pi(R_f^2 - R_H^2)$. Since the interdomain distance (d) is $(2/\sqrt{3})D_m$, where D_m is the lattice spacing, S is given by $(2/\sqrt{3})D_m^2$. Therefore, the area (A_H) of the nanohole due to the removal of the PMMA homopolymer is given:

$$A_H = \pi {R_H}^2 = \frac{f_0\phi_H}{1 - \phi_H + f_0\phi_H}\frac{2}{\sqrt{3}}{D_m}^2 \qquad (1)$$

For the same degree of cross-linking, the area (volume) of the hole arising from cross-linking should be proportional to S_{PS}. If $S_{0,PS}$ and A_0 are defined by the area of PS in neat PS-*b*-PMMA and the pore area produced by cross-linking of neat PS-*b*-PMMA, respectively, then the area of the pore (A_c) from cross-linking the PS matrix in the PS-*b*-PMMA/PMMA mixture film can be written as

$$A_c = \frac{S_{PS}}{S_{0,PS}}A_0 = \left(\frac{1-f_0}{f_0}\right)S_{PMMA,block}\left(\frac{A_0}{S_{0,PS}}\right) = \left(\frac{1-f_0}{f_0}\right)\left(\frac{1-\phi_H}{\phi_H}\right)\frac{A_0}{S_{0,PS}}\pi {R_H}^2 \qquad (2)$$

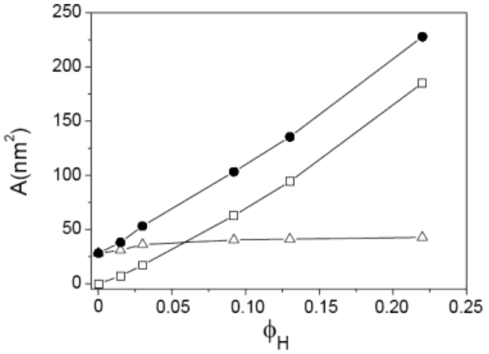

Figure 3. Calculated values of three areas: A_H (□) for homopolymer only, A_c (△) for cross-linking effect, and A_f (●) for the final area which is the sum of A_H and A_c.

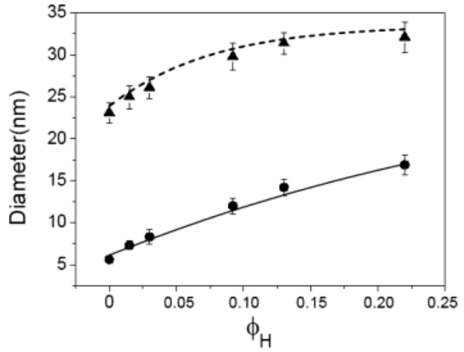

Figure 4. Change of hole diameters ($2R_f$) after selective removal of PMMA homopolymer (●) and entire hole diameter ($2R$) after the removal of all PMMA phases by UV exposure (▲) vs the amount of PMMA homopolymer: Predictions of $2R_f$ and $2R$, given in solid and dotted lines, respectively, are in good agreement with measured ones by TEM images. The error bar in each measured diameter represents one standard deviation.

The total hole area (A_f) is the sum of A_c and A_H:

$$A_f = \pi R_f^{\,2} = \left(\frac{f_0\phi_H}{1-\phi_H+f_0\phi_H}\right)\frac{2}{\sqrt{3}}D_m^{\,2}\left[1+\left(\frac{1-f_0}{f_0}\right)\left(\frac{1-\phi_H}{\phi_H}\right)\frac{A_0}{S_{0,PS}}\right] \quad (3)$$

From the measured values of D_m by FT of TEM images, the areas A_H, A_c, and A_f are shown in Figure 3. In the calculation, the PMMA volume fraction in the block (f_0) was 0.3. A_0 (28 nm^2) and $S_{0,PS}$ (1018 nm^2) were calculated from D_m for the neat PS-*b*-PMMA film.[15,17] A_f was found to increases with increasing ϕ_H.

The prediction of the hole diameters ($2R_f$) by eq 3 (solid line) is given in Figure 4, which is in very good agreement with that measured by TEM (solid circles), indicating that the assumptions made are reasonable. Nanopores with diameters spanning from ~6 to ~18 nm were successfully achieved. Exposing the film to deep UV followed by acetic acid rinsing removes all the PMMA from the film and leaves an array of hexagonally packed nanopores.[4,5] Since the lattice spacing of PS-*b*-PMMA/PMMA mixtures is larger than that of neat PS-*b*-PMMA, the pore size of thin film of mixtures after UV treatment with acetic acid rinsing is expected to be larger than that of neat PS-*b*-PMMA. Since the total area occupied by the PMMA block and homopolymer is written as

$$S_{PMMA,total} = \pi R^2 = \frac{f_0}{1-\phi_H+f_0\phi_H}\frac{2}{\sqrt{3}}D_m^{\,2} \quad (4)$$

then the final hole size after UV etching can be easily calculated. In Figure 4, the measured diameters ($2R$) at various ϕ_H determined from TEM (solid triangles) are consistent with the predicted ones (dotted line) by eq 4 using known values of D_m. Thus, the nanopores with diameters ranging from ~23 to ~32 nm were also generated.

In summary, arrays of nanopores with diameters ranging from ~6 to ~32 nm were produced by selective removal of the PMMA homopolymer after cross-linking the PS matrix or UV etching of the entire cylindrical microdomains. Since the hole size depends on the molecular weight of the block copolymers, the range of achievable hole sizes can be significantly extended.

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