Carbohydrate Polymers 88 (2012) 789–792

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

Cellulose nanowhisker foams by freeze casting

Rajalaxmi Dash, Yang Li, Arthur J. Ragauskas*

Institute of Paper Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA

ARTICLE INFO

Article history:
Received 26 October 2011
Received in revised form 5 December 2011
Accepted 21 December 2011
Available online 31 December 2011

Keywords:
Cellulose nanowhiskers
Foams
Freeze casting
Porous structure
Multilayered composites

ABSTRACT

Cellulose nanowhisker foams with uniform layer structure were successfully prepared via freeze casting method. Here, we investigate the relationship between freezing rate, slurry concentration and the microstructure of the porous nanowhisker architecture. The results indicate that the above freezing parameters significantly influence the microstructure and morphological features and the structures obtained could have numerous applications, including scaffolds, filters and specifically as a template for dense multilayered composites after infusion with a second phase.

1. Introduction

Fabrication of materials with homogeneous and well defined architectures has received increasing research interest owing to their broad applications such as tissue engineering, delivery matrices, green packaging, nanocomposites, and automotive industry (Hoepfner, Ratke, & Milow, 2008; Kim, Park, Kim, Wada, & Kaplan, 2005; Rosenau, Liebner, Potthast, Haimer, & Wendland, 2007; Xinhong, Dairong, & Xiuling, 2008). Several methods including spin coating, layer-by-layer, freeze casting, and eutectic growth in two phase system has been utilized to organize micron/nano size particles to obtain ordered structures. Among the different techniques used, freeze casting has been shown as a versatile, easily implemented, and promising technique to build structures such as scaffolds, porous nanocomposites, and microwire networks with well aligned and controlled porosity (Barr & Luijten, 2010; Deville, Saiz, Nalla, & Tomsia, 2006; Deville, Saiz, & Tomsia, 2007).

Freeze casting technique involves freezing a liquid suspension and sublimation of the solvent there after under reduced pressure. During the freezing process, the suspended particles are organized by rejection from the growing ice crystal front to the intervening space, which results in an ordered structure after sublimation. Fabrication of various materials by this technique suggests that the underlying principle of freeze casting is strongly dependent on simple physics of ice crystals and the physical interaction between the growing solidification front and the inert particles of the slurry (Kawata et al., 2003; Tsioptsias, Stefopoulos, Kokkinomalis, Papadopoulou, & Panayiotou, 2008; Zhang et al., 2005). Depending on the choice of solvent, slurry formulation, and solidification conditions, the final porosity and pore morphologies can be readily tuned. However, the solidification conditions remain as the key factor since all the features of porosity are created during this stage and thereby, controlling the formation and growth of ice crystals would yield materials with specific microstructure. For instance, in case of unidirectional freezing, a porous structure with unidirectional channel is obtained. In fact, this approach has been utilized to prepare variety of ceramic structures such as silica fiber bundles, tubular supports with radially aligned pores, micro-honeycombs as well as polymeric scaffolds (Mahler & Bechtold, 1980; Moon, Hwang, Awano, & Maeda, 2003; Mukai, Nishihara, & Tamon, 2004).

Cellulose nanowhiskers, derived sustainably from biomass represent a relatively new raw material that has gained significant attention due to their intrinsically appealing physical, chemical as well as mechanical properties (Azizi Samir, Alloin, & Dufresne, 2005; Eichhorn, 2011; Gavillon & Budtova, 2008; Habibi, Lucia, & Rojas, 2010). Cellulose nanowhiskers designate a class of rod like nanoparticles which are mainly prepared by controlled acid hydrolysis of native cellulose fibers. The size and properties of nanowhiskers depend on the source and hydrolysis conditions of cellulose fibers and typically are 5–10 nm in width and 100–300 nm in length for wood-based nanowhiskers (Beck-Candanedo, Roman, & Gray, 2005; Bondeson, Mathew, & Oksman, 2006). A number of non-periodic highly porous structures known as aerogels from micro and nano cellulose fibers as well as cellulose derivatives has been reported in literature and they are commonly prepared by solvent exchange of a wet gel followed by supercritical CO_2 drying (Aaltonen & Jauhiainen, 2009; Fischer, Rigacci, Pirard, Berthon-Fabry, & Achard, 2006; Gavillon & Budtova, 2008; Heath

* Corresponding author. Fax: +1 404 894 4778.
E-mail address: arthur.ragauskas@ipst.gatech.edu (A.J. Ragauskas).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.12.035

& Thielemans, 2010; Sehaqui, Salajkov, Zhou, & Berglund, 2010). However, porous structures with regular pattern can be obtained by controlling the freezing temperature of the slurry followed by subsequent freeze drying.

Recently, Lee and Deng (2011) reported the preparation of layered cellulose foams through directional freezing technique emphasizing the effect of fiber concentration and freezing temperature on the microstructure and mechanical properties of microfibril foams. They have also measured the compressive strength of cellulose nanowhisker foams but a detailed examination on their microstructure is lacking. Utilizing the facile freeze casting technique, we attempt to fabricate aligned porous cellulose nanowhisker structures and investigate the relationship between the freezing conditions and the microstructures obtained, which has not been reported so far. We expect that ice growth strategy of freeze casting technique will allow the fabrication of well ordered cellulose nanowhisker structures, opening their use as a template for layered composites, filters, and storage material.

2. Materials

A fully bleached commercial softwood Kraft pulp was used as a source for cellulose nanowhiskers preparation. Polyvinyl alcohol (PVA) was purchased from VWR International (M_w: 15,000, degree of hydrolysis: 87–89%).

3. Experimental

3.1. Preparation of H_2SO_4-hydrolyzed cellulose nanowhiskers

The cellulose nanowhiskers were prepared by sulfuric acid hydrolysis of a bleached softwood pulp based on a literature procedure (Bondeson et al., 2006). In brief, 60.00 g (oven dried weight) of the pulp was mixed with H_2SO_4 solution (64%, w/w, 1:10 g mL^{-1}) with continuous stirring at 45 °C for 45 min. The hydrolysis reaction was halted by adding excess (10-fold) of distilled water followed by the removal of acidic solution through successive centrifugation at 12,000 rpm for 10 min until the supernatant became turbid. The sediment was collected and dialyzed (MWCO: 12–14,000) against tap water until the solution pH did not change anymore. After dialysis, the content was sonicated for 10 min and centrifuged for 5 min at 10,000 rpm. The cloudy supernatant, containing nanowhiskers, was collected and the remaining sediment was again mixed with distilled water, sonicated, and centrifuged to obtain additional nanowhisker; this step was repeated till the supernatant was clear.

3.2. Preparation of porous samples

Porous cellulose nanowhisker samples were prepared by freezing a suspension of nanowhiskers and polyvinyl alcohol under different freezing conditions and then drying under vacuum. Cellulose nanowhisker suspension (10 mL, 2 wt%) was mixed with different amounts of PVA (20% and 50%, w/w) and slowly stirred at room temperature for 4 h in order to avoid the generation of bubbles. Then, the mixture was poured in to small glass vials and freezed by two methods: (i) dipping in liquid nitrogen (ii) placing these vials in two different freezers for 2 h, where the cooling rates were measured to be 4.5 and 13 °C min^{-1}, respectively. Frozen solids were subsequently dried in a freeze dryer for 24 h to sublimate the water under vacuum. Control samples were prepared in absence of PVA.

3.3. Characterization

Surface morphology of the porous samples was studied by JEOL-1530 thermally assisted field emission (TFE) scanning electron microscope (SEM). Before acquiring images, the surfaces of all the samples were coated with gold in a sputter coater.

4. Results and discussion

Cellulose nanowhisker suspension was mixed with PVA and solidification of the slurry was carried out by two ways: (i) quenching the slurry in liquid nitrogen (ii) freezing the slurry at two different cooling rates, i.e., 13 °C min^{-1} and 4.5 °C min^{-1}. Freeze drying of the solvent created the final nanowhisker porous structure as a replica of ice crystals that generated during freezing. PVA was used as a binder due to its solubility in water and its compatibility with cellulose nanowhiskers (Kvien & Oksman, 2007). Cellulose whisker concentration (2.0 wt%) was chosen as an attempt to be in semi-dilute concentration range especially to obtain a template for potential multilayered nano-composite applications.

It was observed that irrespective of the cooling rate, when compared to the samples in PVA, the samples prepared in absence of PVA (Fig. 1) collapsed during the sublimation process resulting in a structure with no particular alignment of the pores created. It suggests that PVA acts as a support to the nanowhiskers, which could be due to the hydrogen bonding between PVA and nanowhiksers, facilitating the formation of a stable oriented porous architecture. The influence of PVA content on the microstructure of the nanowhisker materials prepared was also studied. The images of the samples freezed at 13 °C min^{-1} cooling rate are shown here (Fig. 1). At 20 wt% PVA content, the samples exhibited a well oriented porous structure with equally spaced lamellar walls (Fig. 1b), while at 50 wt% of PVA, a dense structure with some locally aligned pores were found (Fig. 1c) instead of the long range order lamellar walls. The possible physical interactions among nanowhiskers and between nanowhiskers and the growing solidification fronts during the freezing leads to different growth mechanisms, which could be the reason for the loss in alignment at high slurry concentrations. Similar phenomenon was also observed for samples prepared at 4.5 °C min^{-1} cooling rate, however, for samples freezed in liquid nitrogen, the effect of PVA concentration on the alignment of pores and its morphology was found to be insignificant.

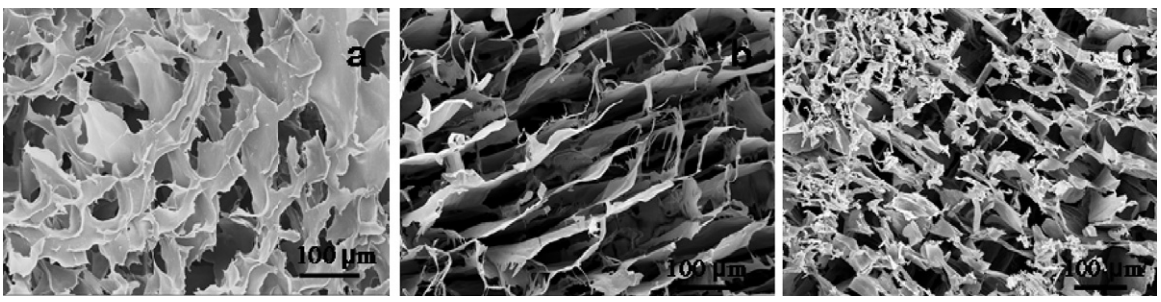

Fig. 1. Morphology of cellulose nanowhisker samples freezed at 13 °C min^{-1} cooling rate (a) 0 wt%, (b) 20 wt% and (c) 50 wt% of PVA.

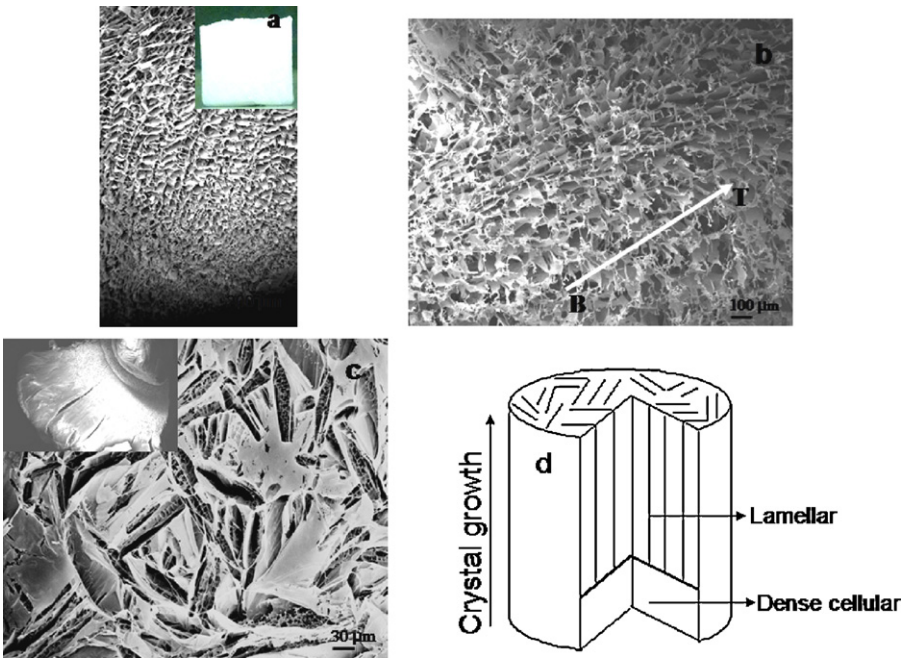

Fig. 2. (a) Overview of the sample and its microstructure. (b) Side (B: bottom and T: top of the sample) and (c) top view of the porous nanowhisker structure and (d) schematic diagram showing the growth pattern of ice crystals.

An overview of the porous cellulose nanowhisker material and its microstructure is shown in Fig. 2a. The bottom part of the microstructure can be characterized as a dense cellular structure with some randomly distributed pores whereas the upper part exhibits an oriented and highly porous structure. It implies that after growth initiation step at the bottom, the ice crystals started growing regularly in a vertical direction leaving behind open pore channels after sublimation. Eventually, the growth was terminated at the top of the suspension and formed a surface which has a different microstructure (Fig. 2c) as compared to the outer side of the sample, where open, uniform, and oriented pores were observed as shown in Fig. 2b. Based on the detailed microstructural observation of the sample a schematic diagram is shown in Fig. 2d simply indicating the growth pattern of ice crystals.

Studies on various materials including ceramic and metallic particles reveal that solidification has a critical role in determining the final pore morphology and microstructure of the porous materials (Deville, 2008; Deville, Saiz, & Tomsia, 2006). Our results are well consistent with literature results as the pore size of the resulted cellulose nanowhisker structure and the pore orientation were both affected by the cooling rate. It was observed that freezing the slurry in liquid nitrogen created a fine and perfectly aligned lamellar structure in the vertical direction with a small pore size of 10–20 μm. The lamellae walls are thinner and inter lamellae spaces are smaller at this fast freezing condition (Fig. 3a), whereas a decrease in cooling rate gradually increased the pore size (~100 μm) and lamellae thickness as observed in Fig. 3b and c. Similar behavior was also found in other polymeric and ceramics materials; as faster the freezing rate, finer the resulting structure, on the other hand slow cooling noticeably scaled up the microstructure (Deville, Saiz, Nalla, et al., 2006; Deville, Saiz, & Tomsia, 2006).

In each case, the cellulose nanowhiskers and PVA slurries were frozen at a constant cooling rate starting from room temperature. As a consequence, the subsequent drying process resulted in a lamellar porous microstructure with long range order (Fig. 4). This is a typical phenomenon observed under steady state freezing conditions as well as in cases where water is being used as a solvent. The mechanism of lamellar structure formation can be well understood through the basic physics of water freezing which has been already explained in literature (Deville, Saiz, Nalla, et al., 2006; Deville, Saiz, & Tomsia, 2006). Moreover, the lamellar surface exhibits two different types of surface dendrites. The first type of dendrite grows in between the lamellae whereas the second type corresponds to a fine tortuous morphology protruding from the top of the lamellae. The relative size of these dendrites depends not only on different freezing conditions applied to the suspension but also on the concentration of the solution. For instance, faster cooling rates with liquid nitrogen leads to finer and smaller dendrites while the dendrite size increases in case of slow cooling or with a more concentrated solution. The formation of the dendritic

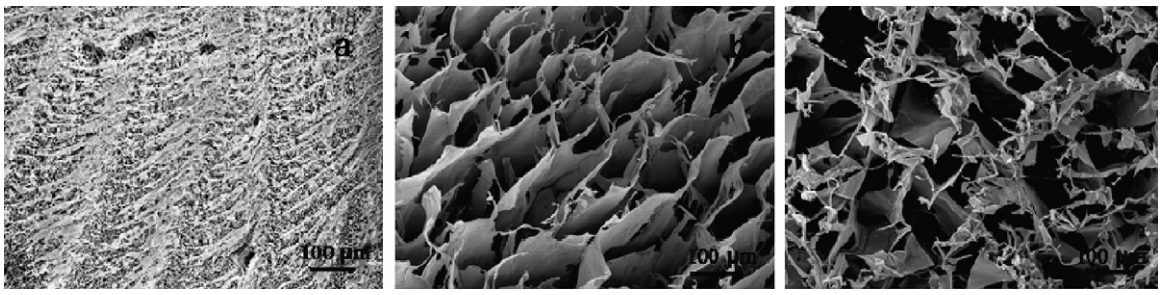

Fig. 3. Effect of cooling rate on the pore structure of 20 wt% PVA samples (a) liquid nitrogen, (b) 13 °C min^{-1} and (c) 4.5 °C min^{-1}.

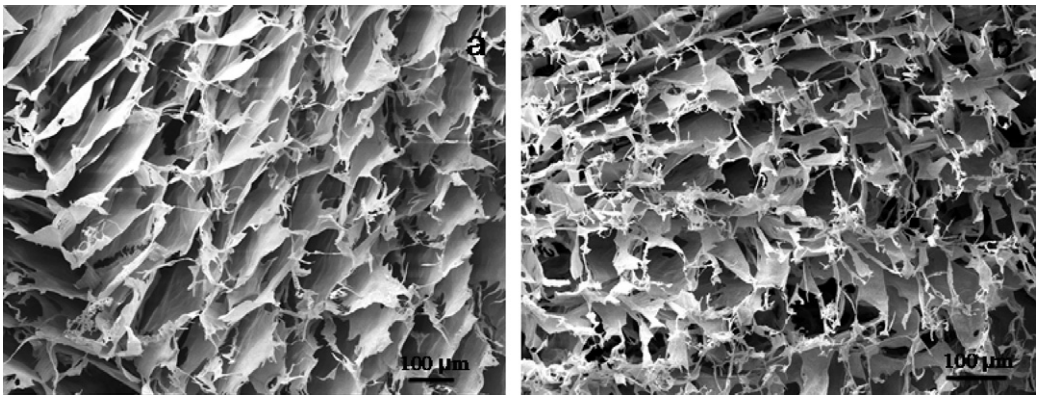

Fig. 4. Microstructure showing (a) lamellar walls and (b) surface dendrites.

feature was also observed in porous ceramic structures and it was proposed to be influenced by a number of factors such as nature of the solvent, freezing conditions, and the characteristics of starting powder (Fukasawa, Deng, Ando, Ohji, & Kanzaki, 2002; Sekhar & Trivedi, 1991).

5. Conclusion

In conclusion, our results illustrate a simple approach to produce long range ordered porous cellulose nanowhisker structure with PVA as a support material. The resultant microstructure and pore morphology can be controlled by modifying the freezing rate and the slurry concentration. Finally, considering their lamellar and interconnected pore structure combined with the renewable nature of cellulose, ordered cellulose nanowhisker based materials with designed orientation of pore channels can be prepared through precise control of thermal gradients, which has potential applications especially as a template for layered composites, molecular filtration, delivery matrix, and tissue engineering scaffold.

Acknowledgments

The authors would like to acknowledge DOE (DE-EE0003144) and PSE Fellowship program at IPST@GT for the financial support of this study.

References

Aaltonen, O., & Jauhiainen, O. (2009). The preparation of lignocellulosic aerogels from ionic liquid solutions. *Carbohydrate Polymers*, *75*, 125–129.
Azizi Samir, M. A. S., Alloin, F., & Dufresne, A. (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules*, *6*, 612–626.
Barr, S. A., & Luijten, E. (2010). Structural properties of materials created through freeze casting. *Acta Materialia*, *58*, 709–715.
Beck-Candanedo, S., Roman, M., & Gray, D. G. (2005). Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. *Biomacromolecules*, *6*, 1048–1054.
Bondeson, D., Mathew, A., & Oksman, K. (2006). Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose*, *13*, 171–180.
Fischer, F., Rigacci, A., Pirard, R., Berthon-Fabry, S., & Achard, P. (2006). Cellulose based aerogels. *Polymer*, *47*, 7636–7645.
Deville, S. (2008). Freeze-casting of porous ceramics: A review of current achievements and issues. *Advanced Engineering Materials*, *10*, 155–169.
Deville, E., Saiz, E., Nalla, R. K., & Tomsia, A. P. (2006). Freezing as a path to build complex composites. *Science*, *311*, 515–518.
Deville, S., Saiz, E., & Tomsia, A. P. (2006). Freeze casting of hydroxyapatite scaffolds for bone tissue engineering. *Biomaterials*, *27*, 5480–5489.
Deville, S., Saiz, E., & Tomsia, A. P. (2007). Ice-templated porous alumina structures. *Acta Materialia*, *55*, 1965–1974.
Eichhorn, S. J. (2011). Cellulose nanowhiskers: Promising materials for advanced applications. *Soft Matter*, *7*, 303–315.
Fukasawa, T., Deng, Z. Y., Ando, M., Ohji, T., & Kanzaki, S. (2002). Synthesis of porous silicon nitride with unidirectionally aligned channels using freeze-drying process. *Journal of American Ceramic Society*, *85*, 2151–2155.
Gavillon, R., & Budtova, T. (2008). Aerocellulose: New highly porous cellulose prepared from cellulose-NaOH aqueous solutions. *Biomacromolecules*, *9*, 269–277.
Habibi, H., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chemical Review*, *110*, 3479–3500.
Heath, L., & Thielemans, W. (2010). Cellulose nanowhisker aerogels. *Green Chemistry*, *12*, 1448–1453.
Hoepfner, S., Ratke, L., & Milow, B. (2008). Synthesis and characterization of nanofibrillar cellulose aerogels. *Cellulose*, *15*, 121–129.
Kawata, M., Uchida, H., Itatani, K., Okada, I., Koda, S., & Aizawa, M. (2003). Development of porous ceramics with well-controlled porosities and pore sizes from apatite fibers and their evaluations. *Journal of Materials Science: Materials in Medicine*, *24–242*, 647–650.
Kim, U.-J., Park, J., Kim, H. J., Wada, M., & Kaplan, D. L. (2005). Three-dimensional aqueous-derives biomaterials scaffolds from silk fibroin. *Biomaterials*, *26*, 2775–2785.
Kvien, I., & Oksman, K. (2007). Orientation of cellulose nanowhiskers in polyvinyl alcohol. *Applied Physics A*, *87*, 641–643.
Lee, J., & Deng, Y. (2011). The morphology and mechanical properties of layer structured cellulose microfibril foams from ice-templating methods. *Soft Matter*, *7*, 6034–6040.
Mahler, W., & Bechtold, M. F. (1980). Freeze-formed silica fibers. *Nature*, *285*, 27–28.
Moon, J. W., Hwang, H. J., Awano, M., & Maeda, M. (2003). Preparation of NiO-YSZ tubular support with radially aligned pore channels. *Materials Letters*, *57*, 1428–1434.
Mukai, S. R., Nishihara, H., & Tamon, H. (2004). Formation of monolithic silica gel microhoneycombs (SMHs) using pseudosteady state growth of microstructural ice crystals. *Chemical Communication*, *10*, 874–875.
Rosenau, T., Liebner, F., Potthast, A., Haimer, E., & Wendland, M. (2007). Ultra-lightweight cellulose aerogels from NBnMO-stabilized lyocell dopes. *Research Letters in Materials Science*, *2007*. Article ID 73724.
Sehaqui, H., Salajkov, M., Zhou, Q., & Berglund, L. A. (2010). Mechanical performance tailoring of tough ultra-high porosity foams prepared from cellulose I nanofiber suspensions. *Soft Matter*, *6*, 1824–1832.
Sekhar, J. A., & Trivedi, R. (1991). Solidification microstructure evolution in the presence of inert particle. *Materials Science and Engineering A*, *147*, 9–21.
Tsioptsias, C., Stefopoulos, A., Kokkinomalis, I., Papadopoulou, L., & Panayiotou, C. (2008). Development of micro- and nano-porous composite materials by processing cellulose with ionic liquids and supercritical CO_2. *Green Chemistry*, *10*, 965–971.
Xinhong, C., Dairong, C., & Xiuling, J. (2008). Chitosan-based aerogels with high adsorption performance. *Journal of Physical Chemistry B*, *112*, 7721–7725.
Zhang, H., Hussain, I., Brust, M., Butler, M. F., Rannard, S. P., & Cooper, A. I. (2005). Aligned two- and three-dimensional structures by directional freezing of polymers and nanoparticles. *Nature Materials*, *4*, 787–793.