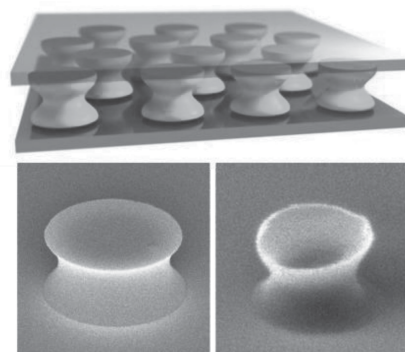


Nanopressing: Toward Tailored Polymer Microstructures and Nanostructures

Yi-Huei Kao, Mu-Huan Chi, Chia-Chan Tsai, Jiun-Tai Chen*

A simple and versatile method is developed for preparing anisotropic polymer particles by pressing polymer microspheres at elevated temperatures. Polystyrene (PS) microspheres are used to demonstrate this approach. Depending on the mechanical deformation and wetting of the polymers on the substrates, polymer structures with special shapes such as barrel-like or dumbbell-like shapes can be prepared. The morphology of polymer structures can be controlled by the experimental parameters such as the pressing pressure, the pressing temperature, and the pressing time. The wetting of the polymers on the substrates dominates when the samples are annealing at higher temperatures for longer times.



1. Introduction

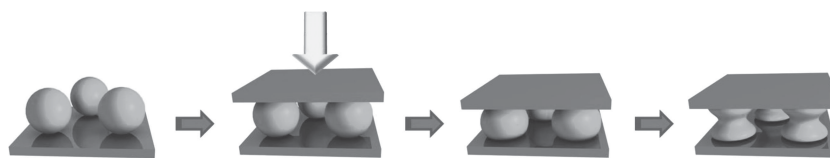
Polymer microspheres and nanospheres have been extensively studied because of their applications in areas such as drug delivery, biosensing, affinity chromatography, and cosmetics.^[1–4] The spherical polymer particles can be prepared by chemical or physical methods such as heterogeneous polymerization, coacervation, emulsification, and spray-drying.^[5–12] To overcome the intrinsic limitations of isotropic polymer particles and to prepare polymer particles with multiple functionalities, one of the common design strategies is to use anisotropic polymer particles.^[13] The shapes of nonspherical polymer particles are essential in determining their properties and functionalities. For example, Yunker et al.^[14] studied that the coffee ring effect, which is commonly observed for polymer spheres, can be eliminated by using ellipsoidal particles. The anisotropic shape of the particles deforms the air–water interfaces significantly, producing strong interparticle capillary interactions and leading to the uniform deposition of particles.

To fabricate nonspherical polymer microparticles or nanoparticles, various approaches have been developed,^[13,15] such as the stretching method,^[16,17] the seeded polymerization,^[18,19] microfluidics,^[20] and micro-molding.^[21] Among these approaches, the stretching method is commonly used to prepare ellipsoidal polymer particles through the uniform deformation of polymer microspheres in a matrix of another polymer. For example, Ho et al.^[16] embedded monodisperse spherical polystyrene (PS) particles in a deformable poly(vinyl alcohol) (PVA) matrix. The samples were then stretched above their glass transition temperatures to various predetermined macroscopic draw ratios. Later, Champion et al.^[17] modified the stretching method to generate polymer particles of over 20 distinct shapes in large quantities.

Despite these methods, however, the preparation of precisely shaped polymer particles is still a great challenge. Here, we report a simple and versatile method that directly addresses this need. The method involves placing polymer microspheres on a flat substrate and pressing the microspheres with another substrate, while the samples are thermally annealed. Unique structures such as barrel-like or dumbbell-like polymer structures, which are not accessible by other traditional methods, can be prepared. Various experimental factors including the pressing

Y.-H. Kao, M.-H. Chi, C.-C. Tsai, Prof. J.-T. Chen
Department of Applied Chemistry, National Chiao Tung
University, Hsinchu 30050, Taiwan
E-mail: jtchen@mail.nctu.edu.tw

pressure, the pressing temperature, and the pressing time are discussed for their effects on the sizes and shapes of the resultant particles. At shorter pressing times, barrel-like polymer structures are formed because the mechanical stress dominates the deformation process. At longer pressing times, however, the wetting of the polymer becomes more important, and dumbbell-like polymer structures can be obtained.



Scheme 1. The schematic illustration of the experimental process to prepare anisotropic polymer particles by pressing polymer microspheres, while the samples are thermally annealed.

2. Experimental Section

2.1. Materials

Polystyrene microspheres with a mean diameter of 2 μm (variation: 5%) were purchased from Polyscience. Four-inch Si (1 0 0) wafers were obtained from Guv Team International Co., Ltd. Deionized water was obtained from Milli-Q system. Ethanol, acetone, and isopropyl alcohol were purchased from ECHO Chemical.

2.2. Preparation of PS Microspheres on Silicon Substrates

The silicon wafers were cut into smaller substrates ($\approx 1.2 \text{ cm} \times 1.2 \text{ cm}$) and were cleaned by deionized water, acetone, and isopropyl alcohol. Before use, the silicon substrates were dried by N_2 gas. The PS microspheres in a 2.5 wt% aqueous suspension were first diluted with ethanol (weight ratio = 1:1). The PS microspheres were then spread on the silicon substrates by spin-coating the aqueous suspension at 4000 rpm for 90 s. Under this condition, separated PS microspheres on silicon substrates can be prepared.

2.3. Nanopressing of PS Microspheres

After spin-coating the PS microspheres on a silicon substrate, the sample was dried to evaporate the residual solvent. Subsequently, another silicon substrate was placed on top of the microspheres. A force was then applied on top of the sample by using a weight or a clip, whereas the whole sample was annealed at the preset temperature (170 $^\circ\text{C}$) in an oven. After the sample was pressed and annealed for the desired time such as 5 min, the force was released and the sample was cooled to room temperature. The two silicon substrates were separated, and the polymer microstructures were characterized.

2.4. Structure Analysis and Characterization

The distribution of the PS microspheres spread on the silicon substrates before the pressing process was investigated by an optical microscope (OM, Zeiss). A scanning electron microscope (SEM, JEOL JSM-7401F) with an accelerating voltage of 5.0 kV was also used to investigate the polymer microstructures before and after the pressing processes. Before the SEM measurement, the samples were dried in a vacuum oven and coated with 4 nm of platinum.

3. Results and Discussion

The experimental scheme to fabricate the anisotropic polymer particles is shown in Scheme 1. Commercially available PS microspheres with an average diameter of $\approx 2 \mu\text{m}$ are used as the starting materials. At first, separated PS microspheres are deposited on a silicon substrate by spin-coating a suspension of PS microspheres. A second silicon substrate is then placed on top of the microspheres. By putting a weight or applying a force on the second substrate, the microspheres are deformed, while the samples are annealed above the glass transition temperature (T_g) of the polymer. When the pressing temperatures are higher than the T_g of the polymer, the microspheres can wet the silicon substrates. Depending on the pressing pressure, the pressing temperature, and the pressing time, barrel-like or dumbbell-like PS particles can be prepared. The shape deformations of the PS particles are mainly controlled by both the pressing pressure from the weight and the wetting behavior of polymers on the silicon substrates.

The pristine PS microspheres can be obtained commercially or synthesized by the emulsion polymerization technique.^[22] In this work, we use PS microspheres with an average diameter of $\approx 2 \mu\text{m}$. The sizes of the microspheres can be measured by SEM, as shown in Figure 1. The distribution of the microspheres on the silicon substrates can be controlled by changing the sphere concentration of the suspension and the spin-coating speed. By using suspensions with higher sphere concentrations or spinning the suspensions at lower speeds, multilayers of stacked polymer microspheres can be formed on the silicon substrates. For the purpose of this work, separated polymer microspheres are necessary. Therefore, suspensions with a lower sphere concentration ($\approx 0.078 \text{ wt}\%$) and a high spin-coating speed ($\approx 4000 \text{ rpm}$) are applied. The SEM image of separated PS microspheres on a silicon substrate is shown in Figure 1a. The separation distances between the microspheres are ≈ 10 to $50 \mu\text{m}$. Figure 1b shows the SEM image of a single PS microsphere on the silicon substrate. The contact area of the PS microsphere on the silicon substrate is small, due to the spherical geometry of the microsphere.

Because of the monodisperse size distribution of the PS microspheres, monolayers of the microspheres can also

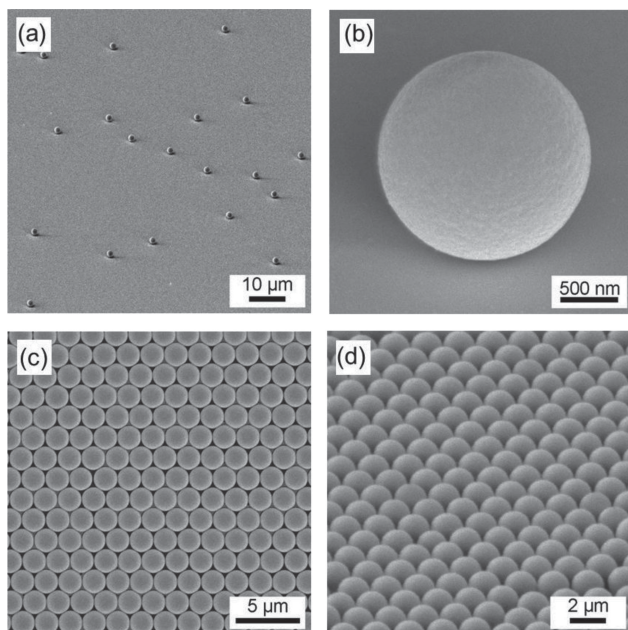


Figure 1. The SEM images of PS microspheres on silicon substrates before the pressing and the thermal annealing processes. The average diameter of PS microspheres is $\approx 2 \mu\text{m}$. a) The tilted view of many PS microspheres; b) The tilted view of a single PS microsphere; c) The top view of a monolayer of hexagonally packed PS microspheres; d) The tilted view of a monolayer of hexagonally packed PS microspheres.

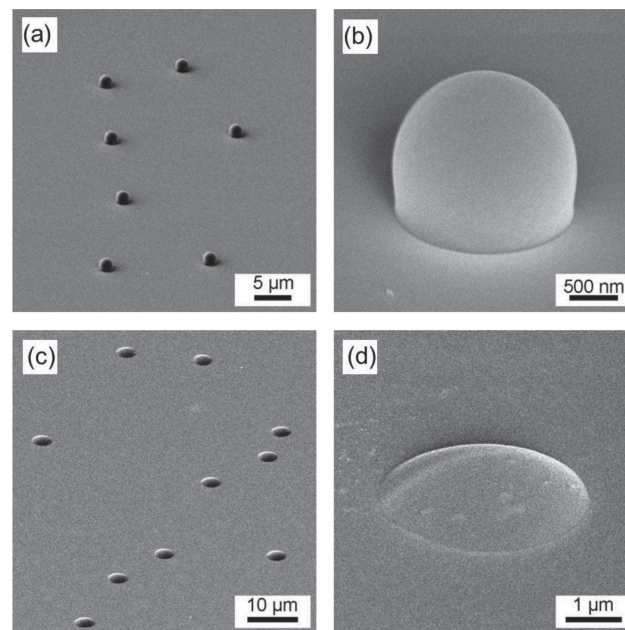


Figure 2. The SEM images of PS microspheres annealed at $170 \text{ }^\circ\text{C}$ for (a,b) 2 and (c,d) 10 min without pressing by weights. a) Many annealed PS microspheres; b) A single-annealed PS microsphere. The contact angle at the air–polymer–substrate interface is $\approx 95^\circ$; c) Many annealed PS microspheres; d) A single-annealed PS microsphere. The contact angle at the air–polymer–substrate interface is $\approx 35^\circ$.

be obtained by using techniques such as spin-coating,^[23] electrophoresis,^[24] electrostatic deposition,^[25] and the self-assembly method on the liquid–gas interface.^[26] The microsphere monolayers can be used as masks for the application of nanosphere lithography.^[27] SEM images of hexagonally packed monolayers of PS microspheres prepared by the self-assembly method on the liquid–gas interface are demonstrated in Figure 1c,d.^[26,28]

In order to study the pressing effect during the thermal annealing process, we first anneal the PS microspheres on the silicon substrates without pressing. The annealing temperatures ($170 \text{ }^\circ\text{C}$) are higher than the T_g of PS ($T_g \approx 100 \text{ }^\circ\text{C}$), and the wetting of the polymer microspheres can occur on the silicon substrates. When the samples are annealed at $170 \text{ }^\circ\text{C}$ for 2 min, wetting of the microspheres occurs on the substrates, as shown in Figure 2a,b. Compared with the unannealed microspheres, more polymer chains are in contact with the substrate after the annealing process, and the contact angle at the air–polymer–substrate interface is $\approx 95^\circ$. When the annealing time is increased to 10 min ($170 \text{ }^\circ\text{C}$), the contact angle at the air–polymer–substrate interface is decreased to $\approx 35^\circ$, as shown in Figure 2c,d. The samples annealed for longer times can wet more on the substrates, and finally the measured contact angles are closer to the equilibrium contact angle (θ_E), which is determined by Young's equation:

$$\theta_E = \cos^{-1} (\gamma_{SG} - \gamma_{SL}) / \gamma \quad (1)$$

where γ is the interfacial tension between the liquid and the gas, γ_{SL} is the interfacial tension between the solid and the liquid, and γ_{SG} is the interfacial tension between the solid and the gas.^[29]

To fabricate anisotropic polymer structures by the pressing process, several parameters are involved such as the type of the polymers, the size of the spheres, the arrangement of the spheres, the type of the substrates, the pressing pressure, the pressing temperature, and the pressing time. Among these parameters, the pressing temperature and the pressing time are the easiest parameters to be controlled. Figure 3 shows the SEM images of the pressed polymer structures by using a weight of 300 g, while the samples are annealed at $170 \text{ }^\circ\text{C}$ for 3 and 10 min. Similar structures over large areas can be obtained, as shown in Figure 3a,c. For the samples annealed at $170 \text{ }^\circ\text{C}$ for 3 min, barrel-like PS structures are generated. The detailed wetting behavior and the formation of a single barrel-like polymer structure can be observed from the SEM image with a larger magnification (Figure 3b). The top and the bottom surfaces of the barrel-like PS structures are flat, reflecting the planar nature of the silicon substrates. The convex shape of the side of the structures is caused by both

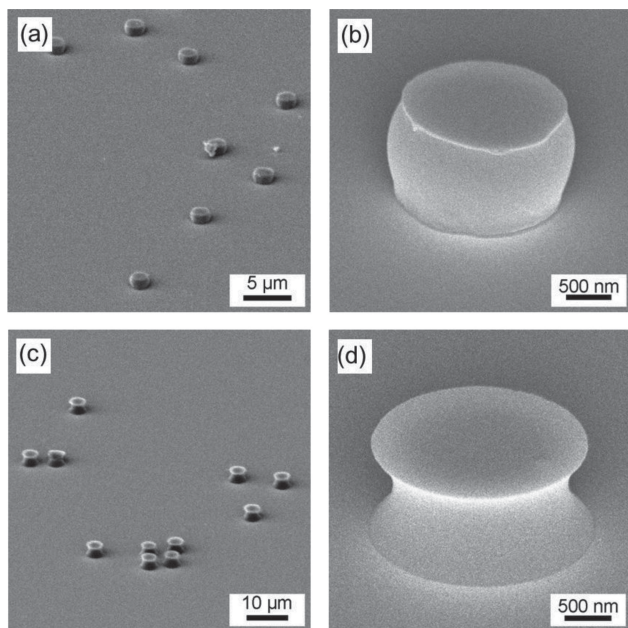


Figure 3. The SEM images of annealed PS particles by pressing the samples with a weight of 300 g, while annealing at 170 °C for (a,b) 3 and (c,d) 10 min. a) Many barrel-like polymer particles; b) A single barrel-like polymer particle. The contact angle between the polymer melt and the Si wafer is $\approx 110^\circ$. c) Many dumbbell-like polymer particles; d) A single dumbbell-like polymer particle. The contact angle between the polymer melt and the Si wafer is $\approx 50^\circ$.

the pressing effect and the original spherical shape of microspheres. The contact angle at the air–polymer–substrate interface is $\approx 110^\circ$. When the annealing time is increased to 10 min (170 °C), dumbbell-like PS structures can be obtained, as shown in Figure 3b,d. The SEM image of the dumbbell-like PS structure with a larger magnification (Figure 3d) indicates that the contact angle at the air–polymer–substrate interface is decreased to $\approx 50^\circ$. Therefore, with a longer annealing time, the wetting effect becomes more important. The contact angles keep decreasing with the annealing time and can achieve equilibrium contact angles after a certain period of time.

The detailed formation mechanism of the pressed microstructures can be explained as follows: At first, the pressing pressure dominates, and the top surfaces of the microspheres are flattened by the substrates. Later, the wetting force by thermal annealing becomes more important, and polymer chains can wet both silicon substrates. The initial contact areas between the microspheres and the substrates are small because of the spherical shape of the microspheres. The ideal contact angle of a microsphere with a very large diameter on a flat substrate is close to 180° . After the initial pressing for a short time, the contact areas of the polymer particles on

the substrates increase, while the contact angles are still larger than 90° . With a longer annealing time, the contact angles gradually decrease, and eventually reach equilibrium contact angles.

The pressing process is carried out, while the samples are thermally annealed at high temperatures. Without thermal annealing, the polymer chains are in the glassy states. Therefore, if the polymer microspheres are pressed without thermal annealing, wrinkled or broken structures can be observed. Figure S1a,b (Supporting Information) shows the tilted and top views of the SEM images of pressed PS structures by pressing the PS microspheres at room temperature. The wrinkles and the broken edges of the pressed structures shown in the images are caused by the mechanical stress of the pressing weights.^[30] Wetting is not involved in the shape changes of the PS structures, since the pressing process is carried out at room temperature, which is lower than the T_g of the polymers. Although PS microspheres can be deformed at room temperature and flattened microstructures can be obtained, the surfaces of the structures are rough, compared with the structures pressed at elevated temperatures. In addition, dumbbell-like polymer microstructures, which are related to the wetting of polymers, cannot be obtained under these conditions.

A simple morphology diagram can be drawn on the basis of the shapes of the polymer structures pressed under different conditions (Figure 4). The morphology of the pressed polymer structures can be controlled by both the pressing pressure and the pressing time. For a constant pressing pressure, the shapes of the polymer structures change with the pressing time. At a shorter pressing time, the mechanical stress dominates, and barrel-like structures can be obtained. At a longer pressing time, the wetting of polymers on the substrates becomes more important, and dumbbell-like polymer structures are formed. The dependence of the shape changes of the structures on the pressing time in the case of applying a

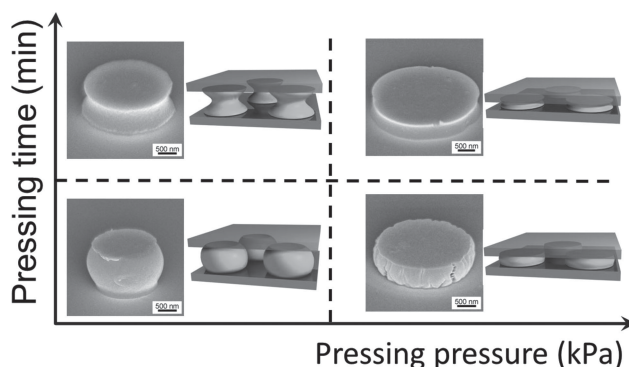


Figure 4. The graphical illustrations and the corresponding SEM images of polymer particles pressed and annealed under different conditions.

weaker pressing pressure is similar to the case of applying a stronger pressing pressure, as shown in Figure 4. But the heights of the pressed structures are shorter by applying stronger pressures, when the same pressing temperatures and times are used.

The shapes and morphologies of the polymer structures by the pressing technique can also be controlled by changing the pressing temperatures (data not shown). The results demonstrate that the dumbbell-like structures can also be obtained even at lower temperatures once longer annealing times are used. At high pressing temperatures, the degree of wetting is higher, and dumbbell-like structures can be generated at shorter annealing times.

In order to prepare the anisotropic structures with uniform sizes and shapes, it is important to keep the two silicon substrates parallel. If the two substrates are perfectly aligned, the heights of all the pressed microstructures are the same, which are equal to the length of the gap between the two silicon substrates. If the substrates are not perfectly aligned or the edge of one substrate is in contact with the edge of the other substrate, the length of the gap between the two substrates is gradient. In this case, pressed microstructures with gradient heights at different locations can be obtained.

When PS microspheres are spread on the silicon substrates, separated microspheres can be prepared by using a polymer suspension with a lower sphere density and by spinning at a higher spinning speed. Aggregated or multi-layered microspheres can be formed on the substrates if a polymer suspension with a higher sphere density and a lower spinning speed are used. After the pressing process, aggregated PS microspheres merge together, and larger microstructures can be formed compared with the microstructure pressed from separated microspheres. The shapes of the pressed polymer microstructures from aggregated microspheres are similar to those from separated microspheres, but the sizes of the pressed microstructures from aggregated microspheres are larger than those from separated microspheres.

For the pressing processes from separated polymer microspheres or aggregated polymer microspheres, the relationship between the wetting areas and the heights of the polymer structures can be calculated. For the convenience of calculation, separated polymer microspheres and aggregated polymer microspheres are assumed to form ideal disc-like structures after the pressing processes. The volumes of the polymer structures are assumed to be conserved before and after the pressing processes. For a single polymer microsphere transformed to a polymer disc, the following relation is obeyed:

$$\frac{4}{3}\pi r^3 = \pi R_1^2 h_1 \quad (2)$$

where r is the radius of the original microsphere, R_1 is the radius of the disc by pressing one microsphere, and h_1 is the height of the disc by pressing one microsphere. Assuming that aggregated microspheres also form disc-like structures by the pressing process, the following relation is obeyed:

$$n\frac{4}{3}\pi r^3 = \pi R_n^2 h_n \quad (3)$$

where n is the number of aggregated microspheres, R_n is the radius of the disc by pressing the aggregated microspheres, and h_n is the height of the disc by pressing the aggregated microspheres. For a sample containing separated and aggregated microspheres, the heights of the pressed particles from separated microspheres or aggregated microspheres are the same, which are equal to the gap (h) between the two silicon substrates. Therefore, $h_1 = h_n = h$, and Equations (2) and (3) can be substituted to yield the following equations:

$$\pi R_1^2 h = \frac{1}{n}\pi R_n^2 h \quad (4)$$

$$R_n/R_1 = \sqrt{n} \quad (5)$$

Consequently, the relationship between the radius of the pressed polymer disc and the number of aggregated microspheres can be described by Equation (5), that the ratio between the radius of the disc from aggregated microspheres and the radius of the disc from a single microsphere is equal to the square root of the number of aggregated microspheres.

To study the pressed structures from aggregated microspheres, samples containing separated and aggregated microspheres on silicon substrates are prepared by using a lower spinning speed, as shown in Figure S2a (Supporting Information). Figure S2b (Supporting Information) shows the SEM image of pressed PS structures by pressing separated and aggregated PS microspheres. In Figure S2b (Supporting Information), R_1 , R_2 , R_3 , and R_5 represent the radii of pressed PS structures by pressing one, two, three, and five PS microspheres, respectively. The (R_n/R_1) values are measured and are compared with the theoretical values, as shown in Figure S2c (Supporting Information). The measured values agree well with the theoretical data, even though the theoretical values are calculated on the basis of the assumption that the pressed structures all have ideal shapes of discs.

In this work, the volumes of the polymer structures are assumed to be conserved before and after the pressing processes. This assumption may not be correct. The PS microspheres are prepared by the emulsion polymerization technique, and the polymer chains may pack more loosely before the annealing process. Therefore, slight reductions of the volumes of the particles after the

annealing process are expected. Such reductions, however, are considered to be relatively small compared with the sizes of the polymer particles.

The pressing pressure in this work is controlled by the weights placed on the top of the silicon substrates. The pressures on individual PS particles, however, are related to the particle densities on the substrates and the contact areas between the particles and the substrates. While the particle densities on the substrates can be controlled by the particle density in the suspension and the spin-coating speeds, the contact areas are changing with the pressing time. Therefore, the pressures on individual particle are decreasing with time in a nonlinear fashion. Still, the general trend is maintained that heavier weights can result in stronger mechanical stresses.

The top and the bottom surfaces of the polymer structures are flattened by the silicon substrates whose root-mean-square roughnesses (R_q) are typically in the range of several angstroms. It may also be possible to use patterned silicon substrates by lithography techniques, and patterns can be transferred to the top and the bottom surfaces of the pressed polymer structures.

In order to examine the polymer structures after the pressing process correctly, the separation process of the two silicon substrates is critical. If the silicon substrates are separated when the samples are already cooled to room temperature, the shapes of the pressed polymer structures are maintained. If the silicon substrates are separated at temperatures higher than the T_g of polymers, polymer chains are mobile and polymer structures with special shapes can be obtained. For example, volcano-like structures with deep concave holes on the top sides of the structures can be generated when the second substrate is separated at elevated temperatures, as shown in Figure S3 (Supporting Information). The formation of the volcano-like structures is related to the pinning of the polymer melts at the polymer/air/substrate interfaces, which causes the elongation of the polymer structures during the separation process. The degrees of the elongation in the pinned regions are higher than those in the middle parts of the structures, resulting in the formation of the volcano-like concave shapes. Consequently, the structures are elongated, and the heights of the structures are higher than those before the separation processes. Polymer structures with rough edges can also be observed, when the separation process is performed at elevated temperatures (Figure S3b, Supporting Information).

If lateral movements between the two substrates are involved during the separation processes at elevated temperatures, tilted polymer structures can be formed. As shown in Figure S4 (Supporting Information), PS structures with tilted necks (turtle-like structures) are generated by separating the two substrates in both the

vertical and lateral directions to the planar surfaces of the silicon substrates. The tilt angles of the structures related to the substrates shown in Figure S4 (Supporting Information) are $\approx 50^\circ$. The longitudinal axes of most 1D nanostructures grown on planar substrates reported in the literature are usually perpendicular to the substrate surfaces.^[31] Therefore, the separation process used in this work may provide a unique approach for fabricating tilted microstructures or nanostructures on flat substrates that may exhibit interesting optoelectronic properties. The tilt angles can be controlled by changing the relative velocities of the lateral movement to the vertical movement. Similar approaches may also be applied during the separation processes, and special structures such as helical structures may be generated by twisting or spinning the top or the bottom substrates during the separation process, while the samples are still thermally annealed. As a result, the control over the separation processes of the pressed samples may open a new avenue for generating unique polymer structures with distinct shapes and morphologies that are not accessible by other traditional methods.

4. Conclusions

We study the preparation of anisotropic polymer microstructures by pressing and annealing PS microspheres. The shape of the microstructures can be controlled by the pressing pressure, the pressing time, and the pressing temperature. The shape transformation of the microstructures can be observed by checking the samples at different annealing times. The initial barrel-like polymer structures are transformed to dumbbell-like polymer structures with longer annealing times. This innovative work offers a new branch of investigation in the field of anisotropic polymer particles. In addition to polymers, this strategy can also be applied to other types of polymers, such as block copolymers, polymer blends, and polymer nanocomposites. In the future, we will work on using patterned substrates for the pressing technique and controlling the separation processes. We will also prepare regularly arranged and separated polymer microspheres on a substrate, in an attempt to fabricate ordered arrays of anisotropic polymer structures. Furthermore, the self-assembly behavior of these anisotropic structures and possible applications in biomedical applications such as drug delivery will also be explored.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Received: September 20, 2013; Revised: October 24, 2013; Published online: November 27, 2013; DOI: 10.1002/marc.201300728

Keywords: annealing; microspheres; polystyrene; pressing; wetting

- [1] S. Freiberg, X. Zhu, *Int. J. Pharm.* **2004**, *282*, 1.
- [2] J. N. Wilson, Y. Q. Wang, J. J. Lavigne, U. H. F. Bunz, *Chem. Commun.* **2003**, 1626.
- [3] J. F. Wang, P. A. G. Cormack, D. C. Sherrington, E. Khoshdel, *Angew. Chem Int. Ed.* **2003**, *42*, 5336.
- [4] J. W. Kim, J. W. Shim, J. H. Bae, S. H. Han, H. K. Kim, I. S. Chang, H. H. Kang, K. D. Suh, *Colloid Polym. Sci.* **2002**, *280*, 584.
- [5] H. Kawaguchi, *Prog. Polym. Sci.* **2000**, *25*, 1171.
- [6] K. Landfester, R. Montenegro, U. Scherf, R. Guntner, U. Asawapirom, S. Patil, D. Neher, T. Kietzke, *Adv. Mater.* **2002**, *14*, 651.
- [7] F. Bai, X. L. Yang, R. Li, B. Huang, W. Q. Huang, *Polymer* **2006**, *47*, 5775.
- [8] M. Q. Chu, L. H. Zhou, X. Songi, M. Pan, L. H. Zhang, Y. Sun, J. Zhu, Z. Q. Ding, *Nanotechnology* **2006**, *17*, 1791.
- [9] P. W. Fan, W. L. Chen, T. H. Lee, J. T. Chen, *Macromol. Rapid Commun.* **2012**, *33*, 343.
- [10] G. F. Palmieri, G. Bonacucina, P. Di Martino, S. Martelli, *Int. J. Pharm.* **2002**, *242*, 175.
- [11] C. W. Lee, T. H. Wei, C. W. Chang, J. T. Chen, *Macromol. Rapid Commun.* **2012**, *33*, 1381.
- [12] Y. C. Huang, P. W. Fan, C. W. Lee, C. W. Chu, C. C. Tsai, J. T. Chen, *ACS Appl. Mater. Interfaces* **2013**, *5*, 3134.
- [13] K. J. Lee, J. Yoon, J. Lahann, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 195.
- [14] P. J. Yunker, T. Still, M. A. Lohr, A. G. Yodh, *Nature* **2011**, *476*, 308.
- [15] S. M. Yang, S. H. Kim, J. M. Lim, G. R. Yi, *J. Mater. Chem.* **2008**, *18*, 2177.
- [16] C. C. Ho, A. Keller, J. A. Odell, R. H. Ottewill, *Polym. Int.* **1993**, *30*, 207.
- [17] J. A. Champion, Y. K. Katare, S. Mitragotri, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 11901.
- [18] J. W. Kim, R. J. Larsen, D. A. Weitz, *J. Am. Chem. Soc.* **2006**, *128*, 14374.
- [19] J. W. Kim, R. J. Larsen, D. A. Weitz, *Adv. Mater.* **2007**, *19*, 2005.
- [20] D. Dendukuri, K. Tsoi, T. A. Hatton, P. S. Doyle, *Langmuir* **2005**, *21*, 2113.
- [21] J. P. Rolland, B. W. Maynor, L. E. Euliss, A. E. Exner, G. M. Denison, J. M. DeSimone, *J. Am. Chem. Soc.* **2005**, *127*, 10096.
- [22] C. S. Chern, *Prog. Polym. Sci.* **2006**, *31*, 443.
- [23] J. C. Hulteen, D. A. Treichel, M. T. Smith, M. L. Duval, T. R. Jensen, R. P. Van Duyne, *J. Phys. Chem. B* **1999**, *103*, 3854.
- [24] M. Giersig, P. Mulvaney, *Langmuir* **1993**, *9*, 3408.
- [25] A. Rogach, A. Sussha, F. Caruso, G. Sukhorukov, A. Kornowski, S. Kershaw, H. Mohwald, A. Eychmuller, H. Weller, *Adv. Mater.* **2000**, *12*, 333.
- [26] J. Rybczynski, U. Ebels, M. Giersig, *Colloid Surf. A-Physicochem. Eng. Asp.* **2003**, *219*, 1.
- [27] J. C. Hulteen, R. P. Van Duyne, *J. Vac. Sci. Technol. A-Vac. Surf. Films* **1995**, *13*, 1553.
- [28] J. T. Chen, D. Chen, T. P. Russell, *Langmuir* **2009**, *25*, 4331.
- [29] P. G. Degennes, *Rev. Mod. Phys.* **1985**, *57*, 827.
- [30] C. M. Chen, S. Yang, *Polym. Int.* **2012**, *61*, 1041.
- [31] Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, Y. Q. Yan, *Adv. Mater.* **2003**, *15*, 353.