COMMUNICATION

Microwave-annealing-induced nanowetting: a rapid and facile method for fabrication of one-dimensional polymer nanomaterials†

Chun-Wei Chang, Mu-Huan Chi, Chien-Wei Chu, Hao-Wen Ko, Yi-Hsuan Tu, Chia-Chan Tsai and Jiun-Tai Chen*

Template wetting methods have been broadly applied to fabricate diverse one-dimensional polymer nanomaterials. The currently used template wetting methods, however, have shortcomings and disadvantages such as long processing times, thermal degradation, and difficulties in controlling the lengths. In this work, we develop a novel microwave-annealing-induced nanowetting (MAIN) method to fabricate one-dimensional polymer nanomaterials using porous anodic aluminum oxide (AAO) templates. Upon microwave annealing, the polymer chains are infiltrated into the nanopores of the AAO templates, and the morphologies of the polymer nanomaterials can be controlled by the annealing conditions. The growth rates of the polymer nanomaterials using the MAIN method are faster than those using the traditional thermal annealing method. This work not only provides a time-saving method to fabricate one-dimensional polymer nanomaterials with controlled morphologies, but also offers a better understanding of the effect of microwave annealing on the wetting behaviors of polymer melts.

Introduction

One-dimensional (1-D) polymer nanomaterials have attracted great attention in recent years because of their applications in areas such as tissue engineering, sensors, energy storage, field-effect transistors, and photovoltaics.[1–5] One of the most commonly used approaches to prepare 1-D polymer nanomaterials is the template method using porous templates.[6,7] In the template method, polymer solutions or melts are first introduced into the nanopores of porous templates, and polymer nanomaterials can be obtained after the solidification of the polymers. One of the major advantages of the template method is that the dimensions and morphologies of the

polymer nanomaterials can be controlled by the sizes and shapes of the porous templates.

Anodic aluminum oxide (AAO) membranes are commonly used as porous templates.[8,9] Using a second-step electrochemical anodization process, AAO templates with ordered cylindrical nanopores can be prepared.[10] The pore diameters, pore lengths, and pore-to-pore distances can be varied by changing the anodization parameters such as the type of the electrolyte, the electrolyte concentration, the applied voltage, the working temperature, and the working time.[11,12]

In the template wetting method, several ways have been developed to infiltrate polymers into the nanopores of the templates including the solution method, the thermal annealing method, and the solvent annealing method.[13–18] In the solution method, which was pioneered by Martin *et al.*, polymers are first dissolved in a suitable solvent and the polymer solution wets the nanopores of the template *via* capillary force. After the evaporation of the solvent, polymer nanostructures can be obtained.[13] Normally, polymer nanotubes are prepared using this method due to the deposition of polymer chains on the wall surfaces of the templates. The thicknesses of the nanotubes can be controlled by the concentrations or the viscosities of the polymer solution.[16,19] Recently, different polymer nanostructures other than nanotubes are also reported by changing the experimental conditions in the solution method such as the type of polymer, the molecular weight of the polymer, the type of solvent, or the solution concentration.[20–22] Although the solution method can be used to prepare versatile polymer nanostructures, the experimental conditions are usually difficult to control, which may cause irregular polymer nanostructures or non-reproducible results. Furthermore, residual polymer films are usually present on both sides of the templates after the evaporation of the solvents, which is problematic on the characterizations of the samples.

Another commonly used method to infiltrate polymer chains into the nanopores of the templates is the thermal annealing method, which was pioneered by Steinhart *et al.*[15] In the thermal annealing method, polymer powders or films are

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050. E-mail: jtchen@mail.nctu.edu.tw

† Electronic supplementary information (ESI) available: SEM images of the AAO templates, TEM image of a PS nanotube, and size distributions of the polymer nanostructures. See DOI: 10.1039/c5ra03037d

heated above the glass transition temperatures (T_g) or the melting temperatures (T_m) of the polymers, and polymer melts can wet the nanopores, resulting in the formation of polymer nanotubes. The morphologies and the lengths of the polymer nanomaterials prepared by the thermal annealing method are mainly controlled by the temperature, the molecular weight, and the annealing time.[23–25]

Although different polymer nanomaterials can be prepared using various template-based wetting methods, the traditional methods usually require long processing times, which can cause the problem of degradation, especially when the polymers are infiltrated at elevated temperatures. For applications such as organic solar cells, the optoelectronic properties of conjugated polymer nanostructures prepared by the template method may also be deteriorated due to the long processing times. For the newly developed solvent-annealing-based template wetting method, the required infiltration times are even longer, from hours to days due to the low mobilities of the polymer chains in the solvent vapors.[17,18] Therefore, there is an urgent need to develop new template-based methods to prepare polymer nanomaterials with shorter processing times, while the lengths and morphologies can be controlled.

Here, we develop a novel microwave-annealing-induced nanowetting (MAIN) method for the fabrication of one-dimensional polymer nanomaterials. In the MAIN method, a porous template is first placed on top of a polymer film coated on a silicon substrate. The sample is then annealed by microwave irradiation, during which the polymer chains wet the nanopores of the template. After solidification and removal of the template, one-dimensional polymer nanomaterials can be obtained. Using the MAIN method, the polymer chains can be infiltrated into the nanopores in shorter times comparing to the traditional thermal annealing method, enabling the MAIN method a more promising approach for future industrial manufacturing. In addition to the shorter processing times, the MAIN method also offers considerable flexibility in controlling the morphologies of the prepared polymer nanomaterials. Depending on whether the polymer melts are in the complete wetting or the partial wetting regimes, for example, polystyrene (PS) nanotubes or nanorods in the AAO templates can be prepared by annealing PS films at different microwave annealing temperatures.

Results and discussion

Fig. 1 shows the schematic illustration of the experimental processes to prepare PS nanostructures using the MAIN method. First, an AAO template is placed on top of a PS-coated silicon wafer. A glass substrate is then placed on top of the AAO template to ensure a good contact between the template and the polymer film. Subsequently, the sample is moved into a microwave-safe glass holder. The microwave annealing experiments are conducted in a microwave synthesizer, where the annealing temperatures are controlled by an in-built microwave feedback system. After the annealing process, the sample is cooled and the AAO template is removed selectively using a 5 wt% NaOH(aq) solution.
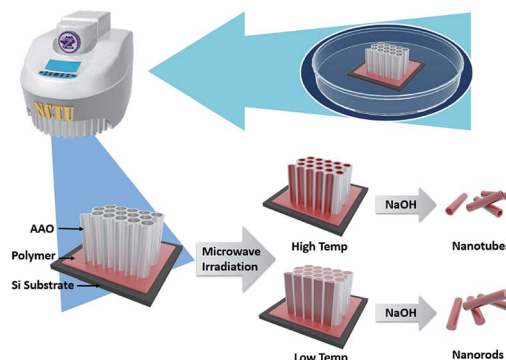

Fig. 1 Schematic illustration of the experimental processes to prepare one-dimensional polymer nanostructures.

Both commercial and synthesized AAO templates are used in this work. The average pore diameters of the commercial and synthesized AAO template are ~237 and ~60 nm, respectively, as shown in Fig. S1.† Before evaluating the feasibility of the MAIN method, we fabricate polymer nanomaterials using the traditional thermal annealing method. A PS (M_w: 35 kg mol^{-1}) solution in toluene is first spin-coated on a silicon wafer. After the solvent is evaporated, an AAO template is placed on top of the PS film, and the samples are annealed at 120 or 190 °C for 30 min. When the annealing temperatures are higher than the glass transition temperature of PS ($T_g \sim 100$ °C), the polymer chains can wet the nanopores of the AAO templates via capillary force. After the AAO templates are removed selectively by NaOH(aq), PS nanostructures can be obtained.

Fig. 2 shows the SEM images of the PS nanorods and nanotubes prepared by the thermal annealing method at different annealing conditions. At lower annealing temperatures, the PS chains wet the nanopores in the partial wetting regimes and PS nanorods are formed, as shown in Fig. 2a and b where the samples are annealed at 120 °C for 30 min.[26] The average diameter of the PS nanorods is ~233 nm (Fig. S2a†) that
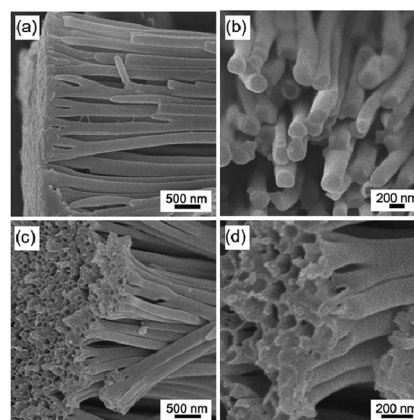

Fig. 2 PS (M_w: 35 kg mol^{-1}) nanorods and nanotubes fabricated by the thermal annealing method. (a and b) SEM images of PS nanorods with lower and higher magnifications. The samples are annealed at 120 °C for 30 min. (c and d) SEM images of PS nanotubes with lower and higher magnifications. The samples are annealed at 190 °C for 30 min.

is close to the pore size of the AAO templates (∼237 nm), indicating the replication process of the cylindrical nanopores of the AAO templates. At higher annealing temperatures, the PS chains wet the nanopores in the complete wetting regime and PS nanotubes are formed, as shown in Fig. 2c and d where the samples are annealed at 190 °C for 30 min.[26] The average diameter of the PS nanotubes is ∼247 nm (Fig. S2b†) that is also close to the pore size of the AAO templates (∼237 nm).

Our results using the thermal annealing method agree well with those observed by Zhang *et al.*, who studied the morphologies of PS melts in cylindrical nanopores at different annealing temperatures.[26] They reported that there is a transition from partial to complete wetting when the annealing temperature is raised above a critical temperature (T_w). At temperatures lower than the T_w, partial wetting occurs and polymer nanorods are obtained. By comparison, complete wetting occurs at temperatures higher than the T_w and polymer nanotubes are obtained.[26]

Although the thermal annealing method has been used to fabricate 1-D polymer nanomaterials with controlled lengths and morphologies, the long processing time of this method is still a major problem, especially for future industrial applications. Therefore, we develop the microwave-annealing-induced nanowetting (MAIN) method to shorten the processing time.

In the microwave annealing process, both the annealing temperature and the heating rate are critical parameters and need to be controlled carefully. The heating profiles are recorded by an in-built infrared sensor, as shown in Fig. S3a and b.† The heating rate can be controlled by the power of the microwave synthesizer and increases with the applied power. Once the temperature in the annealing chamber reaches the preset temperature, the power is adjusted automatically to keep the temperature. After the heating process, the chamber is cooled to room temperature.
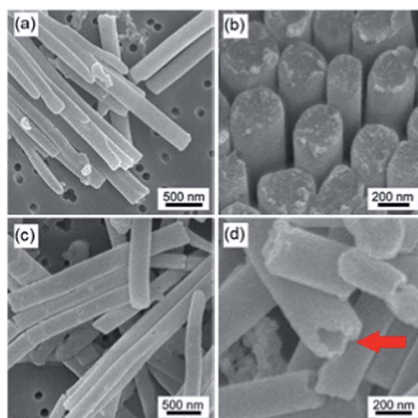
Similar to the results from the thermal annealing method, the morphologies of the polymer nanostructures can be controlled by annealing the samples under microwave irradiation at different temperatures.[26] Fig. 3a and b shows the PS nanorods fabricated at 120 °C for 15 min under microwave irradiation, where the polymer melts wet the nanopores in the partial wetting regime. From the top-view SEM image, the solid nature of the rod-like nanostructures can be observed (Fig. 3b). PS nanotubes can also be prepared using the MAIN method by annealing the samples at higher temperatures. Fig. 3c and d shows the PS nanotubes fabricated at 190 °C for 15 min under microwave irradiation, where the polymer melts wet the nanopores in the complete wetting regime. The open end of a PS nanotube is indicated by a red arrow in Fig. 3d. To characterize the nanotube samples further, we have also performed TEM measurement. As shown in Fig. S4,† the tubular structure of the PS nanotube can be confirmed. The size distributions of the PS nanorods and nanotubes are shown in Fig. S5,† which are close to those of the AAO templates. Therefore, the morphologies of the polymer nanostructures fabricated using the MAIN method can also be controlled, similar to those using the traditional thermal annealing method.

To compare the infiltration behaviors of polymer melts into the nanopores of the AAO templates using the thermal annealing method and the MAIN method, we also measure the lengths of the nanostructures quantitatively. In general, the lengths of the polymer nanostructures are difficult to be measured after the nanostructures are released from the templates, due to the high aspect ratios and flexibility of the nanostructures. Therefore, we measure the lengths of the
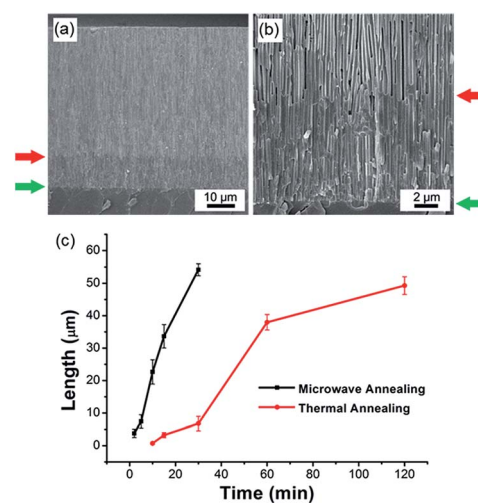

Fig. 4 (a and b) Cross-sectional SEM images of PS (M_w: 35 kg mol^{-1}) nanorods in nanopores of AAO templates fabricated by thermal annealing at 120 °C for 30 min with lower and higher magnifications, respectively. The green arrows indicate the interfaces between the bulk PS films and the AAO templates. The red arrows indicate the regions where the polymer melts have reached, representing the heights of the PS nanorods. (c) Plot of the average lengths of the PS (M_w: 35 kg mol^{-1}) nanorods fabricated by microwave annealing (black line with square dots) and conventional thermal annealing (red line with round dots) in the nanopores *versus* the annealing times. The annealing temperatures are both fixed at 120 °C.

Fig. 3 PS (M_w: 35 kg mol^{-1}) nanorods and nanotubes fabricated by the MAIN method. (a and b) SEM images of PS nanorods with lower and higher magnifications. The samples are annealed under microwave irradiation at 120 °C at 10 W for 15 min. (c and d) SEM images of PS nanotubes with lower and higher magnifications. The samples are annealed under microwave irradiation at 190 °C at 30 W for 15 min. The red arrow indicates the location of the open end of a nanotube.
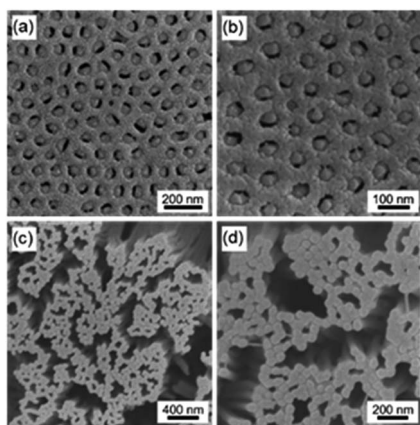
Fig. 5 SEM images of PS (M_w: 35 kg mol^{-1}) nanorods using the synthesized AAO templates with pore diameters of ∼60 nm. The nanorods are fabricated by the MAIN method at 5 W and 120 °C for 3 min with lower and higher magnifications. (a and b) The AAO templates are partially removed by etching the templates using a 5 wt% phosphoric acid solution for 30 min, revealing the nanorods embedded in the AAO templates. (c and d) The templates are mostly removed by etching the templates using a 5 wt% phosphoric acid solution for 60 min.

polymer nanostructures by breaking the nanostructures-containing templates and observing the cross-sectional SEM images. Without removing the templates, aggregation or collapsing of the polymer nanostructures are not observed. Since the wetting velocity of the polymer melt increases with the annealing temperature, we measure the lengths of the PS nanostructures prepared by the two different wetting methods at lower annealing temperatures (120 °C). Fig. 4a and b shows the SEM images of PS (M_w: 35 kg mol^{-1}) nanorods embedded in the nanopores of AAO templates fabricated by the thermal annealing method at 120 °C for 30 min with different magnifications. The total length of the nanopores in the AAO template is ∼60 μm, as shown in Fig. 4a. The bulk PS film, the polymer-filled AAO channels, and the unfilled AAO channels can be distinguished by the different contrasts in the SEM images. The green arrows indicate the interfaces between the bulk PS film and the AAO templates. The red arrows indicate the regions where the polymer melts have reached, representing the lengths of the PS nanorods. In Fig. 4a and b, the average length of the PS nanorods is measured to be ∼10 μm. There are also some deviations of the lengths of the PS nanorods due to the size distributions of the nanopores. The meniscus on the top of the PS nanorods, a signature of the capillary-force-driven infiltration of the polymer melts, can also be observed in the cross-sectional SEM images with a higher magnification, as shown in Fig. 4b. Fig. 4c shows the average lengths of the PS nanorods fabricated by both the thermal annealing method and the MAIN method at 120 °C for different times. For the thermal annealing method, it takes ∼120 min to fill the whole AAO nanopores (total lengths of the nanopores are ∼60 μm), while it takes only ∼30 min for the MAIN method, demonstrating the faster infiltration velocity of the polymer melts under microwave irradiation.

The faster wetting velocity using the MAIN method enables it a more promising approach for industrial manufacturing. Since

polystyrene is a poor microwave absorber due to its low dielectric loss tangent (0.0049 at 3 GHz), the faster wetting velocity is probably due to the local heating under microwave irradiation.[27] Morris *et al.* studied the microphase separation of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) and polystyrene-*block*-poly(dimethylsiloxane) (PS-*b*-PDMS) thin films using a microwave-assisted annealing technique. They suggested that the PMMA and PDMS blocks are polar and can interact with the oscillating field which drives the microphase separation while the PS block is microwave transparent.[28] In another work, they also studied the rapid microphase separation of polystyrene-*block*-poly(lactic acid) (PS-*b*-PLA) thin films using a solvo-microwave technique.[29] They proposed that some very high energy states can be created during microwave annealing that can pass into the polymer and cause efficient local heating. We think that the effect of local heating might also occur in our work, resulting a faster wetting velocity under microwave irradiation.

In addition to commercial AAO templates, synthesized AAO templates with interpore distances of ∼110 nm and pore diameters of ∼60 nm (Fig. S1c and d†) are also used for the MAIN method. A PS (M_w: 35 kg mol^{-1}) film is annealed on a synthesized AAO template using microwave irradiation at 120 °C for 3 min. By partially etching the AAO templates using a 5 wt% phosphoric acid solution for 30 min, the PS nanorods can be revealed while the template can still be observed, as shown in Fig. 5a and b. After the template are further etched using a 5 wt% phosphoric acid solution for 60 min, aggregated PS nanorods can be observed, as shown in Fig. 5c and d. The size distribution of the PS nanorods using the synthesized templates is shown in Fig. S6,† where the average diameter of the nanorods (∼50 nm) is slightly smaller than that of the synthesized AAO templates (∼60 nm).

Conclusions

We successfully fabricate one-dimensional polymer nanomaterials by the microwave-annealing-induced nanowetting (MAIN) method. Compared to the traditional template wetting method, the MAIN method requires less processing times and still has good control over the morphologies of the nanomaterials. By varying the microwave annealing temperatures, partial wetting or complete wetting regimes are obtained and polymer nanorods or nanotubes can be fabricated. This work not only provides a facile and efficient method to fabricate one-dimensional polymer nanomaterials with controlled morphologies, but also offers a new research direction on the microwave annealing of polymer chains in confined environments. In the future, we will apply this method to fabricate polymer nanostructures using multi-component polymers such as block copolymers or polymer blends, in an attempt to understand the effect of microwave annealing on phase-separated morphologies.

Experimental section

Materials

Polystyrene (PS) with a weight-average molecular weight (M_w) of 35 kg mol^{-1} was purchased from Sigma Aldrich. Toluene was purchased from Echo Chemical. Sodium hydroxide (NaOH) was

obtained from Tedia. Commercial AAO templates (pore diameter ~150–400 nm, thickness ~60 μm) were purchased from Whatman. Polycarbonate filters (VCTP, pore size: 0.1 μm) were obtained from Millipore. Four-inch Si (1 0 0) wafers were purchased from Guv Team International Co., Ltd.

Fabrication of the synthesized AAO templates

The synthesized AAO templates were prepared by the two-step anodization method reported by Masuda *et al.*[10,30] Briefly, a flat aluminum foil with a purity of 99.9997% was first cleaned by ultrasonication in isopropyl alcohol (IPA) for 10 min. The foil was then electropolished at 20 V in a mixed solution of ethanol–perchloric acid (80 : 20) at 4 °C for 2 min. After the foil was rinsed by deionized (DI) water, it was anodized at 40 V in 0.3 M oxalic acid solution at 16 °C for 1 h. Then the aluminum foil was etched in a mixed solution of phosphoric acid (H_3PO_4) (6 wt%) and potassium dichromate ($K_2Cr_2O_7$) (1.8 wt%) for 1 h to dissolve the aluminum oxide layer. The second anodization was conducted at 40 V in 0.3 M oxalic acid solution at 16 °C for 2 h. Finally, the sample was immersed in phosphoric acid (5 wt%) at 30 °C for 35 min to widen the pores. The pore diameter of the synthesized AAO template is ~60 nm.

Preparation of polymer films on silicon substrates

A silicon wafer (1 cm^2) was first cleaned by ultrasonication in DI water, isopropyl alcohol, and acetone solution for 15 min. The residual solvent on the substrate was removed by N_2 purge. Subsequently, 25 μL of a 5 wt% of PS–toluene solution were dropped onto the silicon substrate. After the evaporation of the solvent, the PS film was annealed at 150 °C for 2 h to eliminate the residual stress.

Fabrication of polymer nanomaterials by the thermal annealing method

An AAO template was first placed on top of a polymer-coated substrate. The sample was annealed in an oven at 120 or 190 °C for 10 to 120 min. Before the annealing process, the oven was pre-heated to the desired temperature. After the thermal annealing process, the sample was cooled to room temperature. The AAO template was removed selectively by a 5 wt% NaOH(aq) solution. Finally, the nanomaterials-containing solution was filtered with a polycarbonate filter while the sample was rinsed with DI water for two times.

Fabrication of polymer nanomaterials by the microwave-annealing-induced nanowetting (MAIN) method

The microwave-annealing-induced nanowetting experiments were performed by a microwave synthesis system (CEM Discover BenchMate). An AAO template was first placed on top of a polymer-coated silicon wafer. A glass slide was then put on top of the sample to ensure a good contact between the polymer film and the template during the annealing process. Subsequently, the sample was irradiated by 2.45 GHz microwave at 120 or 190 °C for 30 s to 30 min. The powers of 10 and 30 W were used for reaching the temperatures at 120 and 190 °C, respectively.

During the annealing process, an in-built infrared sensor was used to control the chamber temperature. After the annealing process, the sample was cooled to room temperature and the AAO template was removed selectively by a 5 wt% NaOH(aq) solution. Finally, the nanomaterials-containing solution was filtered with a polycarbonate filter while the sample was rinsed with DI water for two times.

Structure analysis and characterization

The morphologies of the PS nanostructures were examined by a scanning electron microscope (SEM, JEOL JSM-7401F) at an accelerating voltage of 5 kV. The samples were dried by a vacuum pump and coated with 4 nm of platinum before the SEM measurement. TEM measurements were also performed by a bright-field transmission electron microscope (TEM, JEOL JEM-2100) at an accelerating voltage of 200 kV. Before the TEM measurements, the samples were placed onto copper grids coated with carbon or Formvar.

Notes and references

1 Q. P. Pham, U. Sharma and A. G. Mikos, *Tissue Eng.*, 2006, **12**, 1197–1211.
2 H. D. Tran, D. Li and R. B. Kaner, *Adv. Mater.*, 2009, **21**, 1487–1499.
3 S. I. Cho and S. B. Lee, *Acc. Chem. Res.*, 2008, **41**, 699–707.
4 A. N. Aleshin, *Adv. Mater.*, 2006, **18**, 17–27.
5 J. T. Chen and C. S. Hsu, *Polym. Chem.*, 2011, **2**, 2707–2722.
6 C. R. Martin, *Acc. Chem. Res.*, 1995, **28**, 61–68.
7 M. Steinhart, R. B. Wehrspohn, U. Gosele and J. H. Wendorff, *Angew. Chem., Int. Ed.*, 2004, **43**, 1334–1344.
8 R. O. Al-Kaysi, T. H. Ghaddar and G. J. Guirado, *Nanomaterials*, 2009, 436375.
9 W. Lee and S. J. Park, *Chem. Rev.*, 2014, **114**, 7487–7556.
10 H. Masuda and K. Fukuda, *Science*, 1995, **268**, 1466–1468.
11 A. P. Li, F. Muller, A. Birner, K. Nielsch and U. Gosele, *J. Appl. Phys.*, 1998, **84**, 6023–6026.
12 K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspohn and U. Gosele, *Nano Lett.*, 2002, **2**, 677–680.
13 V. M. Cepak and C. R. Martin, *Chem. Mater.*, 1999, **11**, 1363–1367.
14 J. Martin, J. Maiz, J. Sacristan and C. Mijangos, *Polymer*, 2012, **53**, 1149–1166.
15 M. Steinhart, J. H. Wendorff, A. Greiner, R. B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi and U. Gosele, *Science*, 2002, **296**, 1997.
16 S. Schlitt, A. Greiner and J. H. Wendorff, *Macromolecules*, 2008, **41**, 3228–3234.
17 S. L. Mei, X. D. Feng and Z. X. Jin, *Soft Matter*, 2013, **9**, 945–951.
18 J. T. Chen, C. W. Lee, M. H. Chi and I. C. Yao, *Macromol. Rapid Commun.*, 2013, **34**, 348–354.
19 S. Dougherty and J. Liang, *Nanotechnology*, 2009, **20**, 295301.
20 M. Pasquali, J. Liang and S. Shivkumar, *Nanotechnology*, 2011, **22**, 375605.

21 C. W. Lee, T. H. Wei, C. W. Chang and J. T. Chen, *Macromol. Rapid Commun.*, 2012, **33**, 1381–1387.

22 M. H. Chi, Y. H. Kao, T. H. Wei, C. W. Lee and J. T. Chen, *Nanoscale*, 2014, **6**, 1340–1346.

23 H. Wu, W. Wang, H. X. Yang and Z. H. Su, *Macromolecules*, 2007, **40**, 4244–4249.

24 G. J. Song, X. L. She, Z. F. Fu and J. J. Li, *J. Mater. Res.*, 2004, **19**, 3324–3328.

25 G. Chen, S. A. Soper and R. L. McCarley, *Langmuir*, 2007, **23**, 11777–11781.

26 M. F. Zhang, P. Dobriyal, J. T. Chen, T. P. Russell, J. Olmo and A. Merry, *Nano Lett.*, 2006, **6**, 1075–1079.

27 C. Jin, J. N. Murphy, K. D. Harris and J. M. Buriak, *ACS Nano*, 2014, **8**, 3979–3991.

28 D. Borah, R. Senthamaraikannan, S. Rasappa, B. Kosmala, J. D. Holmes and M. A. Morris, *ACS Nano*, 2013, 7, 6583–6596.

29 P. Mokarian-Tabari, C. Cummins, S. Rasappa, C. Simao, C. M. S. Torres, J. D. Holmes and M. A. Morris, *Langmuir*, 2014, **30**, 10728–10739.

30 X. Y. Han and W. Z. J. Shen, *Electroanal. Chem.*, 2011, **655**, 56–64.