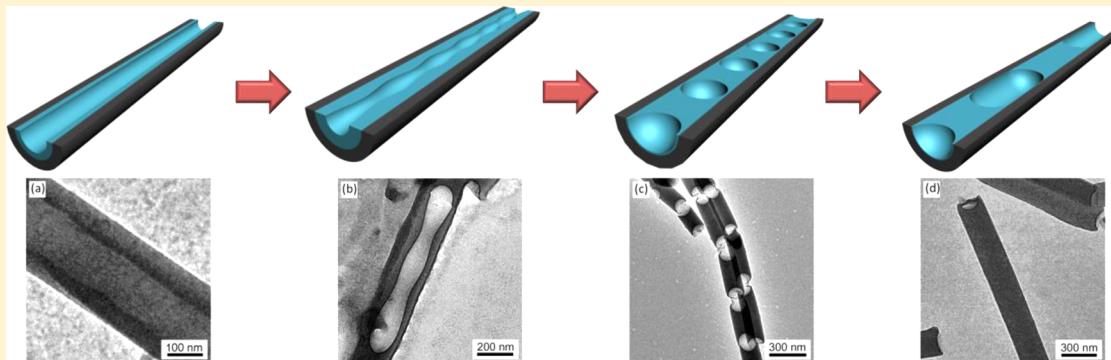


Rayleigh Instability in Polymer Thin Films Coated in the Nanopores of Anodic Aluminum Oxide Templates

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Supporting Information



ABSTRACT: We study the Rayleigh instability of polystyrene (PS) thin films coated in the nanopores of anodic aluminum oxide (AAO) templates. After thermal annealing, the surface of the PS thin films undulates and the nanostructures transform from nanotubes to Rayleigh-instability-induced nanostructures (short nanorods with encapsulated air bubbles). With longer annealing times, the nanostructures further transform to nanorods with longer lengths. PS samples with two different molecular weights (24 and 100 kg/mol) are used, and their instability transformation processes are compared. The morphology diagrams of the nanostructures at different stages are also constructed to elucidate the mechanism of the morphology transformation.

INTRODUCTION

In recent years, polymer nanomaterials have attracted great interests in both academia and industry because of their unique properties and applications in various fields.^{1–4} Polymer nanostructures, such as nanospheres, nanotubes, nanorods, or nanofibers, are synthesized and fabricated by different methods.^{5–7} The shapes and properties of these nanostructures are strongly affected by the preparation methods. For example, the emulsion method is often used to fabricate polymer nanospheres,⁸ and the electrospinning technique is frequently applied to fabricate polymer nanofibers.^{9,10} Despite these methods, there are still limitations to control the morphology of polymer-based nanostructures. In the electrospinning process, for example, many interrelated factors are involved in the fabrication of polymer fibers, and these factors are sometimes difficult to be controlled.¹¹ One of the newly developed methods to prepare polymer nanostructures is the template method.^{12–17} Porous templates are used as scaffolds, and the sizes of the polymer nanostructures are mainly determined by the sizes of the nanopores of the templates.¹⁸ The porous templates can be selectively removed to release the polymer nanostructures. A commonly used template is the anodic aluminum oxide (AAO) template, which is prepared by the anodization of aluminum foils.¹⁹ AAO templates have regular pore sizes and interpore distances, which can be

controlled by the anodization conditions and pore-widening processes.²⁰

In 2007, Russell et al. studied the transformation of poly(methyl methacrylate) (PMMA) thin films coated in the nanopores of AAO templates driven by the Rayleigh instability.²¹ They found that hierarchical polymer nanostructures containing nanorods with encapsulated air bubbles can be formed.^{21,22} Their studies not only provide experimental evidence for the Rayleigh instability of polymer thin films in confined geometries but also are important for understanding the instability behaviors of polymer nanomaterials by post-treatment.²³ Despite their works, many factors involved in the transformation process of polymer thin films coated in cylindrical nanopores are still not understood. For example, it is not clear whether the transformation process is affected by the polymer properties, such as the molecular weights, transition temperatures, and surface tensions. In addition, the morphology diagrams of the transformed morphology of polymer nanostructures at different annealing temperatures and times need to be constructed to further understand the transformation mechanism. Furthermore, the relationship

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between the kinetic pathway and the transformation process has not been discussed before.

To address these issues, here, we study the transformation of polystyrene (PS) thin films coated in the nanopores of AAO templates. The polymer used by Russell et al. to study the Rayleigh-instability-driven transformation of polymer thin films in cylindrical nanopores is PMMA.²¹ Therefore, we intentionally choose a different polymer, PS, for comparison purposes and proving the universality of the transformation processes. Similar to PMMA, PS is a common amorphous polymer with a glass transition temperature (T_g) of ~ 100 °C, but the interaction between PS and alumina is weaker than that between PMMA and alumina.

The Rayleigh instability is a common and important phenomenon in our daily life.²⁴ When we turn on a faucet, we can see that a falling stream breaks into individual droplets at the end of the water stream. The Rayleigh instability was first studied by Plateau.²⁵ He reported that a liquid cylinder undulates and disintegrates into a chain of droplets when the undulation wavelength (λ) is larger than the perimeter ($2\pi R_0$) of the liquid cylinder. Later, Rayleigh studied the phenomenon with theoretical calculations and developed useful equations to predict the relationship between the wavelength of the undulation and the diameter of the original liquid cylinder.²⁴ This phenomenon has been referred to as the Plateau-Rayleigh instability or simply the Rayleigh instability.

In the original theory of the Rayleigh instability, the driving force is the reduction of the surface energy between air and liquid. At the beginning, the surface energy between air and liquid is large and the system is unstable. The surface of the liquid cylinder undulates to reduce its surface area and the surface energy. Finally, the liquid cylinder breaks into individual spheres, as shown in Figure 1. More stable structures are

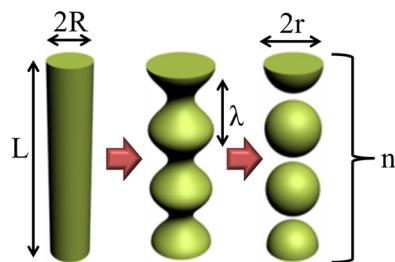


Figure 1. Graphical illustration of the Rayleigh instability. A liquid cylinder undulates and transforms into a chain of spheres.

achieved because of the reduction of the surface energy. According to Rayleigh, the wavelength of the undulation is determined by the fastest distortion mode.^{24,26}

The Rayleigh-instability-driven transformation is observed for not only simple liquids but also metals and viscoelastic

materials, such as polymers.^{27–30} For metal or polymer nanomaterials, the morphology transformation driven by the Rayleigh instability is important for understanding the property changes of nanomaterials by post-treatments and for applications in areas such as patterning or lithography. For example, Toimil-Molares et al. investigated the fragmentation of copper nanowires into copper nanospheres driven by the Rayleigh instability.²⁷ After the copper nanowires are annealed on a SiO₂ substrate at 600 °C, they decay into a chain of nanospheres with a spacing that is in agreement with the theory of the Rayleigh instability. For polymer nanomaterials, the Rayleigh-instability-type transformation is also observed.^{31–34} For example, Park et al. studied the fabrication of ordered Teflon nanospheres driven by the Rayleigh instability.³¹ They first placed a sawtoothed polydimethylsiloxane (PDMS) pattern on a spin-coated Teflon film. After the annealing process, Teflon nanospheres with different sizes and separation distances can be obtained.³¹

In this work, we study the Rayleigh instability of PS thin films confined in the nanopores of the AAO templates. The transformation process of polymer nanostructures is shown in Figure 2. There are four states in the transformation process, including (A) nanotubes, (B) undulated structures, (C) Rayleigh-instability-induced structures, and (D) nanorods. The Rayleigh-instability-induced structures in the third state are short nanorod structures with encapsulated air bubbles. Different from simple liquids, polymers are viscoelastic materials. The viscosity and chain entanglements are controlled by the molecular weight and the conformation of the polymer chains. To investigate the effect of the polymer molecular weight on the transformation process, PS with two different molecular weights ($M_w = 24$ and 100 kg/mol) are used. In addition, the morphology diagrams of the transformed morphology of polymer nanostructures at different annealing temperatures and times are constructed to elucidate the mechanism of the morphology transformation. Furthermore, the relationship between the kinetic pathway and the transformation process is discussed.

EXPERIMENTAL SECTION

Materials. PS with weight average molecular weights (M_w) of 24 kg/mol [polydispersity index (PDI) = 1.06] and 100 kg/mol (PDI = 1.06) was purchased from Polymer Source, Inc. Toluene and sodium hydroxide (NaOH) were obtained from Tedia. The AAO templates (pore diameter ≈ 150 –400 nm, and thickness ≈ 60 μm) were purchased from Whatman. Membrane filters with the pore size of 0.1 and 0.2 μm were obtained from Millipore and Toyo Roshi Kaisha, respectively. The glass substrates were purchased from the FEA Company, with the width, length, and thickness of 26, 76, and 1.2 mm, respectively.

PS Nanotubes by Wetting AAO Templates with Polymer Solutions. The PS nanotubes were prepared by the solution wetting method. At first, a PS solution (5 wt %) in toluene was prepared. A

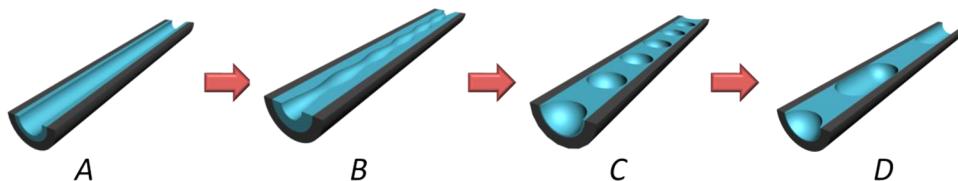


Figure 2. Schematic mechanism of the transformation process by thermally annealing polymer nanotubes confined in the nanopores of AAO templates. The polymer nanotubes (A) are transformed to undulated structures (B), Rayleigh-instability-induced structures (C), and finally nanorods (D).

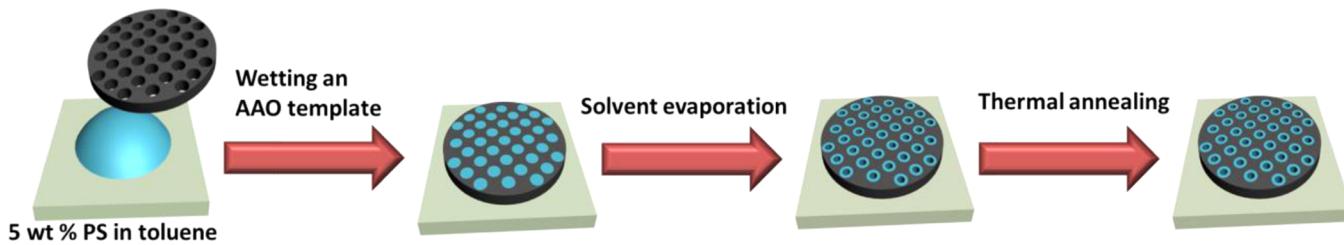


Figure 3. Experimental processes to fabricate PS nanotubes confined in the nanopores of AAO templates. The nanopores of an AAO template are first wetted by a 5 wt % PS in toluene. After the evaporation of the solvent, PS nanotubes are formed. The samples are further treated by thermal annealing, and the PS nanostructures induced by Rayleigh instability are obtained.

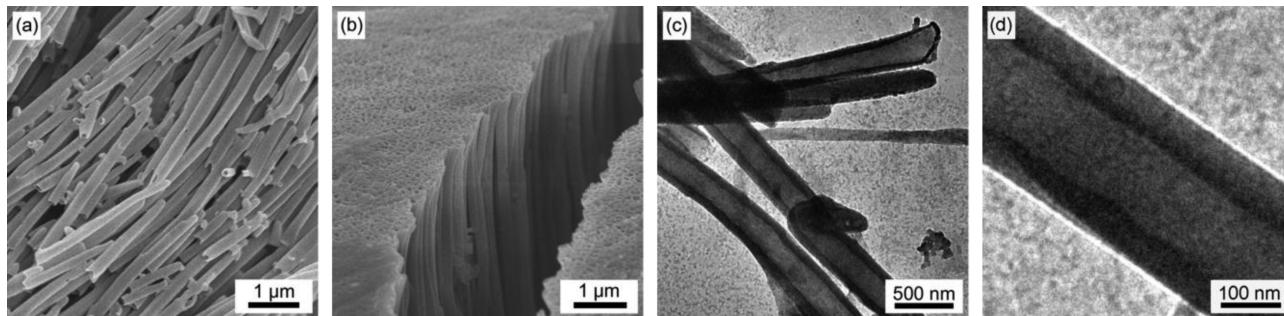


Figure 4. (a and b) SEM images of PS ($M_w = 100 \text{ kg/mol}$) nanotubes: (a) side view and (b) tilt view. (c and d) TEM images of PS ($M_w = 100 \text{ kg/mol}$) nanotubes at different magnifications. In panel d, the diameter of the PS nanotube is $\sim 250 \text{ nm}$ and the wall thickness is $\sim 60 \text{ nm}$.

drop of the PS solution in toluene was dropped onto a glass substrate. Subsequently, an AAO template with an average pore diameter $\sim 250 \text{ nm}$ was placed on top of the PS solution. The nanopores in the AAO template were filled by the PS solution via capillary force. The sample was then dried in ambient condition for 30 min and in a desiccator for 3 h. Later, the sample was further dried in a vacuum oven at room temperature for 3 h and at 60°C for 16 h to ensure the complete removal of the solvent.

Thermal Annealing Process of PS Nanotubes in the Nanopores of AAO Templates. After the fabrication of the PS nanotubes confined in the nanopores of AAO templates, the samples were annealed at different temperatures for different times. Before the samples were annealed, the oven was preheated to desired temperatures. After the annealing processes, the samples were placed in a desiccator under vacuum for 3 h. $\text{NaOH}_{(\text{aq})}$ (5 wt %) was used to remove selectively the AAO templates and release the polymer samples. Finally, the samples were filtered with membrane filters with pore diameters of 0.1 or $0.2 \mu\text{m}$ and washed with deionized water, followed by a drying process using a vacuum pump.

Structure Analysis and Characterization. The samples were characterized using a JEOL JSM-7401F scanning electron microscope (SEM) at an accelerating voltage of 5 kV and a JEOL-2100 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. Before the SEM measurements, the samples were coated with platinum. All of the TEM samples were placed on carbon-coated copper grids. Quantitative studies of the SEM and TEM data were performed using Image J software.

RESULTS AND DISCUSSION

The experimental scheme is illustrated in Figure 3. At first, PS nanotubes are fabricated by the solution wetting method, which was pioneered by Martin et al.³⁵ When the polymer solution is in contact with the AAO template, the polymer solution can wet the nanopores of the AAO templates to reduce the surface and interfacial energies. After the evaporation of the solvent, PS nanotubes are formed in the nanopores of the templates. The samples are then thermally annealed at different conditions. After the AAO templates are selectively removed by 5 wt %

$\text{NaOH}_{(\text{aq})}$, the resultant PS nanostructures are examined by SEM and TEM.

By wetting the AAO templates with a polymer solution, the polymer chains adsorb on the pore walls and polymer nanotubes are usually obtained.³⁵ The wall thickness of the polymer nanotubes is mainly determined by the polymer concentration.^{36,37} Other than the effect of the polymer concentration, the effects of other experimental factors on the morphologies and properties of polymer nanostructures using the solution wetting method have been studied.^{37–39} For example, Wendorff et al. found that polymer nanorods, nanotubes, and nanorods with regular void structures can also be obtained using the solution template wetting method by controlling the molecular weight.³⁷ Feng and Jin also studied that polymer nanospheres and nanorods can be formed by wetting AAO templates with polymer solutions, in which the solvents have preferential affinity to alumina walls.³⁸ Recently, we also found that polymer nanospheres and nanorods can be obtained by introducing non-solvent (water) during the solution wetting process.³⁹

First, we examine the morphology of the PS nanotubes without the thermal annealing processes. The tubular morphology can be observed in the SEM images, as shown in panels a and b of Figure 4. The diameters of the nanotubes correspond to those of the nanopores of the templates (~ 200 – 300 nm). Some branched tube structures are also observed in the SEM images, representing the defects of the original templates. The opening ends of the nanotubes can be seen in the tilt view (see Figure 4b). To further confirm the tubular morphology of the PS nanostructures, TEM measurements are performed. The tube walls can be seen in the TEM images (see panels c and d of Figure 4). The PS nanotubes are prepared from a PS solution of 5 wt %, and the wall thickness of the nanotube is $\sim 60 \text{ nm}$ when the tube diameter is $\sim 250 \text{ nm}$, as shown in Figure 4d.

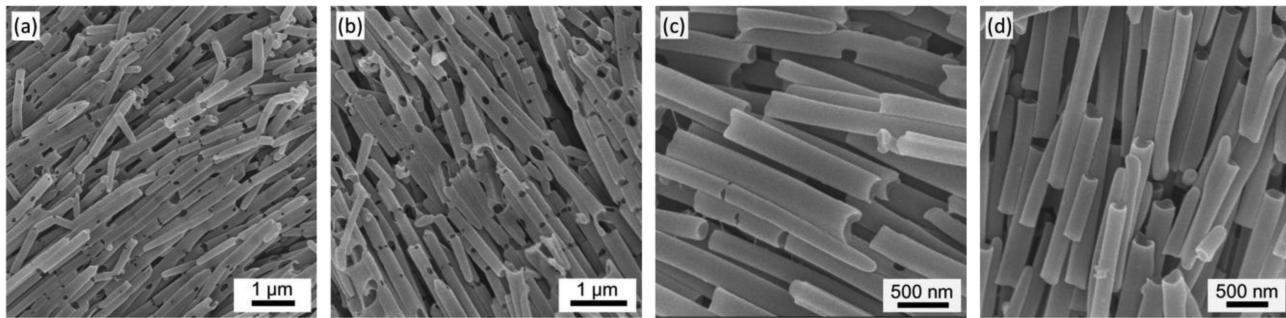


Figure 5. SEM images of PS ($M_w = 100 \text{ kg/mol}$) nanostructures by annealing PS nanotubes in the nanopores of AAO templates at 150°C for different times: (a) 30 min, (b) 1 h, (c) 8 h, and (d) 24 h. The morphologies of the nanostructures shown in panels a and b correspond to structure C shown in Figure 2. The morphologies of the nanostructures shown in panels c and d correspond to structure D shown in Figure 2.

When the PS nanotubes confined in the nanopores of the AAO templates are annealed, the surface of the tube wall undulates. With increasing the annealing time, the amplitude of the undulation also increases. When the amplitude is large enough, the undulated structures coalesce and form Rayleigh-instability-induced nanostructures (short nanorods with encapsulated air bubbles). Panels a and b of Figure 5 show the PS ($M_w = 100 \text{ kg/mol}$) nanostructures by annealing PS samples at 150°C for 30 min and 1 h, respectively. The morphologies of these nanostructures correspond to structure C shown in Figure 2. The encapsulated air bubbles in these nanostructures are only covered by thin polymer films. Therefore, the thin films can be easily broken during the SEM measurements, and the periodic holes can be observed. With longer annealing times, two or more adjacent short nanorods in the Rayleigh-instability-induced nanostructures combine and form nanorods with longer lengths. Thus, the ratio of the length of the longer nanorods to the length of the original short nanorods should be integer numbers. Panels c and d of Figure 5 shows the PS ($M_w = 100 \text{ kg/mol}$) nanostructures by annealing PS samples at 150°C for 8 and 24 h, respectively. The morphologies of these nanostructures correspond to structure D in Figure 2. The lengths of the nanorods can be further increased with even longer annealing time. In addition to SEM, TEM measurements are also performed to study the instability structures. Figure 6a shows the TEM image of the Rayleigh-instability-induced nanostructures by annealing the PS ($M_w = 100 \text{ kg/mol}$) samples at 130°C for 15 h. Solid short nanorods between encapsulated air bubbles are observed. Figure 6b shows the TEM image of the longer nanorod structures by annealing PS ($M_w = 100 \text{ kg/mol}$)

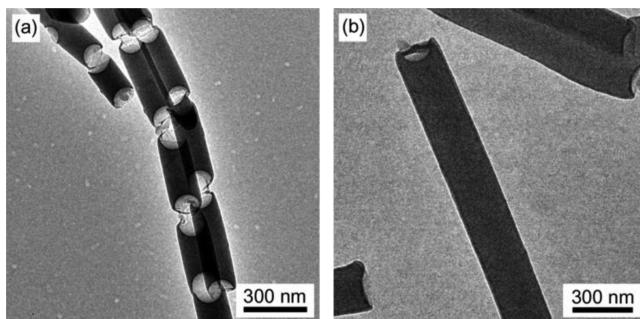


Figure 6. TEM image of PS ($M_w = 100 \text{ kg/mol}$) nanostructures by annealing PS nanotubes at different conditions: (a) 130°C for 15 h and (b) 150°C for 8 h.

samples at 150°C for 8 h. The mechanical strengths of the nanostructures close to the air bubbles are weaker than those close to the nanorods. Consequently, broken nanostructures are usually observed in the TEM measurements.

It is expected that there is a transition state between the nanotubes and the Rayleigh-instability-induced structures.²¹ To prove the existence of the transition state (undulated structures), mild annealing conditions (lower annealing temperatures and shorter annealing times) are applied. The transition states are difficult to be observed and only exist for some specific conditions. For example, the undulated structures can be seen for the PS ($M_w = 24 \text{ kg/mol}$) samples annealed at 120°C for 4 h, as shown in Figure 7a. For PS with a higher

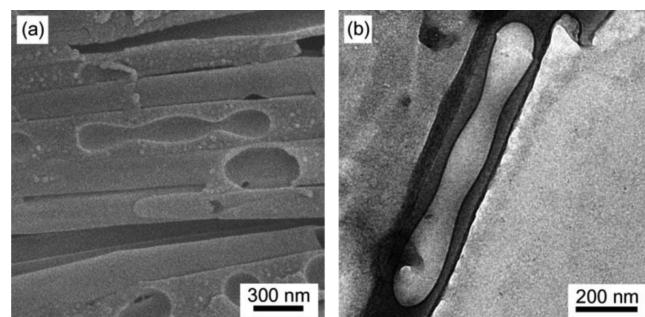


Figure 7. (a) SEM image of undulated PS ($M_w = 24 \text{ kg/mol}$) nanostructures by annealing the PS nanotubes at 120°C for 4 h. (b) TEM image of undulated PS ($M_w = 100 \text{ kg/mol}$) nanostructures by annealing the PS nanotubes at 130°C for 18 h.

molecular weight ($M_w = 100 \text{ kg/mol}$), higher temperatures and longer times are usually required to obtain the undulated structures. For example, undulated PS nanostructures are obtained by annealing the PS sample at 130°C for 18 h, as shown in the TEM image (Figure 7b). It has to be noted that the undulated morphologies can only be observed in very limited regions of the samples, indicating that these morphologies are unstable. Therefore, the data shown in Figure 7 are the combination of undulated morphologies (structure B in Figure 2) and Rayleigh-instability-induced morphologies (structure C in Figure 2). As a result, only undulated structures with closed ends are observed.

We construct the morphology diagrams to elucidate the transformed morphologies of PS nanostructures at different annealing temperatures and times. The morphology diagrams using PS with two different molecular weights ($M_w = 24$ and 100 kg/mol) are shown in Figure 8. Three morphologies are

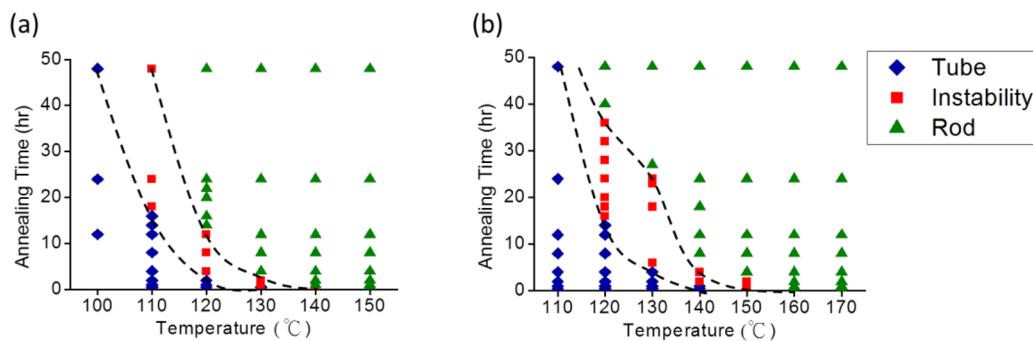


Figure 8. Morphology diagrams of polymer nanostructures from PS with two different molecular weights: (a) $M_w = 24 \text{ kg/mol}$ and (b) $M_w = 100 \text{ kg/mol}$. The solid blue diamond indicates the nanotube structures (structure A in Figure 2). The solid red square indicates the instability structures (structure C in Figure 2). The solid green triangle indicates the nanorod structures (structure D in Figure 2). The black dashed lines are used to guide the eye and to demarcate the different structures.

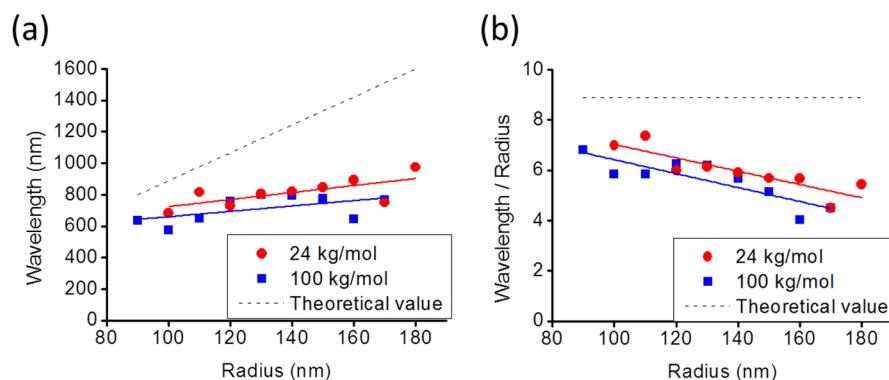


Figure 9. (a) Plot of the undulation wavelength versus the radius of the nanopore. (b) Plot of the wavelength divided by the radius of the nanopore versus the radius.

identified in the transformation process. The first morphology is the morphology of nanotube structures, which are indicated by solid blue diamonds and correspond to structure A in Figure 2. The second morphology is the morphology of instability structures, which are indicated by solid red squares and correspond to structure C in Figure 2. The third morphology is the morphology of nanorod structures, which are indicated by solid green triangles and correspond to structure D in Figure 2. The transition states (undulated structures) that correspond to structure B in Figure 2 are located between the nanotube structures and instability structures and are not indicated in the morphology diagrams.

From the morphology diagrams, it can be observed that the starting point of the instability structure region occurs at shorter times when the annealing temperature is higher. For example, the starting point of the instability PS ($M_w = 24 \text{ kg/mol}$) structure region is $\sim 18 \text{ h}$ when the annealing temperature is 110°C . The starting point of the instability PS ($M_w = 24 \text{ kg/mol}$) structure region is $\sim 1 \text{ h}$ when the annealing temperature is increased to 130°C . Therefore, the time required to transform from the tube structures to the instability structures at 130°C is shorter than that at 110°C . In addition, the instability structure region is larger at lower annealing temperatures. For example, the instability structures are observed when the PS ($M_w = 24 \text{ kg/mol}$) samples are annealed at 120°C from 4 to 12 h, a duration of 8 h. For higher annealing temperatures (130°C), the instability structures are observed when the samples are annealed from 1 to 2 h, a duration of only 1 h. The shorter duration time in the region of instability structures is because of the lower viscosities at higher

annealing temperatures. Polymers with lower viscosities have higher mobilities and transform from the instability structures to the nanorod structures more rapidly.

Similar tendency in the morphology diagram can be observed for PS with higher molecular weight ($M_w = 100 \text{ kg/mol}$), as shown in Figure 8b. However, for PS with higher molecular weights, a slower kinetics is observed. Furthermore, the instability structure region is larger for PS with higher molecular weights than that with lower molecular weights under the same annealing conditions. For example, the instability structures are observed when the PS ($M_w = 24 \text{ kg/mol}$) samples are annealed at 120°C from 4 to 12 h, a duration of 8 h. For PS samples with higher molecular weights ($M_w = 100 \text{ kg/mol}$) and annealed at 120°C , the instability structures are observed by annealing from 16 to 36 h, a duration of 20 h. Similar to the effect of increasing the annealing temperature, polymers with lower molecular weights have higher mobilities and transform from the instability structures to the nanorod structures more rapidly.

The results in the morphology diagrams for PS with these two molecular weights are further examined (see Figure S1 of the Supporting Information). The starting points, middle points, and ending points of the instability regions (structure C in Figure 2) at different annealing temperatures are compared. As shown in Figure S1a of the Supporting Information, the starting points of the instability structure region from PS with a molecular weight of 24 kg/mol are found to be earlier than those from PS with a molecular weight of 100 kg/mol . For polymers with lower molecular weights, the effect of chain entanglement is less, resulting in higher mobilities of the

polymer chains. Similar trends are also observed for the middle points and ending points in the instability regions, as shown in panels b and c of Figure S1 of the Supporting Information.

Quantitative studies of the transformation process are also performed, and the experimental values are compared to the theoretical values. According to the theory of the Rayleigh instability, the relationship between the wavelength of the undulation and the diameter of the cylinder can be shown as the following:

$$\lambda = 2\pi b \sqrt{2} \quad (1)$$

where λ is the wavelength of the undulation and b is the radius of the original tube.⁴⁰ It can be seen that the experimental results follow a linear relation but deviate from the theoretical values, as shown in Figure 9a. To eliminate the effect of different radii, the wavelength is replaced by the values calculated by the wavelength over radius of tube at the longitudinal axis. Discrepancies from the theoretical values are observed (see Figure 9b), which can be explained by the following reasons. First, the interaction between the polymer and AAO wall may affect the transformation process. Such effects should be more evident in AAO templates with smaller diameters. Second, the calculated values are based on cylinders in a non-confined environment. In this work, however, the polymers are confined in the nanopores of AAO templates. Therefore, the sizes of the air bubbles are restricted by the diameters of the nanopores. Such discrepancies are also observed by Russell et al., who used PMMA thin films in the nanopores of AAO templates.²¹

The pore diameters of the AAO template are ~ 150 – 400 nm. The pore diameter distribution gives us the advantage of obtaining data for nanotubes with different diameters (~ 150 – 400 nm) from a single sample. As shown in Figure 9, similar trends are followed for nanotubes with this diameter range. Different behaviors might be observed when the nanotubes are prepared from AAO templates with much smaller diameters. For example, the radius of gyration (R_g) of PS with an average molecular weight of 100 kg/mol is ~ 9 nm. Therefore, the instability phenomena of polymer chains might be significantly different when the radii of the nanotubes are close to or below the radii of gyration of the polymers.

On the basis of the experimental results, the energy states for polymer morphologies at different transformation processes can be realized. The driving force of the morphology transformation is related to the theory of the Rayleigh instability. The transformation process can be regarded as the transformation from an air cylinder embedded in the polymer matrix to a series of air bubbles. At first, nanotubes are formed within the nanopores of AAO templates using the solution wetting method. Because the surface energy between the wall surface of AAO templates and air is larger than that between PS and air, PS chains cover the wall surface of AAO templates to form PS nanotubes after the evaporation of the solvent. Without solvent and below the glass transition temperatures of the polymers, the nanotube morphologies are maintained, even though the morphology is not at the lowest energy state.

Once the samples are annealed at temperatures higher than the glass transition temperature of PS, the morphology of the polymer nanostructures can be changed to reduce the energy state. By assuming the conservation of the volume, the change in the total surface area can be calculated. The interfacial areas between polymer and air are decreased from tube structures to

Rayleigh-instability-induced structures, resulting in lower surface energies. As a result, tube structures undulate and transform to Rayleigh-instability-induced structures to reduce the energy. Even though the energy states of the instability structures are not the most stable states, the instability structures are still formed in a short time because of their relative stable states. With further annealing at high temperatures, the instability structures can be changed to nanorod structures.

When the annealing temperatures are lower, the morphology transformation processes are slower. On the basis of the experimental results, we propose that there are energy barriers between the instability structures (structure C in Figure 2) and the nanorod structures (structure D in Figure 2). Once the polymer has enough energy to overcome the energy barrier, the morphology can be changed from instability structures into nanorod structures, in which the energy state is more stable than that of the instability structures.

There are three regions in the morphology diagram, including the nanotube region, the instability structure region, and the nanorod region. These definitions, however, are roughly defined. There are slight differences between annealing at low and high temperatures. For samples annealed at higher temperatures, more regular structures and clear boundaries between different regions in the morphology diagrams are observed. For samples annealed at lower temperatures, however, two or more different morphologies can sometimes be observed on the same samples. We propose that the polymer chains are more difficult to transform at lower temperatures because of their lower mobilities. For example, when the PS ($M_w = 24$ kg/mol) samples are annealed at 110 °C, the instability structures are still maintained, even the samples annealed for 48 h.

CONCLUSION

We study the Rayleigh instability in PS thin films confined in the cylindrical nanopores of AAO templates. After thermal annealing, the surface of PS nanotubes undulates and transforms into short nanorods with encapsulated air bubbles (Rayleigh-instability-induced nanostructures). The morphology diagrams of the PS nanostructures with two different molecular weights are constructed and compared to demonstrate the morphology transitions at different annealing temperatures and times. Slower kinetics of the morphology transformation is observed for PS with higher molecular weights.

In the future, we will study the Rayleigh-type transformation in cylindrical nanopores using other types of polymers, such as crystalline polymers, block copolymers, or conjugated polymers. The morphology transformation may be affected by properties of these polymers, including the crystallinity and the chain conformation. In addition, the spontaneous formation of the encapsulated air bubbles may be useful for delivery and sensing purposes.

ASSOCIATED CONTENT

S Supporting Information

Plots of the annealing time versus the annealing temperature at different transformation stages for PS with molecular weights of 24 and 100 kg/mol (Figure S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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