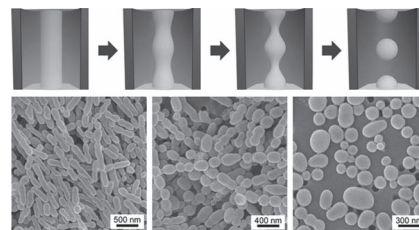


Effect of Nonsolvent on the Formation of Polymer Nanomaterials in the Nanopores of Anodic Aluminum Oxide Templates

Chih-Wei Lee, Tzu-Hui Wei, Chun-Wei Chang, Jiun-Tai Chen*

We study the effect of nonsolvent on the formation of polymer nanomaterials in the nanopores of porous templates. Water (nonsolvent) is added into a poly (methyl methacrylate) (PMMA) solution in dimethylformamide (DMF) confined in the nanopores of an anodic aluminum oxide (AAO) template. Water forms a wetting layer on the pore wall and causes the PMMA solution to be isolated in the center of the nanopore, resulting in the formation of PMMA nanospheres or nanorods after the solvent is evaporated. The formation of the polymer nanomaterials induced by nonsolvent is found to be driven by the Rayleigh-instability-type transformation. Without adding the nonsolvent, PMMA chains precipitate on the walls of the nanopores after the solvent is evaporated, and PMMA nanotubes are obtained.



1. Introduction

In recent years, the fabrication of polymer nanomaterials has aroused great interest because of their unique properties and applications in areas such as sensors, actuators, drug delivery, or photovoltaics.^[1–4] Compared with other fabrication methods, the template method has been proved to be a powerful technique to prepare various kinds of polymer nanomaterials.^[5,6] Polymer melts or solutions are introduced into the nanopores of porous templates by wetting, and polymer nanomaterials are obtained after the removal of the templates.^[7] These polymer nanomaterials possess unique properties and unusual morphologies, which are not accessible in the bulk.^[8–11] One of the most widely used templates is the anodic aluminum oxide (AAO) template, which is prepared by the electrochemical oxidation of aluminum.^[12] By using a two-step anodization process, developed by Masuda and Fukuda,^[13] AAO templates with hexagonally packed nanopores and high pore densities can be prepared. Although many polymer

nanomaterials have been fabricated using templates such as the AAO template, only few studies have focused on the formation mechanism of polymer nanomaterials using the template-based method.^[14] For example, Russell and co-workers^[15] studied the transition from partial to complete wetting of polystyrene (PS) melts by using AAO templates. The wetting transition was found to be related to the spreading coefficient, which is dependent on the annealing temperature and the polymer molecular weight. Wendorff and co-workers^[16] also investigated the effect of polymer molecular weight on the formation of PS nanomaterials by wetting AAO templates with PS solution. They observed that the formation of PS nanorods, nanotubes, or void structures can be controlled by changing the polymer molecular weight. Later, Feng and Jin^[17] studied the effect of interfacial interactions on controlling the polymer nanostructures using template wetting with PS solution. They demonstrated that the nanorod morphology is dependent on the solvents, which have preferential affinity to the pore wall of the template. Despite these works, it is still a challenge to fully understand the formation mechanism of polymer nanomaterials made by templates. The formation process of these materials involves many interrelated factors, such as the type of polymer, the polymer molecular weight, the solution concentration, the type of solvent, the drying

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condition, the size of the nanopore, and the chemistry of the pore wall.^[18–25] These factors are important in controlling the properties, morphologies, and sizes of polymer nanomaterials made by templates, but they still require further investigation.

Here, we study the effect of nonsolvent on the formation of polymer nanomaterials made by templates. Poly(methyl methacrylate) (PMMA) solution in dimethylformamide (DMF) is first introduced to the nanopores of AAO templates by capillary force. Without adding nonsolvent, PMMA chains precipitate on the pore wall, and nanotubes are obtained after the solvent is dried by a vacuum pump. By adding water (nonsolvent), the PMMA solution is isolated in the center of the nanopores of the templates, and PMMA nanospheres or nanorods are formed after the solvent is dried. The aspect ratios of the polymer nanomaterials are also found to be dependent on the polymer concentration. The formation of these nanomaterials is driven not only by the nonfavorable interaction between the polymer and water but also by the confinement effect of the porous template. To demonstrate the versatility of this work, another commonly used polymer, PS, is also studied, and similar results are obtained.

By studying different drying times of the polymer solution in the nanopores before water is added, the formation mechanism of the polymer nanomaterials is found to be related to the Rayleigh-instability-type transformation. The Rayleigh instability was first studied by Plateau, who investigated the instability in liquid cylinders.^[26] He demonstrated that the free surface of a liquid cylinder first distorts, and the liquid cylinder then disintegrates into a chain of drops to reduce the surface energy. Later, Rayleigh showed that the wavelength of the distortion and the size of the drops are determined by the fastest distortion mode.^[27] Similar studies were further conducted by Nichols and Mullins,^[28] who extended Rayleigh's approach to solid cylinders. The Rayleigh-instability-type transformation has been observed for different materials such as metals or polymers.^[29–31] In this study, the polymer solution confined in a nanopore is first isolated by water and forms a cylindrical domain, which later undulates and breaks into spherical domains, resulting in the formation of polymer nanospheres. When some amount of solvent has been evaporated before adding water, the transformation process may not be completed, and intermediate structures can be observed.

2. Experimental Section

2.1. Materials

Poly (methyl methacrylate) with weight-average molecular weights (\bar{M}_w) of 97 and 557 kg mol⁻¹ was purchased from Sigma-Aldrich and Polymer Source, respectively. PS was

purchased from Sigma-Aldrich with the weight-average molecular weight (\bar{M}_w) of 35 kg mol⁻¹. DMF and sodium hydroxide (NaOH) were obtained from TEDIA. The AAO membranes (pore diameter \approx 150–400 nm, thickness \approx 60 μ m) were purchased from Whatman. Polycarbonate filters (VCTP, pore size: 0.1 μ m) were obtained from Millipore. The wipers (Kimwipes) were purchased from Kimberly-Clark.

2.2. Fabrication of Polymer Nanomaterials

PMMA and PS nanomaterials were made under similar conditions. For making PMMA nanomaterials, for example, polymer solutions (PMMA in DMF) with different concentrations (5, 8, 10, 16, and 32 wt%) were first prepared. To fabricate PMMA nanotubes, the AAO templates were immersed into the PMMA solution for 3 s. After the templates were taken out of the solution, the residual solution outside the nanopores of the AAO templates was removed by wiping with wipers (Kimwipes). Subsequently, the samples were dried with a vacuum pump, followed by immersing into NaOH_(aq) to selectively dissolve the AAO template. Finally, the samples were filtered and washed with deionized water using polycarbonate filters. To fabricate PMMA nanospheres or nanorods, similar procedures were performed, but the AAO templates were dipped into a bottle of water before the templates were selectively removed by NaOH_(aq).^[32]

2.3. Structure Analysis and Characterization

A JEOL JSM-7401F model scanning electron microscope (SEM) with an accelerating voltage of 10 kV was used to investigate the polymer nanostructures. Before the SEM measurement, the samples were dried in a vacuum oven at 30 °C and were coated with 4 nm platinum. Bright-field transmission electron microscopy (TEM) studies were conducted with a JEOL JEM-2010 TEM operating at an accelerating voltage of 200 kV. For TEM measurement, the samples were placed onto copper grids coated with Formvar and carbon.

3. Results and Discussion

To study the effect of nonsolvent on the formation of polymer nanomaterials made by templates, we choose water as the nonsolvent. First, we consider the Hildebrand solubility parameters (δ) of the polymers and solvents. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density and is often used as an indicator for solvation and swelling.^[33] Polymers are soluble in solvents with similar values of solubility parameters. The solubility parameters of PMMA, PS, DMF, and water are 19.4, 18.6, 24.8, and 47.9 MPa^{1/2}, respectively. Consequently, PMMA and PS are soluble in DMF and are insoluble in water. It is also important that DMF and water are miscible, so that water can diffuse into the polymer solution confined in the nanopores.

The experimental scheme for preparing the polymer nanomaterials is shown in Figure 1, which is divided into

route A and route B. The main difference between route A and route B is that water (nonsolvent) is not added in route A to demonstrate the effect of the nonsolvent. For both routes, the polymer solution is introduced into the nanopores of the AAO templates by capillary force. The height at which the polymer solution can reach by capillary force is inversely proportional to the radius of the nanopore, given by the Jurin's law:^[34]

$$h = 2\gamma \cos\theta / \rho g r \quad (1)$$

where h is the maximum height, γ is the surface tension of the polymer solution, θ is the contact angle of the solution meniscus at the pore wall, ρ is the density of the polymer solution, g is gravity, and r is the radius of the pore. The maximum height at which the polymer solution can reach is higher than the length of the nanopores ($\approx 60 \mu\text{m}$), mainly due to the small pore diameters ($\approx 150\text{--}400 \text{ nm}$). The low viscosity of the polymer solution also causes the solution to be drawn into the nanopores within a second.

After the AAO templates are taken out from the polymer solution, a wiping step using a wiper is performed to remove the polymer solution outside the nanopores of the AAO templates. This step is to ensure that the polymer nanomaterials obtained after dissolving the templates are from the materials confined in the nanopores. Without the wiping step, the obtained results are disturbed by the materials outside the nanopores. For route A, the solution-containing templates are dried using a vacuum pump, resulting in the precipitation of polymers on the pore walls. After the templates are selectively removed by aqueous NaOH solution, polymer nanotubes are obtained. The vacuum pump is used to ensure that the solvent is dried completely. Otherwise, the residual solvent in the nanopores may cause the morphology change of the polymers

when the samples are exposed to the aqueous NaOH solution. For route B, the solution-containing templates are immersed into a bottle of water immediately after the wiping step. The preferential interaction between water and the pore wall causes the formation of a wetting layer of water on the surface of the pore wall.^[35] Consequently, the polymer solution is isolated in the center of the pores. After the templates are selectively removed by the aqueous NaOH solution, nanospheres or nanorods are obtained, depending on the concentration of the polymer solution.

When water is introduced into the solution-containing nanopores, it is important to make sure that the solvent is not dried. If the solvent has already evaporated completely before introducing water, then polymer nanotubes are obtained, because of the precipitation of the polymers on the pore wall. In this work, the solvent for the polymer is DMF, which has relatively high boiling point ($153 \text{ }^\circ\text{C}$) and low vapor pressure (2.6 mmHg at $20 \text{ }^\circ\text{C}$). Therefore, the polymer solution can stay longer in the nanopores of the AAO template before the nonsolvent is added. For solvents such as THF (boiling point: $66 \text{ }^\circ\text{C}$, vapor pressure: 129 mmHg at $20 \text{ }^\circ\text{C}$) or chloroform (boiling point: $61 \text{ }^\circ\text{C}$, vapor pressure: 159 mmHg at $20 \text{ }^\circ\text{C}$), also good solvents for PMMA at room temperature, they have much higher vapor pressures than that of DMF and evaporate more quickly.

Figure 2 shows the SEM and TEM images of PMMA nanotubes. Without the nonsolvent, PMMA precipitate on the pore wall of the AAO template after the evaporation of the solvent.^[36] The diameters ($150\text{--}400 \text{ nm}$) and length ($\approx 60 \mu\text{m}$) of the PMMA nanotubes correspond to those of the nanopores. Branched structures, indicating the branched pores in the AAO templates, can also be seen from the side view of the nanotubes (Figure 2a). The tubular nature of the structures is seen from the top view shown in Figure 2b. The top parts of the nanotubes are

observed to be inter-connected, demonstrating that the polymer solution also wets the top surface of the template and forms a thin polymer film. Figure 2c and d shows two typical images of a single PMMA nanotube with low and high magnifications, respectively. The tubular structure is evident, and the wall thickness of this nanotube is $\approx 100 \text{ nm}$ with an outer diameter of $\approx 300 \text{ nm}$. The wavy structures with nonuniform thickness on the tube wall may be caused by the fast evaporation of the solvent by the vacuum pump. Because the sample has been dried by the vacuum pump, the tubular polymer structures are retained even after they are exposed to the aqueous NaOH solution.

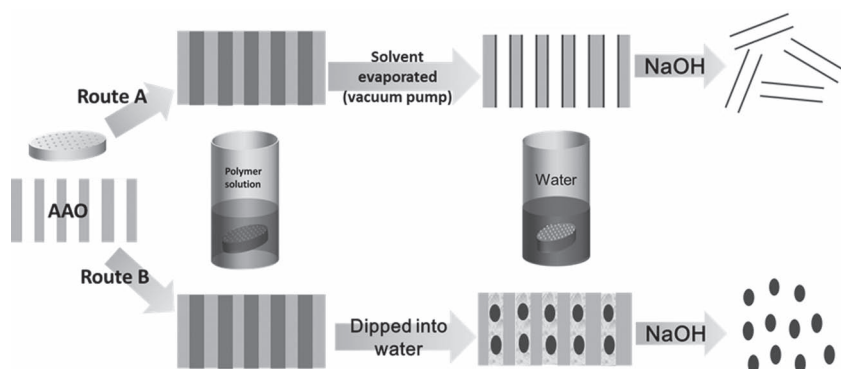


Figure 1. The schematic illustration of the experimental processes, including route A and route B. For route A, the sample is dried directly using a vacuum pump without adding water, and polymer nanotubes are obtained. For route B, the sample is dipped into water before the AAO template is selectively removed by $\text{NaOH}_{(\text{aq})}$. Nanospheres or nanorods are obtained, depending on the concentration of the polymer solution.

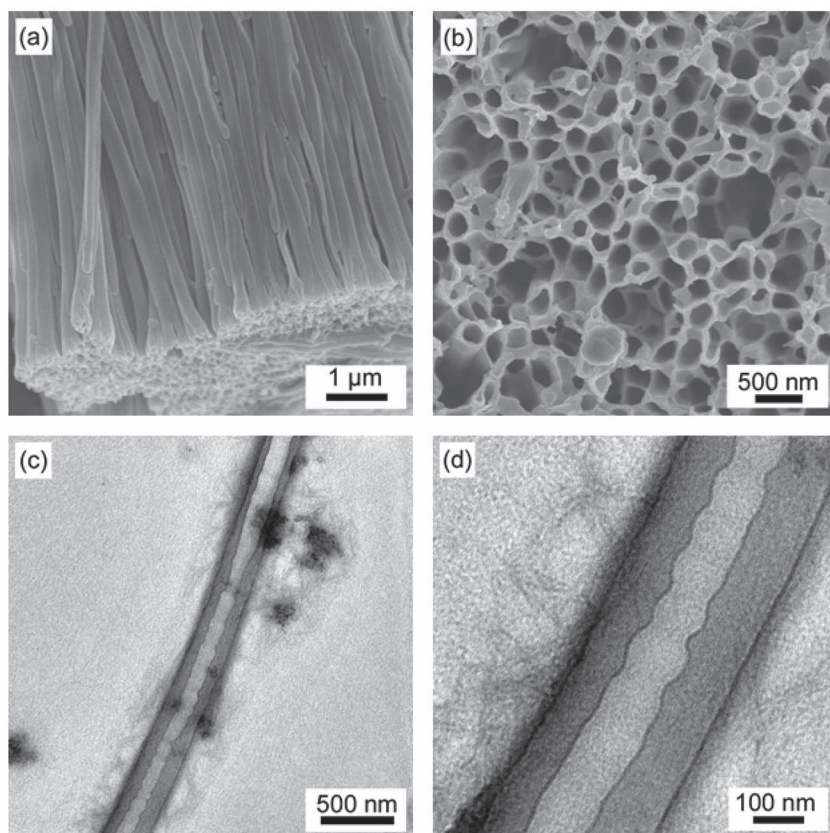


Figure 2. SEM and TEM pictures of PMMA (\overline{M}_w : 97 kg mol⁻¹) nanotubes. (a–b) SEM images of PMMA nanotubes from 5 wt% (a) and 10 wt% (b) PMMA solution. (c–d) TEM images of PMMA nanotubes from 10 wt% PMMA solution with low (c) and high (d) magnifications.

By adding water into the PMMA solution confined in the nanopores of AAO templates, PMMA nanospheres or nanorods are obtained. Figure 3a is the SEM image of PMMA nanostructures by adding water into 5 wt% PMMA solution. Water wets the surface of the pore wall and causes the PMMA solution to precipitate in the center of the nanopores, resulting in the formation of PMMA nanospheres and short nanorods. When the PMMA concentration increases to 10 wt%, longer PMMA nanorods are observed (see Figure 3b). The internal structures of the PMMA nanomaterials from 5 and 10 wt% PMMA solution are further examined by TEM (Figure 3c and d), and the solid nature of the materials is confirmed. The results from 5 and 10 wt% PMMA solution exhibit the dependence of the polymer morphology on the polymer concentration. The PMMA concentrations are further increased to 16 and 32 wt% (Figure 4a and b), and PMMA nanorods with longer lengths are observed. The highest concentration used in this work is 32 wt% because of the solubility issue and the high viscosity of the polymer solution. When the polymer concentration is too high, the viscous solution is difficult to be processed. The relationship between the aspect ratio (the length divided by the diameter) of

the PMMA nanomaterials and the concentration of the polymer solution is plotted in Figure 4c. The aspect ratio of the nanomaterials increases with the polymer concentration.

To understand the formation mechanism of the polymer nanomaterials induced by nonsolvent and the concentration-dependent morphology, we try to study the intermediate states of the formation process by controlling the amount of solvent in the nanopores. The above results are obtained by immersing the solution-containing templates into water without any drying process. The solution-containing (5 wt% PMMA in DMF) templates are also dried in ambient conditions for different periods of time before immersing into water. Figure 5b, c, d, and e are the SEM images of the water-induced PMMA nanomaterials by drying for 30, 20, 10, and 0 min, respectively. Undulated PMMA structures are observed at longer drying time, while PMMA nanospheres are obtained without the drying process. Based on these results, we propose a simple model to explain the possible formation mechanism of the water-induced polymer nanomaterials, as shown in Figure 5a. When

water enters the solution-containing nanopore and wets the pore wall, the polymer solution is isolated and forms a cylindrical domain. The cylindrical solution then undulates and breaks into spherical domains, driven by the Rayleigh instability.^[26,27]

When the Rayleigh instability is applied to viscoelastic materials, the viscosity resists the breakup of the materials.^[37] The characteristic time for the material breakup is

$$\tau_m = \eta R_0 / \sigma \quad (2)$$

where τ_m is the characteristic time for the fastest growing mode, η is the viscosity of the material, R_0 is the radius of the cylinder, and σ is the surface tension of the interface.^[37,38] When the sample is not dried before immersing into water, more solvent is present in the nanopores. Therefore, the characteristic time for the transformation process is shorter because of the lower solution viscosity. Consequently, the cylindrical solution domain undulates and breaks into spherical domains before the solvent is completely dried, resulting in the formation of polymer nanospheres, as shown in Figure 5e. When some amount of solvent is dried before immersing the sample

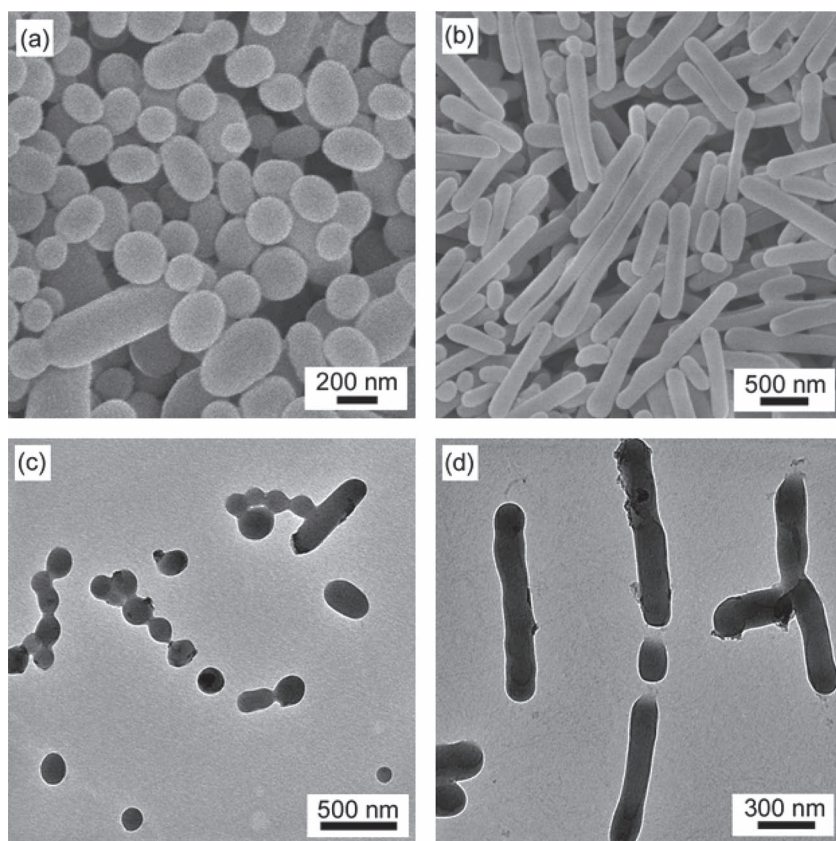


Figure 3. SEM and TEM pictures of PMMA (\bar{M}_w : 97 kg mol⁻¹) nanospheres and nanorods. (a–b) SEM images of PMMA nanospheres from 5 (a) and 10 wt% (b) PMMA solution. (c–d) TEM images of PMMA nanorods from 5 (c) and 10 wt% (d) PMMA solution.

viscosity. For example, PMMA with high molecular weight (\bar{M}_w : 557 kg mol⁻¹) is used, and undulated PMMA structures are obtained, as shown in the Supporting Information.

Even though most of the results can be explained by this simple model, the mechanism of the formation of the polymer nanomaterials induced by nonsolvent is considered to be more complicated. This complexity is due to the fact that water is soluble in DMF, so the interface between water and the polymer domain is not well defined. If water wets the pore wall and diffuses into polymer solution by Fickian diffusion, a broad interface is expected.^[39] If some amount of solvent is dried, water may diffuse into the concentrated polymer solution by non-Fickian diffusion (Case II), in which the diffusion constant is also a function of the concentration, and a sharp interface may be formed.^[40] In addition, the rate of precipitation of the polymers is controlled by the diffusion rate of water molecules. To address these issues, a more complicated model may be required to better reflect the formation process.

The sizes of the polymer nanomaterials made by templates are also compared with the original pore sizes of the AAO templates. The nanopores can be seen from the top view of the AAO templates, as shown in the Supporting Information. The size distribution of the nanopores in the AAO templates is plotted in Figure S3a (Supporting Information). The diameters of the nanopores range from 150 to 400 nm, and the average pore size is 237 nm. Since the pore diameter near the surface is generally larger than the pore diameters away from the surface, the measured values are slightly larger than the actual values. The size distribution of the diameters of the PMMA nanotubes is shown in Figure S3b (Supporting Information). The average diameter of the PMMA nanotubes is 219 nm, which is close to the average pore size of the AAO templates. This result confirms that nanotubes are formed by the precipitation of polymers on the pore walls. But the size distribution of the nanotubes is broader than that of the nanopores of the AAO templates. The broadness may be due to the fact that the nanotubes are not rigid

into water, the characteristic time for the transformation process is longer because of the higher solution viscosity. Therefore, the transformation process may not be completed before the solvent is completely dried, resulting in the formation of undulated structures (see Figure 5b, c, and d). The undulated structures can also be observed by using polymers with higher molecular weights without any drying process because of the higher solution

compared with the original pore sizes of the AAO templates. The nanopores can be seen from the top view of the AAO templates, as shown in the Supporting Information. The size distribution of the nanopores in the AAO templates is plotted in Figure S3a (Supporting Information). The diameters of the nanopores range from 150 to 400 nm, and the average pore size is 237 nm. Since the pore diameter near the surface is generally larger than the pore diameters away from the surface, the measured values are slightly larger than the actual values. The size distribution of the diameters of the PMMA nanotubes is shown in Figure S3b (Supporting Information). The average diameter of the PMMA nanotubes is 219 nm, which is close to the average pore size of the AAO templates. This result confirms that nanotubes are formed by the precipitation of polymers on the pore walls. But the size distribution of the nanotubes is broader than that of the nanopores of the AAO templates. The broadness may be due to the fact that the nanotubes are not rigid

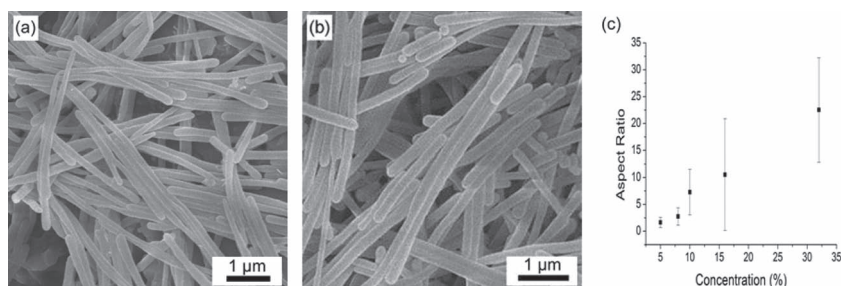


Figure 4. SEM images of PMMA (\bar{M}_w : 97 kg mol⁻¹) nanomaterials prepared from (a) 16 and (b) 32 wt% PMMA solution. (c) Plot of the aspect ratio of the nanorods versus the polymer concentration. The closed boxes indicate the average values of the aspect ratios, and the error bars represent the standard deviation.

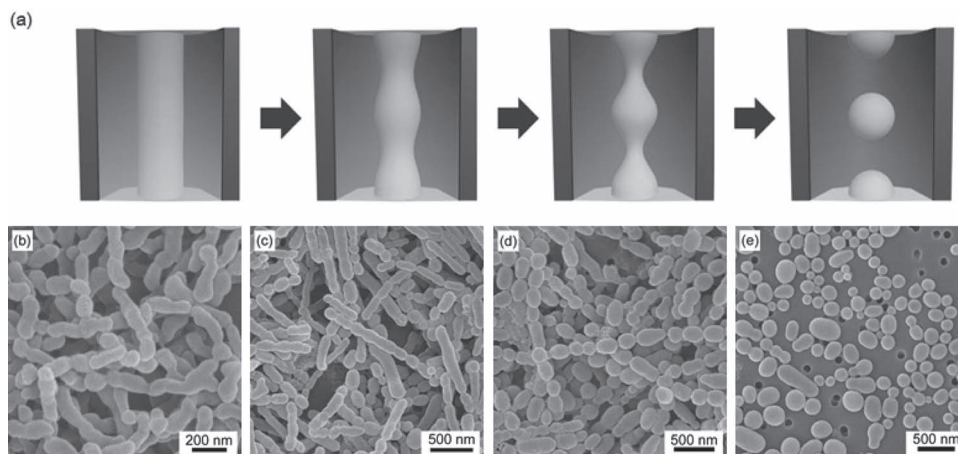


Figure 5. (a) The proposed model of the formation mechanism of polymer nanomaterials induced by nonsolvent. (b–e) SEM images of PMMA (\overline{M}_w : 97 kg mol⁻¹) nanomaterials from 5 wt% PMMA solution under different periods of drying time before immersing into water: (b) 30, (c) 20, (d) 10, and (e) 0 min.

and may be distorted after they are removed from the template. Such distortion causes the discrepancy of the measured diameters from the real diameters. The size distribution of the diameters of the nanospheres made from 5% PMMA solution is shown in Figure S3c (Supporting Information). The average diameter of the nanospheres is 159 nm, which is considerably smaller than the average pore size. The reduction in diameters is reasonable because the polymer chains aggregate in the center of the nanopores instead of precipitating on the pore walls.

PS, another commonly used polymer, is also studied to demonstrate the effect of nonsolvent on the formation of polymer nanomaterials made by templates. As shown in Figure S4 (Supporting Information), the results obtained from PS are similar to those from PMMA. Without adding water, PS nanotubes are obtained. By adding water, PS nanospheres or nanorods are prepared. The lengths of the PS nanorods, however, are shorter than the lengths of the PMMA nanorods, when the same polymer concentration is used. For example, the length of the PS nanorods from 30 wt% PS (\overline{M}_w : 35 kg mol⁻¹) solution is $\approx 1.5 \mu\text{m}$, while the length of the PMMA nanorods from 30 wt% PMMA (\overline{M}_w : 97 kg mol) solution is $\approx 3.5 \mu\text{m}$. Several factors may cause the length difference of the polymer nanorods, including the molecular weight, the solubility of the polymer in DMF, or the interaction between the polymer and the pore wall.

To further clarify the confinement effect of the AAO template on the formation of water-induced polymer nanomaterials, we also study the precipitation of polymers when they are dropped into a beaker of water without the presence of the AAO template. PMMA or PS solution is dropped into water under sonication using a micropipette. The sonication process is to keep the polymers from forming large aggregates. Figure S5

(Supporting Information) shows the SEM images of PMMA and PS aggregates that are formed by dropping 1 wt% polymer solution into water without the presence of the AAO templates. Without the confinement from the template, polymer aggregates with irregular shapes are obtained from both PMMA and PS solution in DMF.

4. Conclusion

In conclusion, we have studied the effect of nonsolvent (water) on the formation of polymer nanomaterials made by templates using PMMA and PS. Without using the nonsolvent, polymer precipitate on the pore walls after the evaporation of the solvent, resulting in the formation of polymer nanotubes. When water (nonsolvent) is added to the polymer solution confined in the nanopores of AAO templates, water wets the pore walls and causes the polymer solutions to be isolated in the central part of the nanopores, resulting in the formation of polymer nanospheres or nanorods. The aspect ratios of the nanomaterials induced by nonsolvent can be controlled by the polymer concentration. This study demonstrates that the morphology and sizes of polymer nanomaterials can be simply controlled by using nonsolvent. Studies are currently being pursued to apply this simple method to other polymer–solvent systems. This concept can also be used to prepare nanomaterials from conjugated polymers or inorganic materials.^[41]

Supporting Information

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

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