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Preparation of Mesoporous Materials from the Flow-Induced Microstructure in Aqueous Surfactant Solutions

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In this study, we synthesized the mesoporous materials under a shear flow at relatively low temperatures using the wormlike micellar solution of a cationic surfactant cetyltrimethylammonium bromide (CTAB). The additive sodium salicylate (NaSal) enhanced the microstructure evolution by forming the micron-order flexible chains, which were stable at low temperatures. The mesoporous structures were prepared from the flow-induced template of wormy CTAB micelles by controlling the composition, flow intensity, reaction time, and temperature. One of the most significant features of the present study is that the shear flow was generated in a Couette cell by a rotating inner cylinder with a coaxial outer cylinder kept stationary. This typical flow configuration produces spring-coil streamlines which eventually stretch and twist a bundle of the long wormy micelles, and thereby form the helical mesoporous silica structures. The X-ray diffraction and transmission electron microscopy analyses showed that the ordered hexagonal phase was formed by the shear flow; otherwise, an amorphous or disordered hexagonal phase prevailed in an equilibrium state. In addition, the presence of cosurfactants or swelling agents also affected the formation of mesoporous material. For example, the primary heptanol enhanced the formation of a stable structure with a well-defined orientation toward the flow direction.

1. Introduction

In the present work, we investigated the effect of shear flow on the formation of mesoporous structures in the presence of wormlike micelles. Wormlike micelles showed a variety of the microstructural behavior under an external field, depending on the surfactant and additive concentrations.[1−4] For example, the micelles in the dilute regime are aligned to the flow direction even in a very weak flow; meanwhile, the micelles exhibit an entangled structure of polymeric chains in the semidilute regime. Thus, the micellar solution displays a viscoelasticity in the semidilute regime. In this study, a template of the silicate−surfactant was prepared from a dilute wormlike micellar solution by utilizing its microstructural evolution under a shear flow. Especially, we examined the relationship between the prepared mesoporous structure and the flow-induced microstructure of wormlike micelles.[1]

Many studies concerning the preparation of mesoporous or microporous materials have used the self-assembled structure, such as surfactants or block copolymers, as a template. The structural phase behavior of the self-assembling system depends on the types of surfactant, added salt, solvent, swelling agent, pH, and temperature. Kresge et al.[5] suggested a new progressive synthetic method for ordered mesoporous molecular sieves (MCM-41) by employing a liquid-crystal template. Lyotropic phases were composed of the ordered arrays of surfactant aggregates, mostly hexagonal array of cylindrical micelles. As expected, the pore size was dependent on both the hydrophobic-chain length of surfactant and the auxiliary organic molecule. The auxiliary organic molecule appeared not only to control the pore size but also to enhance the phase transition from hexagonal phase to cubic phase or vice versa.[6−7] Specifically, the mesoporous structure was changed from cubic phase to hexagonal array by addition of *tert*-amyl alcohol or trimethylbenzene to the surfactant solution.[6] Gallis and Landry used the temperature modification to induce the phase transition from hexagonal MCM-41 to cubic MCM-48 in the presence of ethanol. Ethanol played a role in increasing the effective surfactant volume.[7] Other factors controlling the pore spacing included the charge and length of surfactants,[8−10] solvent property,[11] reaction and processing conditions, and method of the template removal.[12]

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Template-based synthetic methods for mesoporous structure have been extensively studied for its potential applications as catalysts, thin films and membranes, adsorbents, and electronic and optical devices.[13−17] In particular, many studies have been performed recently on the effects of external fields, such as electric,[18] magnetic,[19−20] and flow fields,[15,21−23] on the synthesis of well-ordered structure for the functional materials. These external fields qualitatively endowed the prepared mesophase with long-range alignment and good pore quality. Patterning or orientating the mesoporous phase into a desired arrangement was essential for many of potential applications. Trau et al.[18] described a micromolding in a capillary under an electric field. This method permitted the formation of oriented mesoporous channels with an arbitrary microscopic pattern. In general, an electric field generates three types of phenomena, namely, electro-osmosis, polarization body force, and localized Joule heating, and thereby enhances the formation of a more confined/elongated mesoporous structure. Similarly, an ordered mesoporous structure was developed under a magnetic field since the orientational ordering could be controlled by manipulation of the mesophase composition on the basis of either diamagnetic or dielectric properties. For the electric or magnetic fields,[18−20] the substrate solutions requires a high-order relaxation time to sustain the oriented phase, and thus the highly viscoelastic solutions with liquid crystalline phase have frequently been used. These macroscopically oriented arrangements induced by the external field were not altered during solvent extraction and calcination processes. Meanwhile, an external flow field provides a different route to develop the mesophase in a dilute or liquid crystalline solution. However, most of the substrate micellar solutions behave like a Newtonian fluid with a very short relaxation time in the dilute regime, and it is difficult to form the mesophase and sustain the structure under flow field during sol−gel reactions. Thus, the template fluids must possess appropriate level of viscoelasticity. Several researchers have reported the effects of flow field on the preparation of mesoporous materials. For example, Hillhouse et al.[21] investigated the effects of a continuous capillary flow on the manipulation of the mesoporous film growth and showed that the flow enhanced both the elongated domains along the flow direction and breakage of polydomain conformation. Lin et al. developed the fibrous bundles of MCM-41 fibers into millimeter-sized ropes under a shearing flow.[23]

In this study, the effect of shear flow on the morphology of the mesoporous phase was investigated. We are solely interested in the preparation of mesoporous silica structures by using flow-induced wormlike micelles as a template. Although the rheological and morphological behavior of cetyltrimethylammonium bromide (CTAB) solutions has been studied intensively, the formation of mesoporous structure from the flow-induced template of CTAB micelles has not been reported yet. Indeed, we report here the first formation of helical mesopores in silica substrate from the flow-induced microstructure of wormy CTAB micelles. One of the most significant features of the present study is that the shear flow was generated in a Couette cell by a rotating inner cylinder with a coaxial outer cylinder kept stationary. This typical flow configuration produces spring-coil streamlines which eventually stretch and, at the same time, twist a bundle of the long wormy micelles, and thereby form the helical mesoporous silica structures. In this work, the mesoporous materials were prepared by in situ gelation of a micellar solution of a cationic surfactant of CTAB through the sol−gel chemistry. In particular, the synthesis process of sol−gel reactions was carried at relatively low temperatures to utilize the flow-induced microstructure of the wormlike CTAB micelles in the presence of NaSal as a structure-forming agent. The results showed that the microstructure of the prepared porous materials was well correlated to the rheological behavior of the wormlike micellar solution of CTAB. In addition, the presence of cosurfactants such as primary heptanol changed the microstructure of the prepared mesoporous materials and led to a stable structure with a well-defined orientation toward the flow direction. Finally, the flow-induced alignment of the prepared pore structure was confirmed by XRD (X-ray diffraction), TEM (transmission electron microscopy) and SEM (transmission electron microscopy) analyses.

2. Experimental Section

The surfactant used was cetyltrimethylammonium bromide (Sigma) and the structure-enhancing additive was sodium salicylate (NaSal, Aldrich), both used as received. The cationic surfactant with the structure-enhancing additive forms the wormlike micelles. The micelles exhibit a variety of the flow-induced responses such as alignment to the flow direction and layer fluctuations, depending on the surfactant concentration and the molar ratio, R, of NaSal to CTAB.[1] Specifically, tetraethylorthosilane (TEOS, Aldrich) in hydrochloric acid (HCl, Junsei) was used as a precursor of the silica substrate to prepare the silica−surfactant mesophases. The molar composition of TEOS, CTAB, and HCl was kept at 1:(0.07−0.2):56. In particular, the silica mesopores were formed on the template of wormy CTAB micelles by sol−gel chemistry of silicon alkoxide. Therefore, the acid content was kept very high to produce a very fine, nanoscale structure of silica substrate. In general, the sol−gel route produces a very fine network structure of silica at strong acidity. The molar ratio of NaSal to CTAB was varied from 0.5 to 5.0.

In most cases, the reaction proceeded stepwise at progressively higher temperatures, 25, 40, and 70 °C; in the first two steps, the temperatures were kept low enough to preserve the microstructure of the wormlike micelle. Otherwise, the reaction temperature will be specified. Shear flow was applied to

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the wormlike micellar solution by a lab-built Couette flow cell, which has dimensions of 4.0 cm and 4.4 cm in inner and outer radii, respectively. The shear rate was varied by controlling the revolutions per minute of a servomotor. The shear flow was generated by the rotating inner cylinder with the outer cylinder kept stationary. Temperature was controlled by the usage of an oil bath. The shear viscosity was measured by a commercial rheometer (ARES, Rheometrics) with a cone and plate geometry (cone angle, 0.04 rad; diameter, 50 mm), which was equipped with a temperature vessel. The shear rate was varied from 0.03 to 600 s^{-1}. After the reaction was completed, the solution was aspirated for 1 h and dried at 50 °C for 14 h and at 110 °C for 2 h. The surfactant template was removed by solvent extraction (using ethanol and hydrochloric acid for 1 h), as well as by calcination in an electric furnace at 550 °C for 6 h. The pore spacing and structure of the prepared mesoporous materials were observed by using an X-ray diffractometer (Rigaku, d/max-RC) under the strength of 40 kV and 45 mA. A typical XRD analysis required several hours. The scattering data were collected in a continuous scan mode from 1.2° to 10° (2θ) with a sampling interval of 0.01° at a scanning rate of 1°/min. A transmission electron microscope (EM912, Carl Zeiss in KBSI) was used to examine the microstructure and grain size of the prepared powders. To observe the individual grains, the aggregated powders were dispersed in methanol (0.5 wt %) and sonicated for 30 min. Either a bright-field TEM or a two-dimensional diffraction contrast imaging was taken at 120 kV with a fixed magnification of 100 000 times the individual grains. A fast Fourier transformation (FFT) was performed to examine closely the flow-induced orientational patterns, as suggested by Tolbert.[19] Finally, SEM images of the prepared mesoporous silica were taken to clarify the helical structure of mesopores.

3. Results and Discussion

3.1. Mesoporous Structures Formed in the Absence of an Imposed Flow. Most of the studies concerning synthesis of the silica-based mesoporous materials have examined the effects of surfactant structure, added organic substances, reaction condition, and pH on the formation of the ordered structure. Prior to considering the effect of shear flow on the microstructure of the mesoporous materials, we examined the structure of the porous materials prepared by in situ gelation in the absence of the flow. In this case, the sol–gel reaction proceeded at 25 °C for 3 h and subsequently at 80 °C for 8 h in a reflux condenser. Parts a and b of Figure 1 showed typical X-ray diffraction patterns prepared with 15 and 5 mM CTAB solutions, respectively, for various molar ratios of NaSal to CTAB. As shown in Figure 1a, the XRD peak intensity and resolution were diminished gradually as the molar ratio increased. It could be interpreted that the micelles were transformed from linear to entangled structure as the molar ratio increased in this range of CTAB concentration.[4] This morphological transition inhibited the interaction between the surfactant and the silica precursor. In addition, excess salicylate anions inhibited the congruous formation of surfactant–silicate structure, which was $S^+X^-I^+$ type of organic–inorganic materials. In the present work, we prepared the substrate solutions with the molar composition of TEOS, CTAB, and HCl fixed at 1:0.2:56, following the procedure suggested by Kim and Ryoo.[24] They reported that this composition produced effectively the hexagonal arrays. In the present case, however, the anionic organic substance, Sal^-, was added to the surfactant solutions, and the results were not consistent with their reports. Rather, the intensity peak was blunt, and the XRD patterns were indicative of the formation of disordered hexagonal structure.

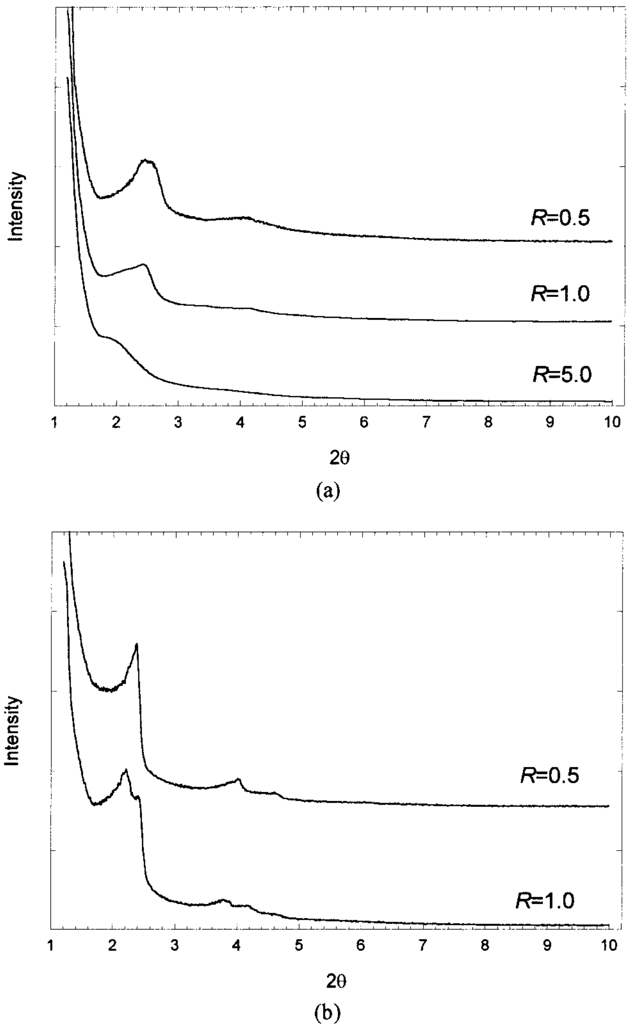

Figure 1. XRD patterns of the porous materials prepared by in situ gelation of wormlike surfactant solutions in the absence of an imposed flow: (a) 15 and (b) 5 mM [CTAB]. The molar ratio R of NaSal to CTAB ranged from 0.5 to 5.0. The samples were prepared by a two-step thermal history, namely, at 25 °C for 3 h and, subsequently, at 80 °C for 8 h.

Meanwhile, for the 5 mM CTAB solution, the XRD pattern indicated the formation of a hexagonal phase at the molar ratio $R = 0.5$ and a mixture of disordered hexagonal and lamellar phases at the equimolar ratio $R = 1.0$. Thus, the higher molar ratio of NaSal to CTAB led to a lamellar phase. The present results confirmed that the ordered hexagonal structure was obviously formed in dilute wormlike micellar solutions especially at low molar ratios. Also, the present X-ray results for the sample prepared in the absence of an imposed shear flow were consistent with the TEM images. In Figure 2a–c, the TEM images were reproduced with different magnifications for the sample corresponding to the XRD pattern of Figure 1a; i.e., the sample was prepared from the 15 mM CTAB solution at the molar ratio $R = 0.5$. As noted, a weak hexagonal structure was formed with large domains for which the XRD peaks were blunt and showed low resolutions. Although the TEM images for the sample corresponding to the XRD pattern of Figure

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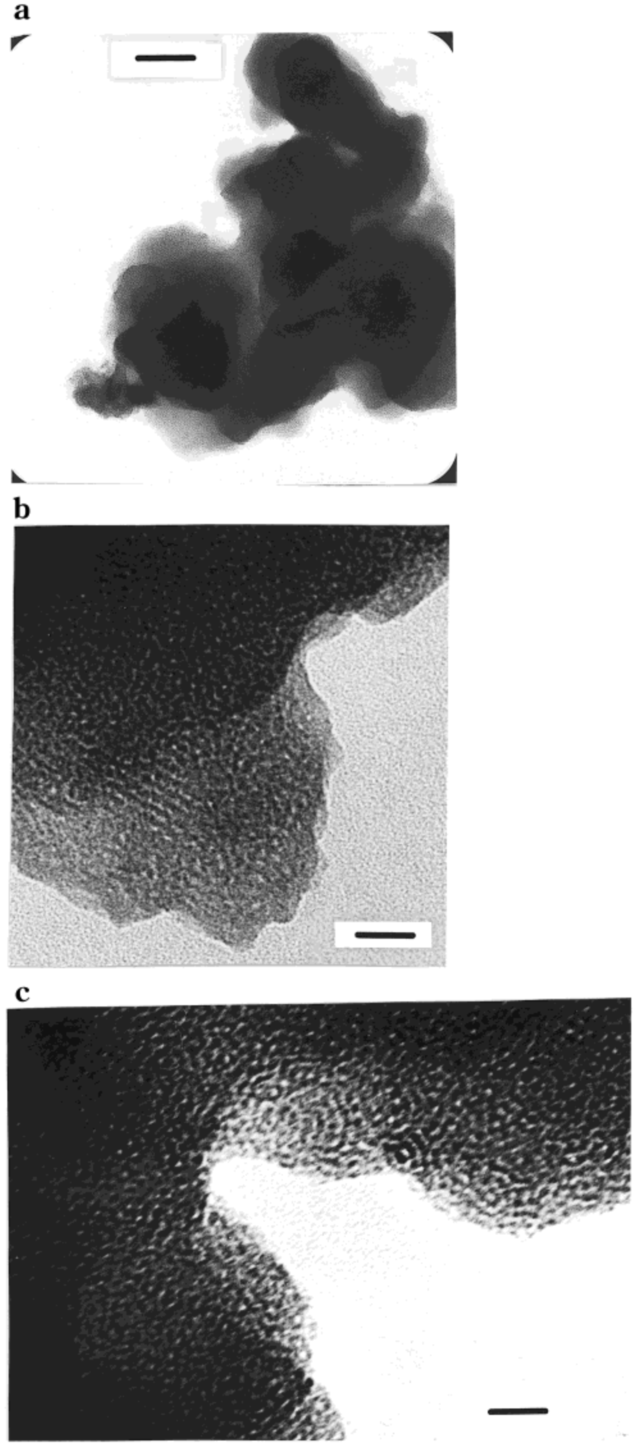

Figure 2. TEM images of the porous materials prepared by the same conditions in Figure 1a. The CTAB concentration was 15 mM with the molar ratio fixed at 0.5. Scale bars indicate (a) 100 and (b) and (c) 20 nm.

1b were not reproduced here, the results showed that a randomly distributed, disordered hexagonal mesophase was also prevalent for the sample with a rather sharp XRD pattern. This was because the second-step reaction temperature of 80 °C was so high that the wormlike micelle conformation was decomposed. Wormlike micelles usually lose their intrinsic properties of long chain structure at temperatures as high as 80 °C, which was also confirmed from the rheological responses. Consequently, the XRD and TEM results were similar to those prepared from a simple surfactant micelle−silicate synthesis process proposed by Kim and Ryoo.[24] Thus, to form a well-ordered hexagonal arrangement, the synthesis temperature should be maintained as low as possible. To see this, the TEM images were reproduced in Figure 3 for the sample prepared by the sol−gel route in which the reactions proceeded at progressively higher temperatures: 25, 40, and 70 °C. Indeed, the TEM images showed that the prepared pores displayed comparatively well-oriented structures at a lower second-step reaction temperature. In the next section, we prepared the mesoporous structure using the same type of wormy micelles under a shear flow and examined the flow effect on the microstructure of the mesopores.

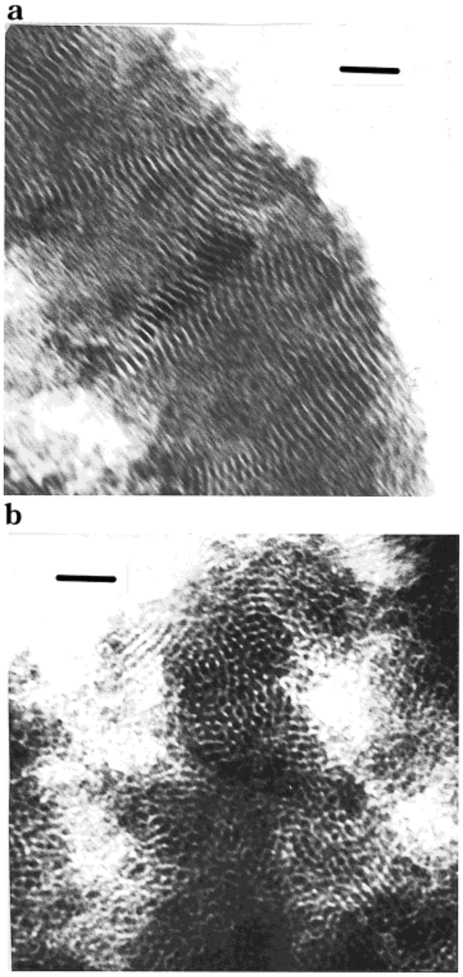

Figure 3. TEM images of various parts of the porous materials prepared by in situ gelation of wormlike surfactant solutions in the absence of an imposed flow. The CTAB concentration was 5 mM with the molar ratio fixed at unity. The samples were prepared by the following three-step thermal history: namely, at 25 °C for 3 h, at 40 °C for 5 h, and subsequently at 70 °C for 1 h. Scale bars indicate 20 nm.

3.2. Mesoporous Structures Formed in the Presence of an Imposed Shear Flow. Let us then consider the microstructural transition in wormlike micellar solutions induced by steady shear flow and its effect on the structure of the prepared mesoporous materials. The shear flow was applied for 9 h to the wormlike micellar solutions to ensure the completely oriented phase toward the flow direction. We performed the synthetic process at high temperatures (70−80 °C) for various reaction time intervals. As noted, temperature change and reaction time affected appreciably the morphology

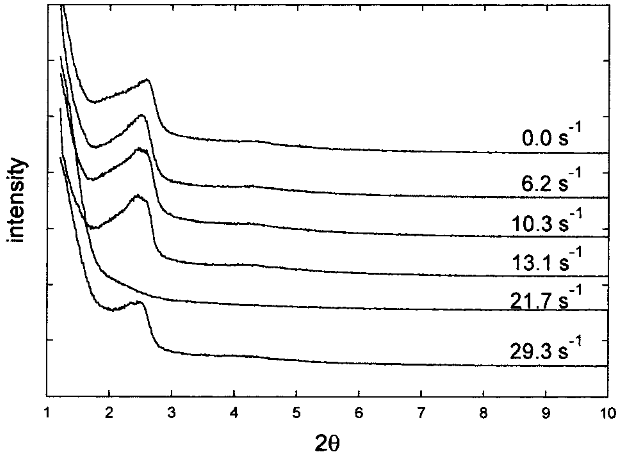

Figure 4. XRD patterns of the prepared samples under various applied shear rates for samples prepared by a three-step thermal history under the continuous flow field. The CTAB concentration was 5 mM with the molar ratio fixed at unity.

of mesoporous structure in the absence of the external flow. In the present study, however, we were interested in the flow-induced microstructure of wormy CTAB micelles, which were used as a template. Therefore, we applied a strong external flow to the CTAB solution, in which the hydrodynamic contribution was dominant over the thermal contribution. By doing this, we could produce the helical tubules of mesopores in silica substrate. The pore arrangement and helical structure remained persistent within the temperature window considered here. Specifically, the three-step reactions proceeded at progressively higher temperatures, 25, 40, and 70 °C, in the presence of the shear flow. Although a dilute CTAB solution with a lower molar ratio R was favorable to the formation of hexagonal structures in the absence of the flow as shown in Figure 1, such a solution was shown to be very unstable under the shear flow. Therefore, for the surfactant template to sustain its structural stability under the flow, the solution should possess an appropriate level of viscoelasticity. To do so, we added the structure-enhancing additive NaSal to an equimolar content for a satisfactorily large relaxation time.[25] In Figure 4, the XRD patterns were plotted versus the scattering angle for the samples prepared at the shear rate ranging from 0 to 29.3 s^{-1}. In this case, the CTAB and NaSal concentrations in the wormlike micellar solution were both 5 mM, and the cryo-TEM images for this equimolar composition showed that the wormlike micelle was transformed into a long linear conformation.[26] Meanwhile, our preceding study confirmed that the long linear chain of wormlike micelles could readily be aligned to the flow direction even in the weak flow regime.[1] Indeed, the XRD patterns in the presence of the shear flow indicate that the prepared pore structure was affected strongly by the intensity of shear flow. As noted, the ordered or disordered hexagonal domains are formed by the imposed flow depending on the flow intensity. One of the most interesting features is that these structures were sustained until the shear rate reached a certain critical value, beyond which no appreciable structure was developed. In the present case, the critical shear rate for disappearance of the flow-induced structure was 21.7 s^{-1}.

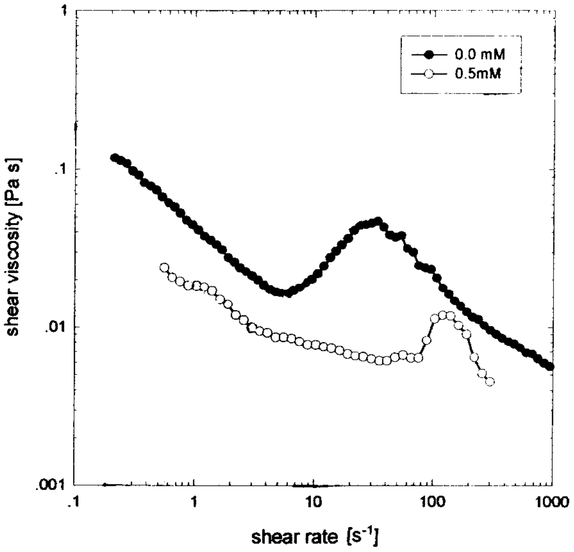

Figure 5. Steady shear viscosity was plotted as a function of the applied shear rate. The CTAB concentration was 5 mM with the molar ratio fixed at unity. Filled symbols are for the sample prepared in the absence of primary heptanol and open symbols for the presence of 0.5 mM heptanol.

To understand the relationship between the flow intensity applied to the surfactant solutions and the development of flow-induced structure, the rheological responses were observed by our group[27] and are reproduced here. In Figure 5, the shear viscosity was plotted as a function of the shear rate for the equimolar micellar solution of CTAB and NaSal. Also included for comparison was the shear viscosity for the presence of primary heptanol at 0.5 mM. The heptanol was added as a cosurfactant, and its effect on the microstructure of the prepared porous materials will be discussed shortly. The result showed that the CTAB solutions without primary heptanol exhibited a typical non-Newtonian behavior of shear thinning throughout the whole shear rate ranges when the concentration was above 0.01 M. As noted in Figure 5, however, when the concentration was below 0.01 M, the viscosity initially shear-thinned as the shear rate was increased up to a certain value, beyond which the viscosity shear-thickened. Moreover, in this case, the viscosity shear-thinned again as the shear rate was increased even higher. At extremely low shear rates, the solution behaved like a Newtonian fluid, and the viscosity was independent of the shear rate. This is because the solution was random and isotropic in its microstructure. However, as the shear rate was increased, the solution underwent the shear-induced transition in which the wormlike micelles were aligned completely in the flow direction so that the micelles were collinear, as observed by the captured SEM image.[1] This structural transition led to the shear thinning like a linear polymer solution. As the flow became much stronger, the collinear aggregation occurred in these solutions. Consequently, the shear thickening of weakly entangled micelles was due to the flow-induced coagula-

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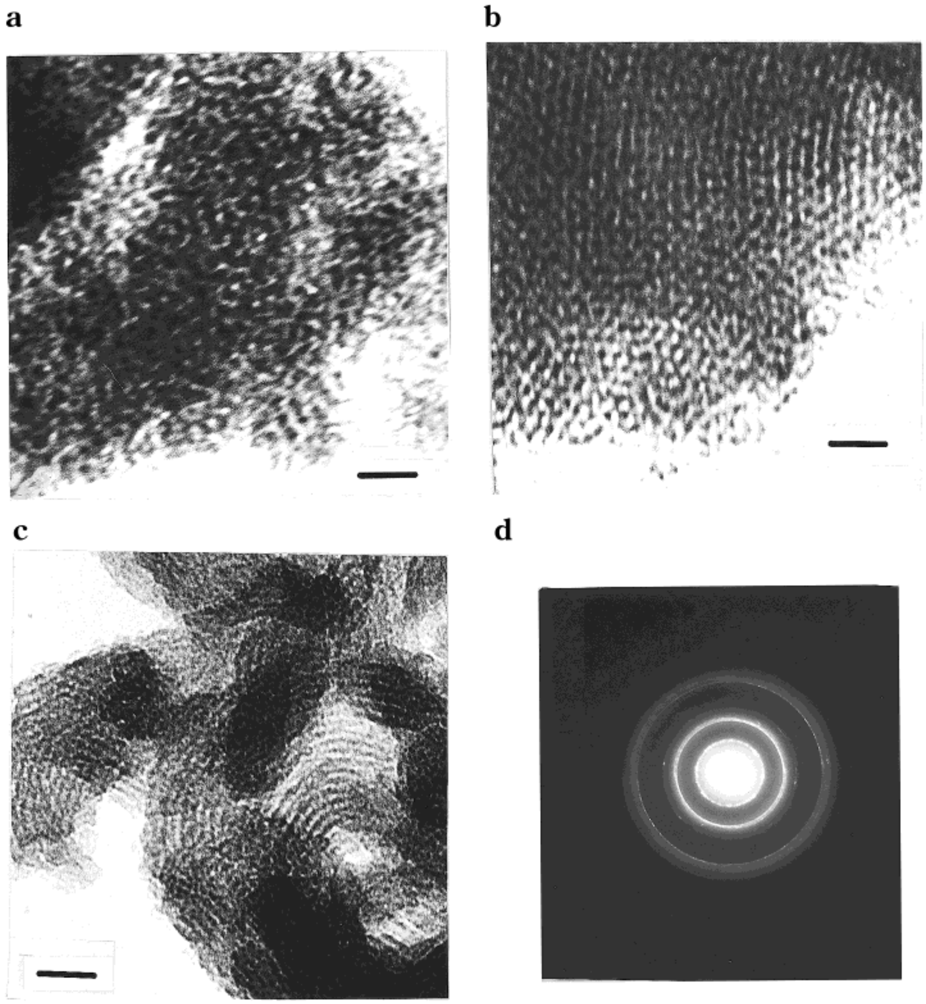


Figure 6. TEM images of the porous samples prepared at different shear rates. CTAB concentration of 5 mM with the molar ratio fixed at unity at (a) 10.26, (b) 10.26, and (c) 13.14 s^{-1}. Scale bar indicates 20 nm. (d) Bright-field image for the sample prepared at 13.14 s^{-1}.

tion by the strong hydrodynamic contribution. It can be noted from Figure 5 that the viscosity shear-thickened for the shear rate ranging from 10 to 25 s^{-1}. This is clearly consistent with the diminishing XRD patterns at the shear rate of 21.7 s^{-1}. Moreover, at even higher shear rates, the solution experienced the shear thinning again since the predominant hydrodynamic forces collapsed the coagulated structure. Indeed, the XRD patterns for the sample prepared at 29.3 s^{-1} indicates the reformation of a weakly layered structure. It is noteworthy that the added silica precursor (TEOS) affected slightly the rheological behavior of surfactant solutions by a dilution effect in the water condensation process. In our previous publication, we reported the flow-induced morphology in the presence of wormlike micelle with silica precursor.[1] The dilution effect led to a time-dependent rheological behavior as the sol−gel reaction proceeded. However, the general rheological features such as shear-thinning and shear-thickening viscosities were not changed by the presence of TEOS. Also noted is that the presence of primary heptanol retarded the onset of shear thickening, which appeared at a shear rate around 100 s^{-1}. As we shall see shortly in section 3.3, the rheological response in the presence of primary heptanol was also consistent with the pore structure of the prepared materials.

Although the XRD patterns were similar for the shear rates below 15.0 s^{-1}, the corresponding TEM images of the prepared mesoporous structures were distinctively different depending on the flow strength. The TEM images in Figure 6a,b, which were prepared at the same shear rate of 10.26 s^{-1}, were not spatially uniform. At this shear rate, both the fully oriented structures and the partially amorphous conformation coexisted. As the shear rate was increased further to 13.14 s^{-1}, the mesoporous structure was transformed into the layered structure with a spatial uniformity, and the typical TEM image was reproduced in Figure 6c. A bright-field image in Figure 6d for the same sample used in Figure 6c showed the crystalline structure without any noticeable orientation, though a fast Fourier transform (FFT) image for spatial region in Figure 6c showed the fully oriented layered structure. In addition, the TEM images for the sample prepared near the critical shear rate of 21.4 s^{-1} indicated that the layer fluctuations at a higher shear rate leading to the shear-thickening viscosity, produced an amorphous phase or a randomly distributed hexagonal phase. The TEM images were similar to those in Figure 6a,b.

Up to now, we have considered the effects of shear flow on the formation of mesoporous structures. Although the wormlike micelles in the dilute surfactant

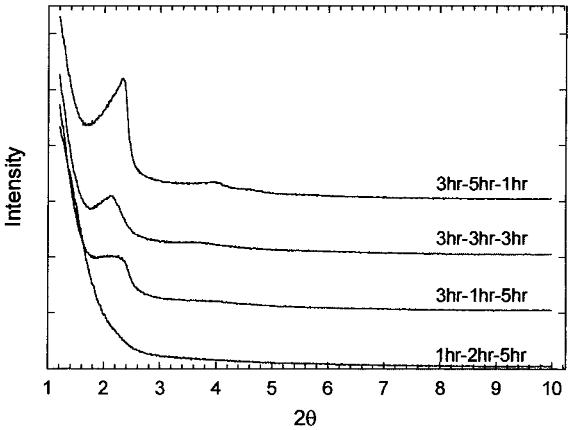


Figure 7. XRD patterns of the samples prepared with different thermal histories. The reaction times at different temperatures, 25, 40, and 70 °C, were indicated in the inset. The CTAB concentration was 5 mM with the molar ratio fixed at unity. The concentration of primary heptanol was 0.5 mM, and the applied shear rate was 10.26 s^{-1}.

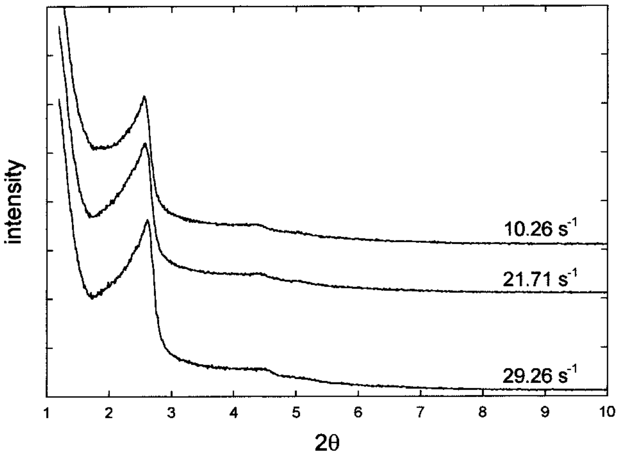


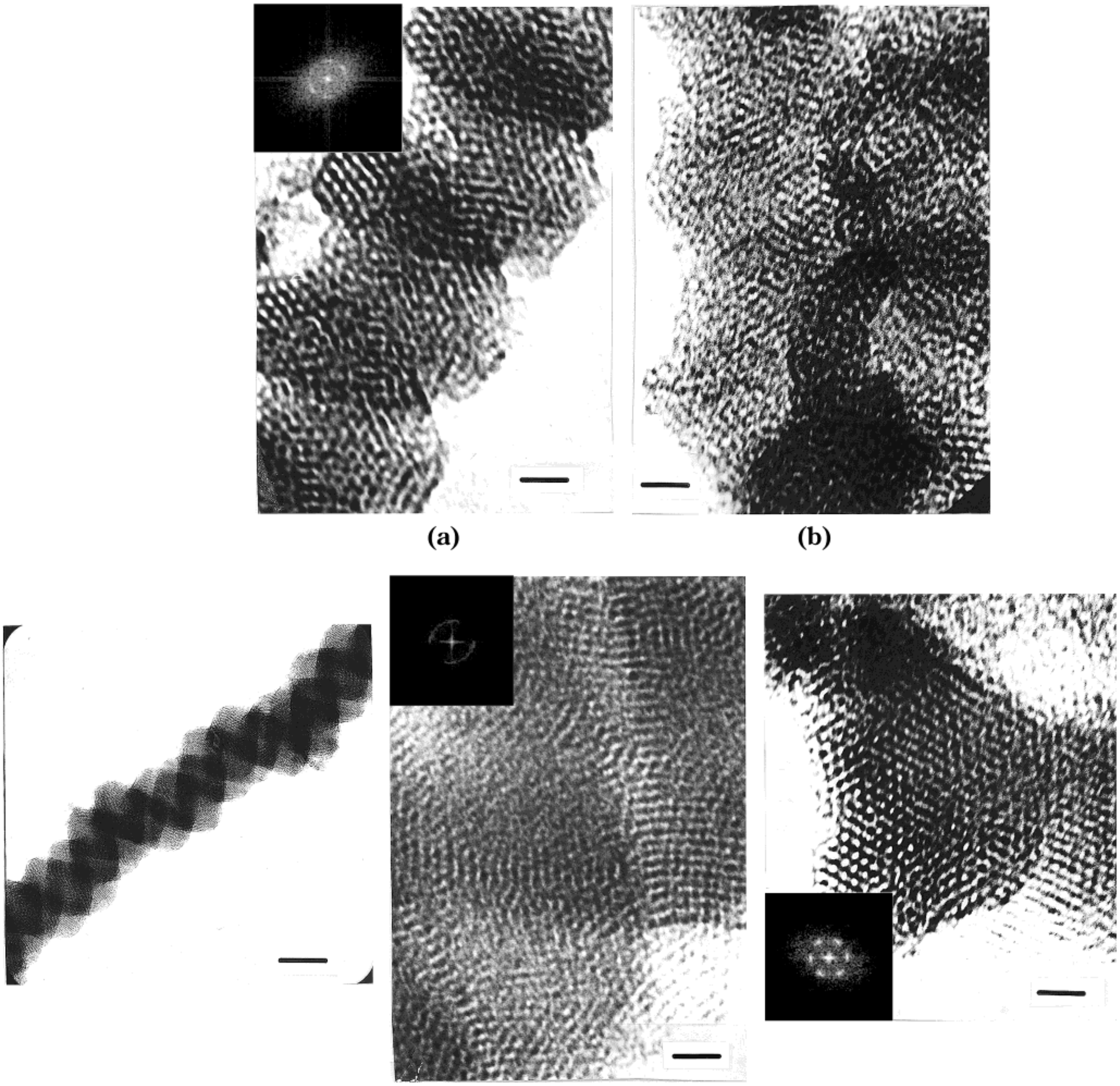
Figure 8. XRD patterns of the porous samples prepared at different shear rates. The CTAB concentration was 5 mM with the molar ratio fixed at unity. The concentration of primary heptanol was 0.5 mM.

regime did not sustain the ordered structure under the shear flow, the linear and long extended micelles in the equimolar solution (i.e., $R = 1.0$) were easily formed into the ordered hexagonal phase under shear flow, as confirmed by the XRD studies. However, in contrast to the phase changes observed from the XRD patterns, the TEM images did not show distinctly the layered structures. In the next section, we will consider the role of primary heptanol in controlling the structural stability and thereby forming well-defined ordered structures.

3.3. Effects of Primary Heptanol on the Mesoporous Structure. In Figure 7, the XRD patterns were illustrated as a function of the scattered angle 2θ for the samples synthesized with the different reaction times of the three-step reactions. In this plot, the CTAB concentration was fixed at 5 mM with the equimolar ratio of NaSal to CTAB. In addition, the primary heptanol was used as a swelling agent or a structure stabilizer. The content of primary heptanol was fixed at 0.5 mM. It can be seen from Figure 7 that the well-ordered hexagonal array was formed either as the reaction time at low temperatures was increased or as the elapsed time at high temperatures was decreased. This is because the wormlike micelles lost their stability when they were exposed to high temperatures. Thus, most of our samples were prepared by the following sequence of reaction time steps: first, 3 h at 25 °C, then 5 h at 40 °C, and finally 1 h at 70 °C. Otherwise, we will specify the reaction conditions.

In general, alcohols play a role in the phase transition of a surfactant solution as cosurfactant or swelling agents, and their presence can change the prepared mesoporous structure.[6–7] A long-chain alcohol forms the so-called surfactant–cosurfactant mixed micelles and increases the micelle size or induces the shape transition. In the CTAB solution, the presence of primary heptanol improved the pore structure as noted in the XRD patterns reproduced in Figure 8. It can be seen from Figure 8 that the prepared hexagonal structure did not depend on the shear rate in the range from 10.26 to 29.26 s^{-1}. In the XRD patterns, we observed the (100) and (110) peaks of the hexagonal phase. The (200) peak was not apparent because the (110) peak is much stronger than the (200) peak in the acidic synthesis route. The pore spacing estimated from the XRD peaks was about 3.6 nm, which was slightly larger than 3.4 nm measured from the TEM images. The discrepancy resulted from the oblique viewing angle in TEM. To investigate closely the effects of primary heptanol, the TEM images were taken for the samples prepared at various shear rates, and the results were shown in Figure 9. Of special interest is that the samples prepared in the presence of primary heptanol exhibited the overlapped, twisted, and anisotropic features of well-defined layers; see Figure 9a,c. In addition, the ordered structures shown in parts a, b, d, and e of Figure 9 were coincident with the X-ray diffraction patterns in Figure 8. Although the XRD patterns indicated that the formation of ordered hexagonal structure was almost independent of the shear rate, the TEM images showed that the layered structure was developed apparently as the shear rate was increased within the range considered here.

The TEM images in Figure 9a for the sample prepared at the shear rate of 10.26 s^{-1} showed a relatively weakly ordered hexagonal phase. As the shear rate was increased up to 29.26 s^{-1}, the formation of ordered structure was enhanced. As noted previously, when the shear rate reached about 10 s^{-1}, which was the onset shear rate of shear thickening without primary heptanol, the ordered structure was disrupted. However, in the presence of heptanol, the onset of shear thickening was retarded up to a much higher shear rate near 100 s^{-1}; see Figure 5. Consequently, when the strong shear flow was applied to the wormlike micellar solution containing primary heptanol, a distinctively well-aligned ordered hexagonal structure was formed. Thus, the general features of the shear-rate dependence were quite different from the case for the absence of primary heptanol, which was shown in Figure 4. The effect of flow intensity was confirmed by performing the fast Fourier transform (FFT) on the TEM images, which determined the degree of orientational order in the calcined mesoporous solid. The FFT images distinguish the morphologies and quantify the material anisotropy. For illustrative purposes, the corresponding FFT images were inset in the TEM images of parts a, d, and e of Figure 9. Indeed, the FFT pattern in Figure 9d,e showed clearly nonuniform distribution of the scattering. Figure



(a) (b)

(c) (d) (e)

Figure 9. TEM images of the porous samples prepared at different shear rates. TEM images for the samples prepared at (a) 10.26, (b) 21.71, and (c) 29.26 s^{-1}. (d) Magnified image of part c. (e) Different local image for the sample in part d. The CTAB concentration was 5 mM with the molar ratio fixed at unity. The concentration of primary heptanol was fixed at 0.5 mM. The FFT images are inset in the corresponding TEM images. Scale bars indicate 100 nm in part b and 20 nm in all the other TEM images.

9e was a different local image for the same sample as in Figure 9d, and the FFT image in Figure 9e distinctly showed the hexagonal crystalline structure. This indicates the formation of orientated structure by a strong shear flow. Meanwhile, the FFT image for a lower shear rate displayed a relatively isotropic distribution of the scattering intensity.

Finally, we added SEM images of the prepared mesoporous silica in Figure 10 to clarify the helical structure of mesopores. This helical structure was produced by the shear flow generated in the Couette flow cell. The prepared helices are a few micrometers long and about a hundred nanometers in the transversal dimension. The SEM images were consistent with the TEM images that showed the twisted and zigzag-typed structures.

4. Summary

We have seen that the wormlike micelles endowed the structural stability of dilute surfactant solutions under a shear flow. Our process has merits of relatively low-temperature process, no need of vacuum, and controllability of the orientational conformation by use of wormlike micelles subjected to an imposing flow. The shear flow was generated in a Couette cell by a rotating inner cylinder with a coaxial outer cylinder kept stationary. This typical flow configuration produces spring-coil streamlines which eventually stretch and, at the

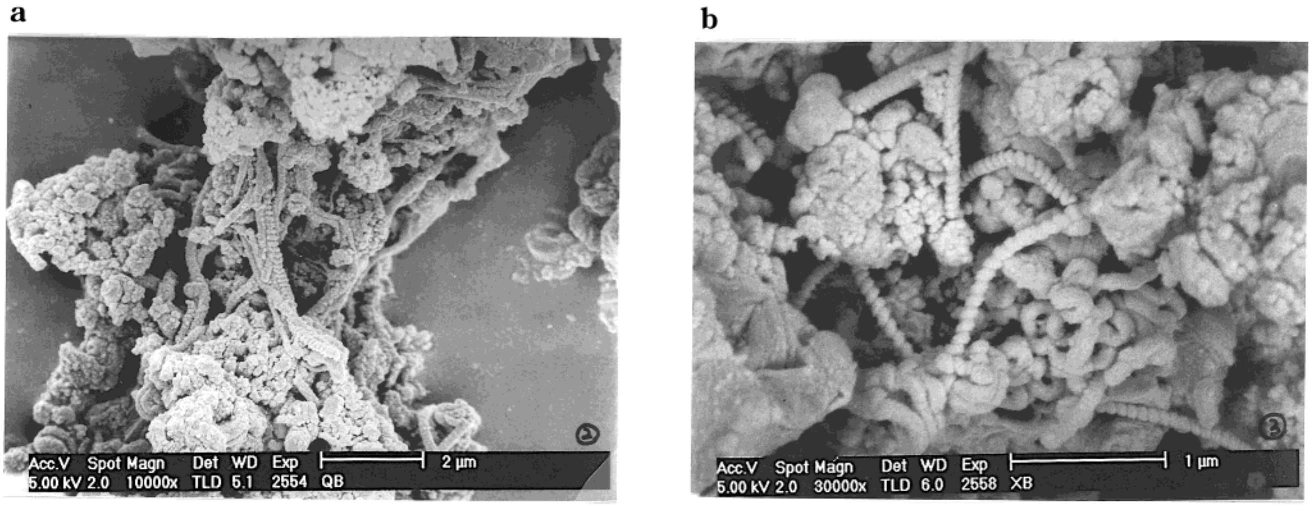


Figure 10. SEM images of the porous samples prepared at two different shear rates: (a) 10.26 and (b) 21.71 s^{-1}. The SEM images in parts a and b corresponds to the TEM images in parts a and b of Figure 9, respectively.

same time, twist a bundle of the long wormy micelles. The helical mesopores in silica substrate were formed successfully from the flow-induced microstructure of wormy CTAB micelles.

In equilibrium conditions without an imposed flow, the prepared porous materials displayed crystalline structure. The crystalline phase was formed favorably as the molar ratio of NaSal to CTAB was decreased, especially in the low-concentration regime. However, when the shear flow was applied to the dilute micellar solution with low molar ratio, the micelle template was not able to sustain its structural stability due to the deficiency in viscoelasticity. Thus, in the presence of an imposed shear flow, the structure-enhancing additive NaSal should be added to an equimolar content for the micelles to possess a required level of relaxation time.

The effects of flow intensity were consistent with the rheological responses of wormlike micellar solution. Any ordered mesoporous structure was not developed when the shear rate was in the range of shear thickening. The presence of primary heptanol produced well-ordered hexagonal phase under a weak or strong shear flow. The oriented structure under a shear flow was confirmed by the FFT images, which displayed nonuniform scattering patterns. The degree of orientation depended strongly on the flow intensity, as confirmed by TEM images.

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