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On-Film Annealing: A Simple Method to Fabricate Heterogeneous Polymer Surfaces, Porous Films, and Hemispheres

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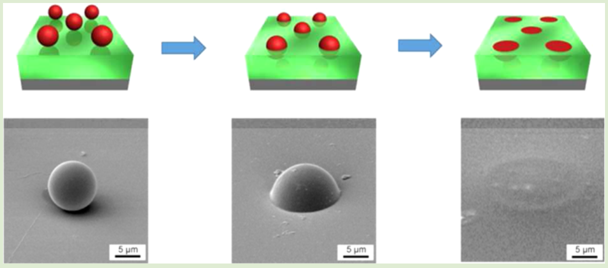
Supporting Information



ABSTRACT: Polymer microspheres have been widely investigated because of their applications in areas such as drug delivery, latex diagnostics, and affinity bioseparators. The effect of annealing on polymer microspheres, however, has been rarely studied. In this work, we demonstrate the morphology transformation of polystyrene (PS) microspheres annealed thermally on poly(methyl methacrylate) (PMMA) films. During the annealing process, the PS microspheres gradually sink into the PMMA films and transform into PS hemispheres, driven by the reduction of the surface and interfacial energies. The effect of the film thicknesses on the morphology transformation is also studied. In addition, porous PMMA films or PS hemispheres can be obtained by removing the PS or the PMMA domains of the polymer composites using cyclohexane or acetic acid, respectively.

Polymer microspheres have attracted significant attention because of their applications in areas such as drug delivery, latex diagnostics, and affinity bioseparators.[1−4] Many fabrication methods have been developed to prepare polymer microspheres such as emulsion polymerization, dispersion polymerization, spray-drying, and distillation precipitation polymerization.[3,5,6] For controlling the morphologies and properties of polymer materials, annealing techniques such as thermal annealing or solvent annealing are commonly used.[7−11] The annealing effects on the morphologies and properties of polymer microspheres, however, have been rarely investigated.

In this work, we report the effect of thermal annealing on polystyrene (PS) microspheres deposited on poly(methyl methacrylate) (PMMA) films. After thermal annealing, the microspheres gradually sink into the PMMA films and transform into hemispheres to minimize the surface and interfacial energies of the polymers. As a result, composites of PS hemispheres encapsulated in PMMA films are obtained. The effect of the PMMA film thicknesses on the morphology transformation is also studied.

To confirm the compositions and morphologies of the PS/PMMA composities, a selective removal technique is applied.[12−14] The PS domains can be removed selectively using cyclohexane, and porous PMMA films can be obtained, where the pore sizes are controlled by the original sizes of the PS microspheres. Besides, the PMMA films can be removed selectively using acetic acid, and PS hemispheres can be released.

This work provides a simple and feasible approach to prepare heterogeneous polymer surfaces with well-defined regions, which could be applied to selective patterning in biomedical applications. In addition, the polymer composites can be used to prepare hemispheres and porous polymer films, which can not be easily prepared by other means.

The experimental scheme to fabricate the PS/PMMA composites is illustrated in Figure 1. PMMA films with different thicknesses are first prepared by blade-coating on glass substrates, followed by an annealing process at 120 °C for 3 h to reduce the roughness of the films. Subsequently, PS microspheres with an average diameter of 6 or 10 μm are spin-coated on the PMMA films. The samples are then annealed for different times at 240 °C, which is higher than the glass transition temperatures (T_g) of both polymers (T_g of PS ~ 100 °C, T_g of PMMA ~ 105 °C). During the annealing processes, the PS microspheres gradually sink into the PMMA film and transform into PS hemispheres.

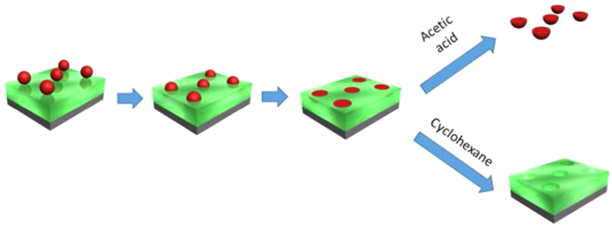


Figure 1. Schematic illustration of the experimental process to prepare PS/PMMA composites by annealing PS microspheres on PMMA films. PS hemispheres and porous PMMA films can be obtained by the selective removal technique.

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The morphology transformation of the PS microspheres on the PMMA films is mainly driven by the surface and interfacial tensions of the polymers. Initially, the PMMA films deposited with PS microspheres have higher surface areas. As the microspheres sink into the PMMA films, the surface areas between polymers and air decrease, resulting in lower surface energies. The PS microspheres eventually transform into hemispheres with the top surface exposing to air. In addition to the surface energies between polymers and air, the newly generated PS/PMMA interfaces contribute extra interfacial energies between PS and PMMA. As a result, the PS microspheres transform into PS hemispheres embedded in the PMMA films. It has to be noted that the sinking processes may occur simultaneously as the microspheres transform into hemispheres.

Figure 2 shows the optical microscopy (OM) and scanning electron microscopy (SEM) images of PS microspheres with an average diameter of ∼10 μm. By changing the concentration of the suspension and the speed of spin-coating, the densities of the microspheres on the substrates can be controlled. Figure 2a,b shows the OM and SEM images of monolayers of hexagonally packed PS microspheres formed by the self-assembly method at the liquid−air interface.[15,16]

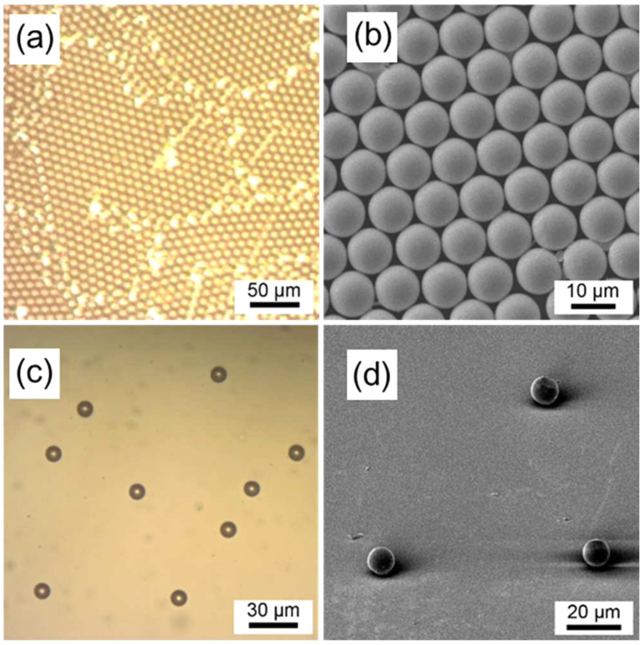

Figure 2. (a, b) OM and SEM images of monolayers of hexagonally packed PS microspheres with an average diameter of ∼10 μm. (c, d) OM and SEM images of separated PS microspheres deposited on PMMA films.

For the purpose of this work, separated polymer microspheres are preferred. Therefore, we use suspensions with lower concentrations and higher speeds of spin-coating to obtain separated PS microspheres.[17] As shown in the OM and SEM images (Figure 2c,d), separated PS microspheres with distances of ∼20−60 μm can be prepared. The tilted-view SEM image also demonstrates that there are only limited contact areas between the PS microspheres and the PMMA films because of the spherical shape of the microspheres.

After the PS microspheres are deposited on the PMMA films, the samples are thermally annealed and in situ observed using OM. Figure 3 shows the OM images of separated PS microspheres annealed on a PMMA film at 240 °C for different times. The diameters of the circles in the OM images increase after the thermal annealing process, which is mainly due to the shape transformation. For the ideal case, the PS spheres transform into hemispheres embedded in the PMMA film. Assuming that the volumes of the PS particles are conserved before and after the annealing processes, the following relation is obeyed:

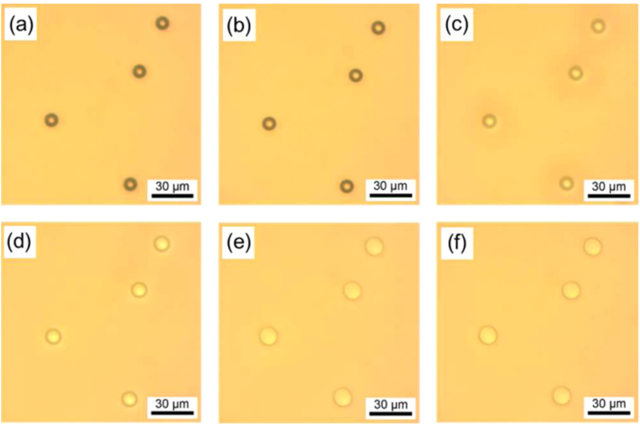

Figure 3. OM images of separated PS microspheres annealed on a PMMA film at 240 °C for different times: (a) 0, (b) 65, (c) 100, (d) 155, (e) 200, and (f) 285 s.

$$\frac{4}{3}\pi r^3 = \frac{1}{2}\frac{4}{3}\pi R_1^{\ 3} \tag{1}$$

where r is the radius of the PS microspheres before annealing and R_1 is the radius of the transformed PS particles. Equation 1 can be rewritten as the following:

$$R_1 = \sqrt[3]{2}\,r \tag{2}$$

Thus, for a single PS sphere, the radius should increase $2^{1/3}$ (≈1.26) times if the PS sphere transforms into a hemisphere. The average radius of the PS spheres before annealing, as shown in Figure 3a, is ∼5 μm. From the OM data, the measured value of the average radius of the PS particles after annealing is ∼6.45 μm, which is close to the calculated value (5 μm × 1.26 = ∼6.3 μm). The deviation between the measured value and the calculated value is probably due to the nonideal hemispherical shape of the particles after annealing. The quantitative study of the size changes of the polymer particles will be discussed in more detail later.

To investigate the transformation processes further, we also study the SEM images of PS microspheres annealed at 240 °C for different annealing times, as shown in Figure 4. The PS microspheres are observed to sink into the PMMA films gradually with the annealing time. When the annealing time is longer than ∼300 s, the PS spheres sink into the PMMA films completely and the surfaces of the PS/PMMA composite films become flat. The results indicate that the surface tension of the PS is lower or very close to that of the PMMA when the samples are annealed at 240 °C. The possible presence of the surfactants, used to synthesize the PS microspheres, might also contribute to the lower surface tension of the PS. It has to be noted that some larger microspheres shown in Figure 4 are formed as the results of many microspheres merging together.

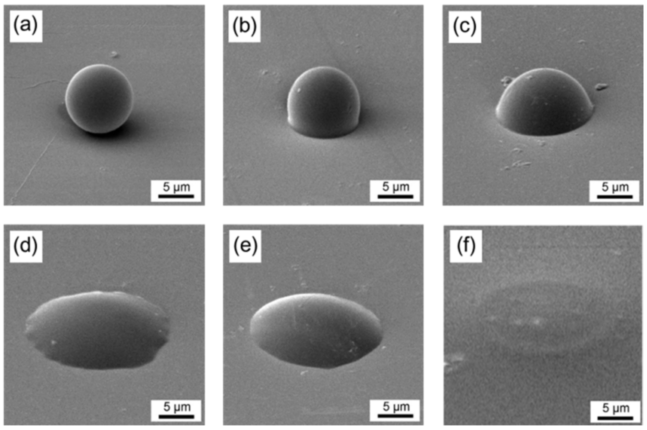

Figure 4. SEM images of PS microspheres annealed on PMMA films at 240 °C for different times: (a) 0, (b) 30, (c) 60, (d) 180, (e) 240, and (f) 300 s.

To confirm the morphologies of the transformed PS/PMMA composites, the selective removal technique is performed.[18,19] The selective removal technique is a powerful tool to characterize the morphology of the composites by using selective solvents. This technique can also help us to understand the effect of film thickness on the morphology of transformation. Here we use samples with thicker (~13 μm) and thinner (~5 μm) PMMA films.

In the case of thicker PMMA films (thickness ~ 13 μm), the PS spheres transform into hemispheres embedded in the PMMA films. Figure 5a shows the schematic illustration of the experimental process to remove the PMMA film or the PS particles selectively in the case of thicker films. The SEM image of a PS hemisphere after the PMMA film is removed selectively by acetic acid is shown in Figure 5b, in which the top flat surface and the curved side surface of the hemisphere can be observed. In addition, porous PMMA films can be obtained by removing PS hemispheres selectively using cyclohexane. Figure 5c shows the cross-sectional SEM image of a PMMA film, where a hemispherical pore can be observed. The results from the samples with thinner PMMA films (thickness ~ 5 μm) are discussed in the Supporting Information.

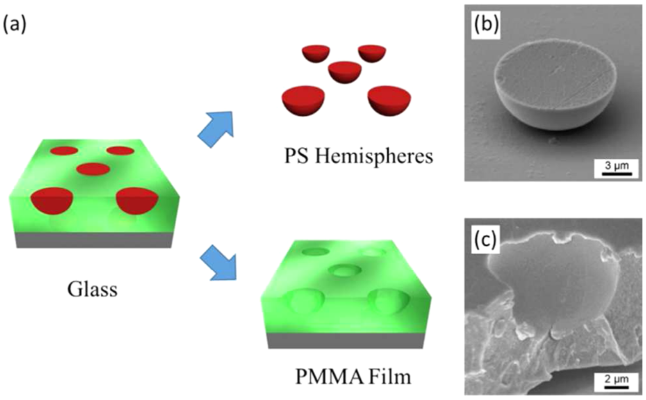

Figure 5. (a) Schematic illustration of the experimental process to remove the PMMA film or the PS particles selectively in the case of thicker PMMA films. (b) SEM image of a PS hemisphere. (c) SEM of a PMMA film, in which the PS particles are removed.

To study the transformation of the polymer particles more quantitatively, the sizes of the particles before and after annealing are measured and compared to the calculated values. Two assumptions are made for obtaining the calculated values. First, the original sizes of the particles are assumed to be uniform. Second, the volumes of the polymer particles before and after annealing are assumed to be unchanged.

Figure 6a shows the graphical illustration of the merging and transformation processes from one or multiple microspheres to hemispheres. For a single microsphere, it transforms to a hemisphere and eqs 1 and 2 described previously are obeyed. For aggregated microspheres that merge and transform to larger hemispheres, the following equation is obeyed.

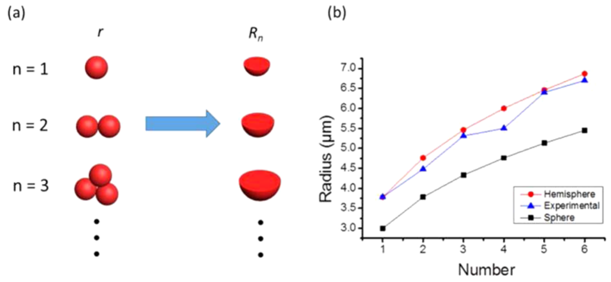

Figure 6. (a) Graphical illustration of single or multiple spheres transforming to hemispheres. (b) Plot of the radius of the merged PS particles vs the number of microspheres. The original radius of the PS microspheres before annealing is ~3 μm. The measured values of the radius of the annealed PS particles are indicated in blue. The calculated values of the radius of the annealed particles assuming spherical shape or hemispherical shape are indicated in black and red, respectively.

$$n\frac{4}{3}\pi r^3 = \frac{1}{2}\frac{4}{3}\pi R_n^{\ 3} \tag{3}$$

where R_n is the radius of the hemispheres by annealing aggregated microspheres and n is the number of aggregated microspheres. From eq 3, the relationship between R_n, n, and r can be established as the following.

$$R_n = \sqrt[3]{2n}\,r \tag{4}$$

Therefore, the radius of the hemisphere (R_n) is proportional to the radius of the original microsphere (r) and the cubic root of the number of the aggregated microspheres (n). The relationship between R_n and R_1 can also be established by combining eqs 2 and 4 as the following.

$$R_n = \sqrt[3]{n}\,R_1 \tag{5}$$

From the samples containing aggregated particles, the sizes before and after annealing can be measured and compared to the calculated values. Figure 6b shows the plot of the radius of the merged PS hemispheres (R_n) versus the number of aggregated microspheres (r) using polymer microspheres with the original radius of ~3 μm. The measured values of the annealed PS particles and the calculated values assuming transformations from spheres to hemispheres are indicated in blue and red, respectively. For comparison purposes, the calculated values assuming transformations from spheres to spheres are also presented, as indicated in black. The measured values agree well with the calculated values that assume transformations from spheres to hemispheres, confirming our hypothesis of the formation the hemispheres.

In conclusion, we study the preparation of heterogeneous polymer surfaces by annealing PS microspheres on PMMA films. The spherical PS microspheres are observed to sink into the PMMA films and transform to hemispheres. The transformation processes can be controlled by the annealing temperature and the annealing time. This work provides a simple way to prepare not only heterogeneous polymer surfaces, but also porous films and hemispheres. In the future, we will study morphology transformations using other polymers. For example, in the case of PMMA spheres annealed on PS films, a reverse case to this work, we expect that the PMMA spheres should sink into the PS films completely while their spherical shapes are maintained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

OM images of PS microspheres annealed on PMMA films. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00316.

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Notes

The authors declare no competing financial interest.

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