Micropatterned Polymer Surfaces Induced by Nonsolvent

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In this work, we present a facile method for fabricating polymer thin films with micropatterned surfaces by evaporating polymer solution containing a small amount of nonsolvent of polymer in air. Poly(methyl methacrylate) (PMMA) and polystyrene (PS) films with densely packed micropores on the surfaces were fabricated. This method was also used to prepare three-dimensional PMMA films with micropatterned surfaces. The effects of nonsolvent content; evaporation temperature; and interactions between the polymer, solvent, and nonsolvent on the specific patterns were investigated, and the formation mechanism of the pores is discussed. This simple route can potentially be used, for example, in the large-scale production of patterned surfaces, three-dimensional painting, and hydrophobicity-enhancing coatings.

1. Introduction

Many techniques, such as soft lithography,[1,2] self-assembly of block copolymers,[3−5] and the breath-figure method,[6−12] are available for the fabrication of micropatterned polymer surfaces because of the potential applications of such materials in modern science and technology.[13,14] Although some more accessible and convenient ways to fabricate micropatterned surfaces have emerged,[8] most of the methods require expensive and delicate equipment and/or specially designed and synthesized starting polymer materials, which limits their applications in some areas to a certain degree. Therefore, it is still desirable to develop simpler and cheaper techniques to prepare micropatterned polymer surfaces. In a previous study, we developed a simple route for fabricating micropatterned polymer films with micro- or nanoscale surface concaves by spreading polymer solutions on a nonsolvent surface (SNS). These films were formed through the phase separation of a polymer solution induced by exchange between the solvent and the nonsolvent across the polymer solution/nonsolvent interface upon the contacting of the polymer solution with the nonsolvent.[15,16] This SNS method is simple, low-cost, and easily accessible.

In addition, almost all of the above-mentioned methods can fabricate only free-standing or substrate-supported micropatterned films in two dimensions, that is, these methods are generally unable to generate micropatterned surfaces on three-dimensional (3D) substrates or objects. Moreover, the area of the micropatterned films produced by these methods is usually small.[1−9] In this article, we present a much easier method for fabricating thin polymer films with micropatterned surfaces. Unlike the spreading of a polymer solution on the surface of a nonsolvent in the SNS method, a small amount of a nonsolvent of the polymer is directly added into the polymer solution to form a stable polymer−solvent−nonsolvent solution system. Then, the solution is coated on a substrate surface, after which the solvent and nonsolvent are evaporated in air, resulting in a porous polymer film with a micropatterned surface. In addition to its simplicity in comparison with other patterning techniques, this method exhibits other two notable advantages. First, it can be employed to fabricate patterned surfaces with very large areas, provided that the substrate is large enough. Second, the present method can be applied not only to smooth surfaces but also to real objects with 3D structures and can make all of their surfaces patterned.

2. Experimental Section

Materials. All of the polymer materials, including polystyrene (PS, M_w = 274 370, M_n = 91 230) and poly(methyl methacrylate) (PMMA, M_w = 103 700, M_n = 37 800), were commercially available. The solvents tetrahydrofuran, acetonitrile, ethanol, and ethylene glycol were analytical grade and were provided by Beijing Chemical Reagent Company. Distilled water was used.

Procedures. The solvent and nonsolvent of the polymer were first mixed at a certain ratio to form a mixed solvent, and then the desired amount of polymer was dissolved in the mixture under agitation, resulting in a stable and clear polymer solution. The substrate materials such as glass flakes, copper flakes, and poly-(tetrafluoroethylene) (PTFE) films were ultrasonically washed with distilled water and ethanol successively and dried in the air. The cleaned substrate was then immersed into the nonsolvent-containing polymer solution and quickly removed. A thin layer of the polymer solution was attached on the surface of the substrate, which was then solidified as a patterned polymer film when the solvent and nonsolvent in the solution were evaporated in a constant-temperature oven with an accuracy of ±2 °C. All experiments were carried out at atmospheric pressure without agitation and air flow, and the evaporation time varied from less than 1 min at 50 °C to over 10 min at 2 °C in air. All experiments were carried out in air with a relative humidity of 30−40%.

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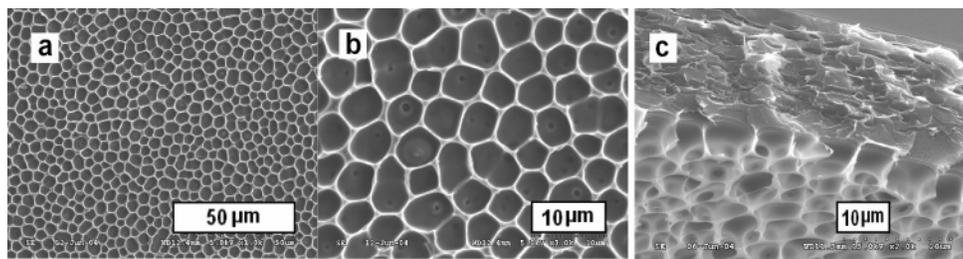
Figure 1. SEM images of PMMA film prepared from the evaporation of 10 wt % PMMA solution in THF with 4 wt % water on the glass substrate at 30 °C: (a,b) surface, (c) cross section.

Characterization. The patterned surfaces and the cross sections of the resulting polymer films were measured by means of scanning electron microscopy (SEM) on a Hitachi S4300F field-emission scanning electron microscope. The cross sections were obtained by fracturing samples in liquid nitrogen, and all samples were sputter-coated with a 10-nm-thick layer of platinum before SEM examination. Contact angles were measured on a dataphysics OCA20 contact-angle system at ambient temperature. Water droplets were dropped carefully onto the surface of samples. The average contact angle value was obtained by measuring at five different positions of the same sample.

3. Results and Discussion

3.1. Morphology of the Surface Patterns. The polymer films obtained through the evaporation of nonsolvent-containing polymer solution were opaque or semitransparent, indicating their porous structure, given that nonporous, dense PMMA or PS films are usually transparent. At 30 °C, a cleaned glass flake with a surface area of about 5 cm^2 was immersed into a 10 wt % PMMA solution in tetrahydrofuran (THF) with 4 wt % water and quickly removed. A thin layer of polymer solution was attached on the surface of the glass substrate, which was solidified as a polymer film with a thickness of about 30 μm when the solvent (THF) and nonsolvent (water) in the solution were evaporated within 3 min. SEM observation indicates that a porous structure formed on the whole surface where the polymer solution was spread, and Figure 1 shows some micrographs of the obtained film.

Densely packed pores with diameters of 4−6 μm and irregular pentagon or hexagon profiles are distributed on the surface (Figure 1a and 1b). From the cross-sectional micrograph of the film (Figure 1c), it can be estimated that the depth of these surface pores is about 5 μm, comparable to their diameter. In addition, it also can be observed that there are pores across the whole depth of the film. Furthermore, there are some smaller pores at the bottom of some surface pores (Figure 1b), which might be generated by the penetration of the pore wall between the sublayer pores and the topmost surface pores.

3.2. Formation Mechanism of the Surface Patterns. As described above, the prepared films were patterned on the surface, and small pores existed in the films. We believe that the pores in the films were formed mainly by a phase-separation mechanism. However, both the breath-figure effect and phase separation play important roles in the formation of the pores on the surface, as discussed below.

In this method, the solution is still a stable solution, although some nonsolvent of the polymer was added into the polymer solution. After the polymer−solvent−nonsolvent mixture had been coated onto the substrate surface, the solvent in the solution began to vaporize into the environment. With the loss of the solvent, phase separation of the polymer solution occurred, and nonsolvent droplets formed by nucleation and growth of the nonsolvent in the solution and on the surface. At the same time,
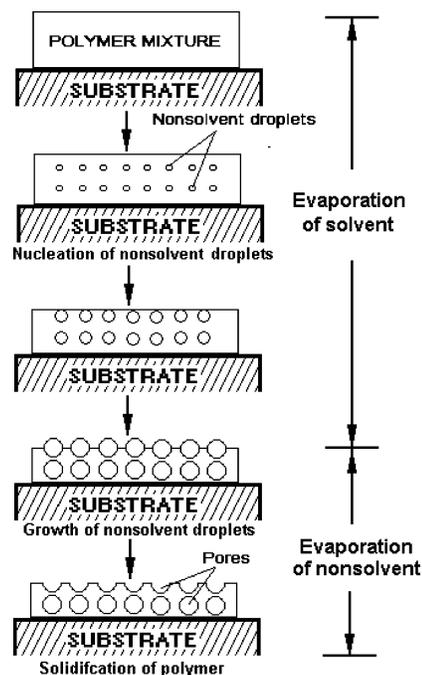

Figure 2. Schematic representation of the process of pore formation.

during the vaporization of the solvent, the breath-figure phenomenon also occurred as water vapor condensed on the surface of the solution.[10] Finally, the nonsolvent droplets also evaporated, and the positions they initially occupied were present as pores on the film surface and inside the film. Figure 2 shows a schematic representation of the process of pore formation.

3.3. Factors Influencing the Surface Pattern. In the present method, the film pores and the surface patterns originate through the nucleation and growth of the nonsolvent droplets in the polymer−solvent−nonsolvent mixture. As a result, factors including the nonsolvent content, evaporation temperature, etc., that influence the phase behaviors of the polymer solution will have considerable effects on the surface patterns. In the following sections, we take the water-containing THF solution of PMMA as an example to discuss the effects of these factors on the surface pattern.

3.3.1. Nonsolvent Content in the Polymer−Solvent−Nonsolvent Mixture. We first prepared solutions of 10 wt % PMMA in THF with 1, 4, and 7 wt % water and then coated them onto separate glass substrates and allowed them to evaporate at 30 °C. SEM images of the resultant patterned surfaces are shown in Figure 3 (see Figure 1a for the case of 4 wt %). Evidently, the diameter of the surface pores increased steadily with the amount of water in the polymer−solvent−nonsolvent mixture. The mixture with the lowest water content, i.e., 1 wt %, gave rise to the patterned surface with the smallest pore diameter of 2−3 μm, whereas the mixtures with 4 and 7 wt % water resulted in surface pores with diameters of 4−6 and 6−10 μm, respectively.
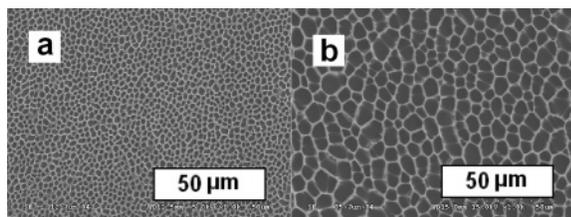
Figure 3. SEM micrographs of the surface patterns prepared from evaporation of 10 wt % PMMA in THF solution with different water contents: (a) 1 and (b) 7 wt %. Figure 1a is for the case of 4 wt %.
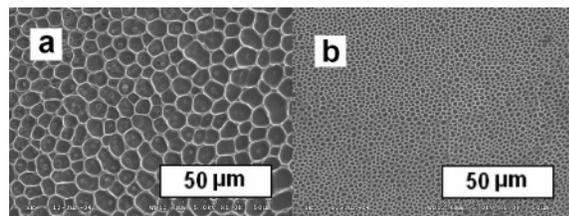

Figure 4. SEM micrographs of surface patterns prepared from the evaporation of 10 wt % PMMA in THF solution with 7 wt % water at different temperatures: (a) 2 and (b) 50 °C. Figure 3b is for the case of 30 °C.

In the mixtures, the concentration of nonsolvent, generally less than 10 wt %, is much lower than the concentration of solvent. Therefore, in mixtures with the same polymer concentration, the initial concentration of the solvent in these solutions can be considered as almost the same. As a result, the times for complete evaporation of the solvent in all of the mixtures are almost identical. However, for mixtures with higher water contents, water droplets begin to form earlier and have more time to grow; on the other hand, the higher water content will provide a sufficient supply of water to ensure the continuous growth of the nucleated water droplets. After successive evaporation of the solvent and nonsolvent, the finally obtained surface pores become correspondingly larger. For the mixture with 7 wt % water content, the pores were notably squeezed and even merged.

3.3.2. Evaporation Temperature. We coated a solution of 10 wt % PMMA in THF with 7 wt % water content on glass substrates and allowed them to evaporate at 2, 30, and 50 °C, obtaining polymer films with different surface patterns, as shown in Figure 4 (see Figure 3b for the case of 30 °C). It is obvious that the diameter of the surface pores decreases with increasing vaporization temperature. For example, the pore diameter decreases from 5−10 to 4−6 μm as the vaporization temperature changes from 2 to 30 °C and further decreases to 1−2 μm at 50 °C. Some smaller holes appear at the bottom of the surface pores formed at 2 °C, suggesting that under these evaporation conditions, the nonsolvent droplets grow fully and lead not only to the approaching and merging of the pores across the film surface, but also to the penetration and merging of the pores in the direction perpendicular to the upper film surface. At a lower temperature, the polymer mixture tends to be less stable, so that it is more prone to phase separation and the breath-figure effect is more effective. Therefore, the nonsolvent droplets in the polymer mixture are generated earlier than during evaporation of the same mixture at a higher temperature. On the other hand, the evaporation of the solvent at lower temperature is slower, and the nucleated nonsolvent droplets have adequate time to grow, whereas at higher temperature, the evaporation of the solvent is quicker, and the growth of the nonsolvent droplets will cease earlier, resulting in smaller surface pores. The time for the completion of the evaporation process varied from less than 1 min at 50 °C to over 10 min at 2 °C. From the above discussion, one can see that

decreasing the evaporation temperature has similar effects on the surface patterns as increasing the nonsolvent content in the solution.

3.3.3. Interactions between Polymer, Solvent, and Non-solvent. Because the interactions between polymer, solvent, and nonsolvent directly determine the phase separation of the three-component mixture,[17] different combinations of the three components will significantly influence the finally obtained polymer surface patterns.

The effect of different solvents for the same polymer−nonsolvent pair, i.e., PMMA−water, was investigated. We replaced THF, whose boiling point is 66 °C, with acetonitrile, which has a higher boiling point of 82 °C, in the PMMA−solvent−water solution. It can be seen by comparing Figures 3a and 5a that the regularity of the resulting surface pattern was much worse and the diameter of the surface pores was larger with acetonitrile than THF. The larger pore diameter can be attributed to the higher boiling point of acetonitrile and the fact that it takes more time to evaporate completely, so that the formed nonsolvent droplets have a longer time to grow. In addition, the solvent power of acetonitrile for PMMA is poorer than that of THF. Consequently, with the evaporation of the solvent, the phase separation of the polymer solution starts earlier.

Ethanol was also used as the nonsolvent. When 10 wt % PMMA in THF solution containing 4 wt % ethanol was vaporized at 30 °C, we obtained only a nonporous film without any notable surface pattern (micrographs not included). However, if 4 wt % water or ethylene glycol (EG) was employed as the nonsolvent, regular micropatterned surfaces were generated in both cases, and the surface pores arising from solution using ethylene glycol as the nonsolvent were denser and more regular than those from the solution using water as the nonsolvent (Figures 3b and 5b). This can be explained as follows. Because ethanol has a boiling point (78 °C) close to that of the solvent THF (66 °C), a large amount of ethanol evaporates simultaneously with the solvent. In addition, the tendency toward phase separation of ethanol is weaker than that of water, which can be deduced from the fact that the solubility parameter of ethanol is much closer to that of PMMA than that of water [δ_{water} = 23.4, $\delta_{ethanol}$ = 12.7, and δ_{PMMA} = 8.9 (cal/cm^3)$^{1/2}$].[18] Therefore, ethanol will evaporate completely before forming droplets, resulting in a nonpatterned film. This suggests that phase separation plays an important role in the formation of the pores. In the case of EG as the nonsolvent, because of its larger molecular size and bulk viscosity, the nucleated EG droplets have a lower mass-transfer rate. As a result, the polymer mixture with EG as the nonsolvent gives rise to smaller surface pores.

Finally, we studied the effect of different polymers on the surface pattern. Figure 5c shows SEM micrographs of the surface pattern originating from the evaporation of 10 wt % PS in THF solution with 4 wt % water as the nonsolvent. Compared to surface pattern from PMMA solution with same concentration and evaporation temperature (Figure 4b), the PS surface pores have a much larger diameter and a wider diameter distribution, and the neighboring pores seldom contact and keep their regular circular profile. The larger pore diameter can be attributed to the stronger phase-separation tendency of water and PS than water and PMMA and the fact that phase separation in PS solution occurs earlier; therefore, the nonsolvent droplets have a longer time to grow, which is favorable to the formation of larger pores in the surface pattern.

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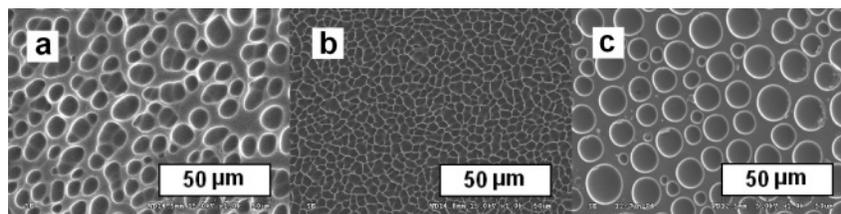(18) Bandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; John Wiley & Sons: New York, 1974.

Figure 5. SEM micrographs of surface patterns obtained from the evaporation of (a) 10 wt % PMMA in acetonitrile solution with 1 wt % water, (b) 10 wt % PMMA in THF solution with 4 wt % ethylene glycol, and (c) 10 wt % PS in THF solution with 4 wt % water. The evaporation temperature was 30 °C in all cases.

3.4. Properties and Potential Applications of the Micropatterned Surfaces. Micropatterned polymer films obtained from the evaporation of nonsolvent-containing polymer solution exhibit huge numbers of compact pores in the range of several micrometers, and owing to the increase of the surface roughness, the hydrophobicity of these patterned surfaces is enhanced considerably compared to that of nonpatterned, smooth surface of the same polymer material.[19] All of the patterned PMMA surfaces prepared in this work have a water contact angle in the range of 100−120°, whereas the contact angle of water on smooth PMMA film is only about 80°.[20]

Compared to our previously reported SNS patterning method, the present method has a unique advantage: The nonsolvent-containing polymer solution can be coated onto substrates composed of different materials via general coating techniques including brushing, immersing, etc. Using this method, we can obtain micropatterned polymer surfaces of very large areas just by brushing the solution on a large substrate. More importantly, by employing this method, we can provide all of the surfaces of 3D objects with micropatterned coatings. Therefore, this method has potential applications in the areas of hydrophobicity enhancement, antislip coatings, etc.

Other than using glass slides as substrates, we also successfully prepared patterned surfaces on different substrates, such as copper flakes and PTFE films. We poured a small amount of 10 wt % PMMA in THF solution with 7 wt % water into a small beaker with a capacity of 10 mL, then tilted and rotated the beaker to coat a thin layer of polymer solution onto the inner wall of the beaker, and poured out the residual solution. After the complete evaporation of the polymer solution on the beaker wall at 30 °C, we tore off the solidified polymer film and obtained a 3D structure that copied the inner profile of the beaker, i.e., a "PMMA beaker". SEM observation showed that the PMMA beaker had a patterned inner surface with regular microscale pores. Figure 6b shows the SEM image of the surface pattern on the upper edge of the PMMA beaker.
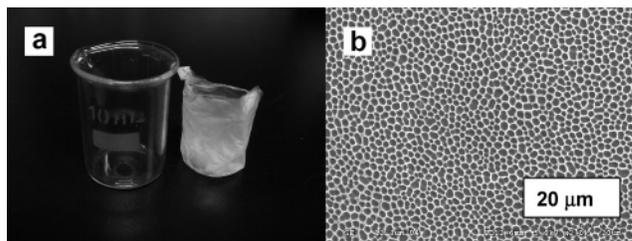

Figure 6. (a) Photograph of a beaker with a capacity of 10 mL (left) and the PMMA beaker copied from the glass beaker (right). (b) SEM image of the surface pattern on the upper edge of the PMMA beaker.

Conclusions

In this work, we describe a new method for preparing patterned polymer films. The principle of the method is that, with vaporization of the solvent in a solvent−nonsolvent−polymer solution, droplets of the nonsolvent are formed and grow through phase separation and the breath-figure effect. Eventually, all of the solvent and nonsolvent are vaporized, resulting in patterned film with dense surface pores. The diameter of the surface pores can be tuned by using suitable polymer−solvent−nonsolvent combinations and changing film-formation factors, such as the nonsolvent concentration and evaporation temperature. These patterned surfaces have enhanced hydrophobicity compared to smooth surfaces of the same materials because of the increased roughness resulting from the huge number of surface pores. This method can be used to prepare patterned films of different polymers, and many materials, such as glasses, metals, and plastics, can be employed as substrates. Large three-dimensional patterned polymer coatings or films can also be prepared.

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