

Fabrication of Pill-Shaped Polyimide Aerogel Particles Using Microfluidic Flows

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suspended in silicone oil are generated in a microfluidic droplet generator. Second, these droplets are guided into a contraction flow channel to deform them into pill-shaped droplets. Third, the pill-shaped droplets undergo sol—gel transition in a heated section of the flow channel and turn into particles. Finally, the pill-shaped aerogel microparticles are recovered via solvent exchange and supercritical drying and characterized. The data indicate that the flow rates of polyimide sol and silicone oil strongly influence the length of the microparticles while surfactants, although not



necessary to obtain pill-shaped particles, exert strong influence on the aspect ratio of the particles. The aspect ratio of particles and the internal morphology are discussed using hydrodynamic and interfacial forces. The ionic dye adsorption capacity of these pill-shaped particles is determined and compared with that of spherical gel microparticles.

■ INTRODUCTION

Aerogels, a class of highly porous materials, are fabricated from organic and inorganic molecules and their hybrids, often via sol–gel transition processes. Kistler first synthesized aerogels using silica.^{1,2} Subsequently, aerogel synthesis processes encompassed a variety of material systems such as resorcinol-formaldehyde,³ graphene,⁴ cellulose,^{5,6} syndiotactic polystyrene,^{7–9} polyurea,^{10–13} polyimide,^{14–17} and polyurethanes.¹⁸ Several inorganic–organic hybrid aerogels have been reported to date.^{19–21} Aerogel articles have also been fabricated in a variety of structural forms, such as monolithic blocks,²² sheets,¹⁷ foams,^{23–26} microparticles,^{27,28} core–shell hollow spheres,²⁹ millimeter size particles with multiple voids as inclusions,³⁰ and even 3D-printed gyroid structures.³¹ This proliferation of aerogels into various structural forms enabled by recent progress in fabrication methods is also accompanied by the expansion of the usage of aerogel porous structures in an array of applications including thermal insulation,³² air filtration,^{33–35} energy storage devices,³⁶ and space shuttle antenna.³⁷

Aerogel microparticles are of strong interest for their usage in a large variety of applications such as double-layer capacitors in energy storage,³⁸ as packed bed reactors in chromatography,³⁹ and as drug reservoirs in drug delivery.^{40,41} Aerogel microparticles of primarily spherical geometry serve in this application space due to the ease of fabrication, e.g., via emulsification,²⁷ although some challenges must be overcome to avoid broken particles and the customary wide particle size distributions originating from the nonuniform distribution of shear rates in an emulsion preparation process via mechanical mixing. The above issues preclude the tight control of the particle size. In a bid to circumvent these challenges, Teo and Jana²⁸ successfully demonstrated the use of a microfluidic setup and fabricated aerogel microparticles of a uniform size. The droplet generation process did not use surfactants, thus eliminating the need for additional processing or cleaning steps to remove undesired surfactants. Teo et al.²⁹ extended the work to obtain core—shell aerogel microparticles with a tight distribution of the particle size. Recently, Yao et al.³⁰ used a balance of buoyancy force and interfacial tension in conjunction with microfluidic flows and fabricated millimeter size aerogel particles with multiple internal voids.

The particle shape has emerged as an important parameter in tuning the properties of micro- and nanoparticles.⁴² Differently shaped micro- and nanoparticles have been fabricated via nonwetting templates,^{43,44} microfluidic flows,^{45–47} film stretching,⁴⁸ and template assemblies.^{49,50} The particle geometry (shape and size) significantly affects

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Figure 1. (a) Complete connection of the droplet generator and (b) schematic representation of the elongation of spherical droplets into pillshaped droplets.

transport processes and absorption and adsorption–desorption properties with the surface area-to-volume ratio being the determining factor.^{50,51} For example, oblate particles improve adhesion to biological substrates, owing to their larger planar surface area.⁵¹ In another example, the addition of platelets to composite materials improve their mechanical properties.⁵²

Different microparticle geometries are reported in the literature in the context of microparticles fabricated via microfluidic flows. Xu et al. described the synthesis of plugs and disk-shaped microparticles by using various microchannel shapes during droplet formation process, followed by a photopolymerization step to lock in the desired microparticle shape.⁴⁵ Dendukuri et al. produced microparticles of various polygonal, nonsymmetrical, and curved shapes using masks, with applications in drug delivery systems.⁴⁷

In this work, a continuous fabrication method is presented for pill-shaped polyimide aerogel microparticles from an oil-inoil emulsion system with and without the use of surfactants. The pill-shaped microparticle geometry was produced by passing deformable, spherical sol droplets through a contraction flow downstream of the microfluidic droplet generator. The train of pill-shaped sol droplets thus produced was guided through a heated tube where an accelerated sol—gel transition process fixed the shape and turned the sol droplets into gel microparticles. The pill-shaped gel microparticles were collected, washed with a solvent, and supercritically dried to yield high surface area aerogel microparticles.

High surface area porous materials are used as media for the adsorption of dyes and other organic pollutants from water, especially from textile effluents. Han et al.⁵³ used surface-modified silica aerogels for the removal of rhodamine B and

methylene blue dyes from aqueous solutions. Methylene blue is a cationic dye widely used in the textile industry. Methylene blue found in textile effluents can cause a variety of harmful effects on the human body, such as vomiting, diarrhea, shock, and gastritis.⁵⁴ In this context, the present study investigated the potential of the pill-shaped gel particles in the adsorption of methylene blue dye initially dissolved in water. The adsorption behavior of pill-shaped particles was compared with that of spherical gel microparticles fabricated using the same flow conditions.²⁸

EXPERIMENTAL SECTION

Materials. Pyromellitic dianhydride (PMDA) was purchased from Alfa-Aesar (Haverhill, MA), and 2,2'-dimethylbenzidine (DMBZ) was purchased from Shanghai Worldyang Chemical Co. Ltd. (Shanghai, China). Tris(2-aminoethyl)amine (TREN) cross-linker, surfactant Pluronic F127 (trademark of BASF), and methylene blue (MB) were purchased from Sigma-Aldrich (Milwaukee, WI). Pyridine, acetic anhydride, acetone, and silicone oil were purchased from Fisher Scientific (Ontario, NY). *N,N*-Dimethylformamide (DMF) was purchased from VWR International (Radnor, PA). The components of the droplet generator, such as 27 G syringe, 0.16 cm ID Tee connector, and Tygon tubing were obtained from McMaster-Carr (Aurora, OH).

Fabrication of a Droplet Generator. The coflow droplet generator used in this work was adapted from the work of Li et al.⁵⁵ and is an extension of the droplet generator used in the work of Teo and Jana.²⁸ The coflow droplet generator was assembled by inserting a 27 G flat tip needle with an inner diameter (ID) of 0.2 mm into a 1.6 mm ID Tee connector, as

shown in Figure 1. The outlet of the Tee connector was attached to a 1.6 mm ID PTFE tube, which in turn was connected to a 1.0 m long, 0.8 mm ID PTFE tube (Figure 1a). The purpose of reducing the PTFE tube ID from 1.6 to 0.8 mm was to produce a contraction flow that elongated the spherical polyimide sol droplets into pill-shaped droplets in the confines of the smaller channel geometry (Figure 1b).

PREPARATION OF POLYIMIDE SOL

The polyimide sol in DMF was used to make spherical droplets in the droplet generator. For this purpose, polyimide precursor solutions were prepared at room temperature by mixing PMDA, DMBZ, and TREN in DMF, as per the process outlined by Teo and Jana.²² Briefly, 0.108 g of PMDA and 0.106 g of DMBZ, dissolved separately each in 2 mL of DMF, were mixed and stirred for 2 min to obtain a solution of polyamic acid. Subsequently, 10 μ L of TREN dissolved in 1 mL of DMF, 0.333 g of acetic anhydride, and 0.313 g of pyridine were added to the polyamic acid solution to trigger cross-linking reactions and to allow for the chemical imidization of the polyamic acid. The resultant solution was used as the polyimide sol in this work. The polyimide sol thus obtained had 3.9 wt % polymer. The sol was transferred immediately after the preparation into the syringe pump designated for polyimide sol in the droplet generation device.

The pill-shaped gel and aerogel microparticles were also prepared in the presence of Pluronic F127 surfactant, a polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymer. It was used as a viscosity modifier to the polyimide sol at 0.0, 1.0, 2.5, and 5.0 wt % with respect to DMF. The surfactant was first dissolved in DMF followed by the addition of other ingredients as presented above.

FABRICATION OF POLYIMIDE AEROGEL MICROPARTICLES

As shown in Figure 1b, polyimide sol was injected into the droplet generator through the 27G needle using a Chemyx syringe pump (Stafford, TX) into silicone oil. Silicone oil was injected into the droplet generator through the Tygon tubing by another Chemyx syringe pump. At the tip of the 27G needle, the polyimide sol extended as a jet, underwent Rayleigh instability, and broke off as spherical polyimide sol droplets that traveled downstream through the 1.6 mm ID PTFE tube. These spherical droplets were guided into the 0.8 mm ID PTFE tube, and the contraction flow of the channel forced the deformation of the spherical droplets into a pill-shaped geometry. The pill-shaped sol droplets further traveled through the 0.8 mm ID PTFE tubing heated at 80 °C, thus undergoing expedited sol-gel transition and preventing coalescence. The PTFE tubing was heated to 80 °C by taping its entire length on a hot plate of an approximate temperature of 90 °C. As a reference, the polyimide sol typically takes 23 min to undergo the sol-gel transition at room temperature (20 °C). In a separate reference experiment, 1 mL of polyimide sol in a glass vial was heated from room temperature to 80 °C in an oil bath. The sol turned into a gel in approximately 50 s. Considering the small volume ($\sim 10^{-4}$ mL) of typical polyimide sol droplets in this work, the sol-gel transition of the pill-shaped polyimide sol droplets occurred in a significantly shorter time. In view of this, no surfactant was needed to stabilize this oil-in-oil (O/O)emulsion system against coalescence. The pill-shaped gel microparticles were collected in a glass jar containing hot

silicone oil at 80 °C. The glass jar with silicone oil was heated to 80 °C using a hot plate. The droplets were exposed to high temperature (80 °C) in PTFE tubing and in hot silicone oil and turned into gel particles. The gel particles settled down at the bottom of the jar and aged in hot silicone oil at 80 °C for 24 h. The particles were removed from silicone oil, cooled to room temperature, and subjected to solvent exchange using a mixture of 50% chloroform/50% silicone oil followed by 100% chloroform after 12 h.

The chloroform-filled gel microparticles were solvent exchanged with mixed solvents, 25 vol % acetone/75 vol % DMF, 50 vol % acetone/50 vol % DMF, 75 vol % acetone/25 vol % DMF, and finally with 100 vol % acetone each at 12 h intervals. The gel microparticles were further washed with 100 vol % acetone for an additional five times at 12 h intervals to remove the residual DMF and chloroform if any. The acetonefilled gels were subsequently solvent exchanged with 100 vol% liquid carbon dioxide six times at 1.5 h intervals in a supercritical dryer and dried under the supercritical condition of carbon dioxide at 50 °C and 11 MPa pressure to yield the pill-shaped aerogel microparticles. The fabrication of spherical polyimide aerogel microparticles is described elsewhere.²⁸ Briefly, the spherical gel particles were obtained after removing the flow contraction zone in Figure 1. In this context, the volumes of the representative ensembles of pill-shaped and spherical particles were the same as they originated from the same droplet generation process.

METHYLENE BLUE (MB) ADSORPTION ON POLYIMIDE GEL MICROPARTICLES

The extent of MB adsorption was assessed by dipping waterfilled polyimide spherical and pill-shaped gel microparticles in aqueous solutions of MB. For this purpose, the acetone-filled gel particles were solvent exchanged with mixed solvents consisting of 25 vol % water/75 vol % acetone, 50 vol % water/ 50 vol % acetone, 75 vol % water/25 vol % acetone, and finally 100 vol % deionized (DI) water, each at 12 h intervals. The gel microparticles were further exchanged with 100 vol % DI water five times at 12 h intervals to remove the residual DMF, chloroform, and acetone. A known weight (12 mg) of an ensemble of DI water-filled spherical and pill-shaped gel microparticles was separately added to 40 mL of 0.001 g/L MB solution in DI water. The concentration of MB in the solution over time was determined from the UV-vis absorbance of MB measured using a UV-vis spectrophotometer (UV-vis Spectrophotometer 8453, Hewlett Packard, Palo Alto, California, USA) and a calibration curve generated from the known MB concentration and corresponding absorbance. The cuvettes containing the gel specimen and MB solution were kept inside aluminum foil enclosures except when spectrophotometer data were taken.

CHARACTERIZATION OF AEROGEL MICROPARTICLES

Gel and Aerogel Microparticle Size Distribution. The size distributions of gel and aerogel microparticles were studied using an Olympus BX51 optical microscope (OM). The images of a population of particles were collected and analyzed using ImageJ software. Typically, the sizes of more than 100 particles were considered in each case.

Aerogel Morphology. The morphology of aerogel microparticles was studied using a scanning electron micro-

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Figure 2. Optical microscopy images of (a) pill-shaped gel and (b) pill-shaped aerogel microparticles. SEM images of (c) pill-shaped aerogel microparticle and (d) cross section of the fractured aerogel microparticle are also shown.

 Table 1. Mean and Standard Deviation of Gel and Aerogel Microparticle Length and Diameter and their Associated Shrinkage at Different Flow Conditions

		gel microparticle		aerogel microparticle		shrinkage	
dispersed phase flow rate $-Q_D$ (mL/min)	continuous phase flow rate – $Q_{\rm C}$ (mL/min)	length (µm)	diameter (µm)	length (µm)	diameter (µm)	length (%)	diameter (%)
0.01	0.5	$1400~\pm~60$	244 ± 11	1330 ± 60	230 ± 14	5.3	5.3
0.02		1680 ± 150	233 ± 15	1610 ± 160	230 ± 13	4.4	2.1
0.03		1740 ± 100	236 ± 12	1680 ± 130	220 ± 11	3.5	5.9
0.04		1830 ± 70	239 ± 13	1740 ± 80	230 ± 12	5.0	5.4
0.02	0.4	1810 ± 110	248 ± 11	1670 ± 110	240 ± 14	7.7	2.0
	0.5	1680 ± 150	233 ± 15	1610 ± 160	230 ± 13	4.4	2.1
	0.6	1470 ± 180	235 ± 12	1440 ± 145	220 ± 2	2.2	6.0
	0.7	1200 ± 130	235 ± 13	1135 ± 120	210 ± 14	5.7	9.4

scope, JSM5310, JEOL, MA at an accelerating voltage of 5 kV and an emission current of 20 mA. A representative piece of the aerogel specimen was mounted on an aluminum stub using a carbon tape, followed by sputter coating with silver (ISI-5400 Sputter Coater, Polaron, UK). Some samples were deliberately fractured to study the cross-sectional morphology of the pillshaped aerogel microparticles.

Fourier Transmission Infrared Spectroscopy (FT-IR). The infrared spectra were collected by a Nicolet iS50 FTIR tridetector spectrophotometer (Thermo Scientific, MA). Aerogel specimens were ground into a powder form. The aerogel powder and F127 powder were mixed separately with KBr pellets, and the mixture was pressed into discs. IR spectroscopy data were taken in transmission mode.

Length and Diameter Shrinkage. The shrinkage of supercritically dried aerogel specimens was obtained from the length and diameter readings of the gel microparticles and the corresponding dried aerogel microparticles. The values of shrinkage were calculated from the average values of the length and diameter of each group of materials. It was difficult to compare the length and diameter of each individual microparticle in the gel state and after supercritical drying.

RESULTS AND DISCUSSION

Morphology. The fabrication method described above successfully generated the pill-shaped gel and corresponding aerogel microparticles, as shown in Figure 2. It is seen that the gel microparticles were typically 1400 μ m long with a diameter of 240 μ m (Figure 2a), while the aerogel microparticles are typically 1330 μ m long with a corresponding diameter of 230 μ m (Figure 2b). A comparison of the images presented in Figure 2a and b suggests that the pill-shaped aerogel microparticles lost some of their straight cylindrical shape. This is attributed to the shrinkage that occurred during the supercritical drying process. The image in Figure 2c indicates that the microparticle surface was smooth at a 100 μ m length scale. A wrinkled surface became apparent at the 100 nm length scale as seen from Figure 2d. Such a wrinkled texture of the surface of core-shell polyimide aerogel microparticles was earlier reported by Teo et al.²⁸ and attributed to the osmotic pressure caused by the higher solubility of DMF and silicone oil at 80 °C. A highly porous internal structure of the microparticles is also apparent from Figure 2d.

Microparticle Size Distribution. The microparticle size distribution was studied as a function of the flow rates of the dispersed phase (Q_D) polyimide sol and the continuous phase



Figure 3. Dependence of mean values of the length of gel and aerogel microparticles on Q_D and Q_C . (a) Average length vs Q_D at constant $Q_C = 0.5$ mL/min and (b) average microparticle length vs Q_C at constant $Q_D = 0.02$ mL/min. Error bars scaling with one standard deviation are shown. The data points are connected using straight line segments to guide the eye.

 $(Q_{\rm C})$ silicone oil. For this purpose, first, $Q_{\rm D}$ was varied in the range of 0.01–0.04 mL/min while keeping the $Q_{\rm C}$ constant at 0.5 mL/min. Subsequently, $Q_{\rm D}$ was maintained at 0.02 mL/min while $Q_{\rm C}$ was varied from 0.4–0.7 mL/min.

A few observations can be made after examining the microparticle length and diameter data presented in Table 1. The distribution of particle lengths is presented in Figure S1. First, the gel microparticles in general had a larger length and diameter than their corresponding aerogel microparticles, irrespective of the flow rates Q_D and Q_C , thereby indicating the appreciable shrinkage in the diameter and length during supercritical drying. This is illustrated using the data obtained with $Q_D = 0.01 \text{ mL/min}$ and $Q_C = 0.5 \text{ mL/min}$. The average gel microparticle length was 1403 \pm 59 μ m, while the corresponding average aerogel microparticle length was 1329 \pm 60 μ m. This corresponds to a mean length shrinkage of 5.3%. This shrinkage occurs both axially and radially as indicated in Table 1. The data presented in Table 1 also show that the mean shrinkage values of 2-9% are consistent with the shrinkage values reported in the previous work.²⁸ We recall that the shrinkage values reported in Table 1 correspond to an ensemble average due to the difficulty associated with tracking the shrinkage values of each individual microparticle.

The data in Table 1 also show the dependence of the microparticle length on Q_D and $Q_{C'}$ while the microparticle diameter shows the weak dependence on flow rates of silicone oil and polyimide sol. For example, the gel microparticle length increased from 1203 \pm 127 μ m to 1828 \pm 69 μ m in this study. In contrast, the gel microparticle diameter only varied from $233 \pm 15 \ \mu m$ to $248 \pm 11 \ \mu m$. The weak dependence of the microparticle diameter on Q_D and Q_C can be attributed to the same degree of contraction of the flow from 1.6 mm to 0.8 mm ID (see Figure 1b) leading to pill-shaped particles of similar diameter irrespective of the combinations of $Q_{\rm C}$ and $Q_{\rm D}$. It is also worthwhile to note that the gel microparticle mean diameter (233–248 μ m) was smaller than the ID (0.8 mm) of the contraction channel. The small variation in the particle diameter can be attributed to the shape relaxation of the elongated pill-shaped droplets before the shapes were fixed via expedited gelation in the heated section of the tube.

For a given Q_C , the particle length increased with an increase in Q_D as is intuitive. As discussed earlier, the contraction flow geometry in Figure 1b kept the diameter of the pill-shaped gel microparticles in a close range of 233–244 μ m (Table 1). Therefore, the effects of Q_C and Q_D are apparent in the values of the length of the pill-shaped microparticles. Table 1 shows that the average gel microparticle length increased from 1403 \pm 59 $\mu \rm m$ to 1828 \pm 69 $\mu \rm m$ for an increase in $Q_{\rm D}$ from 0.01 to 0.04 mL/min for a given $Q_{\rm C}$ of 0.5 mL/min. These trends are illustrated in Figure 3a. The higher droplet mass at higher values of $Q_{\rm D}$ is responsible for the larger particle length. We recall that the extent of contraction in the contraction flow was the same in all cases and thus pill-shaped microparticle diameter was insensitive to both $Q_{\rm C}$ and $Q_{\rm D}$ values.

An increase in Q_D for a given Q_C led to an increase of the mass flow rate of polyimide sol extruded through the 27G needle. This in turn yielded larger spherical droplets of polyimide sol in the first part of the microfluidic droplet generator as schematically presented in Figure 1b. Eq 1, valid for droplet generation in annular co-flow microfluidic systems under jetting regime, presents a relationship between spherical droplet diameter D_0 and the ratio of Q_D and Q_C .⁵⁶ In eq 1, W_0 is the width of the outer channel, and $g(k^*)$ is a function of the wavenumber k^* with $g(k^*) \approx 1.43$. Eq 1 predicts a spherical droplet of diameter 323 μ m for $Q_C = 0.5$ mL/min, $Q_D = 0.01$ mL/min, and $W_0 = 1.6$ mm. The droplet diameter changes to 404 μ m for $Q_C = 0.5$ mL/min and $Q_D = 0.04$ mL/min.

$$\frac{D_0}{W_0} = g(k^*) \left(\frac{Q_D}{Q_C}\right)^{0.5}$$
(1)

An increase of $Q_{\rm C}$ for a given $Q_{\rm D}$ caused a reduction in microparticle length as presented in Figure 3b. For example, the gel microparticle length reduced from $1808 \pm 113 \,\mu$ m for a $Q_{\rm C}$ of 0.4 mL/min to $1203 \pm 127 \,\mu$ m for a $Q_{\rm C}$ of 0.7 mL/min for a given value of $Q_{\rm D} = 0.02 \,$ mL/min. This reduction in the microparticle length can be attributed to two primary factors. First, a smaller droplet is generated in the microfluidic droplet generator at a higher $Q_{\rm C}$, as predicted by eq 1. Second, a higher $Q_{\rm C}$ also leads to a higher shear rate in silicone oil in the microfluidic channel thereby exerting a greater viscous force over the interfacial force and causing a much greater deformation of polyimide sol droplets in the contraction flow.

Effects of a Surfactant. The effects of the Pluronic F127 surfactant in polyimide sol are now discussed. It is worthwhile to note that no surfactant was required for the fabrication of these pill-shaped microparticles as droplet coalescence was not a factor in this work due to the expedited sol–gel transition in the heated section of the microfluidic tube flow (Figure 1b). The addition of a surfactant exerts two effects on polyimide sol.²² First, it increases the room temperature viscosity of the DMF solution, e.g., from 0.85 mPa·s for DMF to 1.15 mPa·s at

Table 2. Average Length and Diameter of Gel and Aerogel Pill-Shaped Microparticles and their Associated Shrinkage at Different Pluronic F127 Concentrations. Flow Rates Were Kept Constant at $Q_D = 0.01 \text{ mL/min}$ and $Q_C = 0.5 \text{ mL/min}$



Figure 4. Gel and aerogel microparticle size distributions at various Pluronic F127 concentrations. Red bars correspond to gel microparticles while gray bars correspond to aerogel microparticles. (a-d) are length distributions while (e-f) are diameter distributions. Flow rates were kept constant at $Q_D = 0.01 \text{ mL/min}$ and $Q_C = 0.5 \text{ mL/min}$.

1 wt % and 2.1 mPa·s at 5 wt % surfactant loading.²² Second, it reduces the interfacial tension between DMF and silicone oil. Accordingly, the presence of the Pluronic F127 surfactant influences both the spherical droplet generation process in the microfluidic droplet generator and the deformation of spherical droplets into pill-shaped droplets in the contraction flow.

The deformation (D) of droplets as defined in eq 2 in the contraction flow is dependent on the balance of hydrodynamic and interfacial stresses.⁵⁷ Christafakis and Tsangaris⁵⁸ studied the deformation of droplets in contraction flows and predicted transient and steady droplet shapes as a function of Reynolds number (Re), Weber number (We), and capillary number (Ca), defined respectively in eqs 3–5. These authors predicted the formation of blunted tail cylindrical droplets, similar to what was discussed earlier in reference to Figure 2a.

$$D = \frac{L - B}{L + B} \tag{2}$$

$$Re = \frac{D_0 U_{\rho_c}}{\eta_c} \tag{3}$$

$$We = \frac{D_0 U_c^2 \rho_c}{\Gamma} \tag{4}$$

$$\eta_0 U_c$$

$$Ca = \frac{-10^{-1}C}{\Gamma} \tag{5}$$

In eqs 2-5, *L* is the length of the pill-shaped droplet, *B* is the diameter of the pill-shaped droplet, D_0 is the diameter of contraction tube, U_c is the mean velocity in the contraction tube, ρ_c is the density of silicone oil, η_0 is the viscosity of silicone oil, and Tis interfacial tension between DMF and silicone oil. The flow rate of the polyimide sol ($Q_D \approx 0.01-$ 0.04 mL/min) was much smaller compared to the flow rate of silicone oil ($Q_c \approx 0.5-0.7 \text{ mL/min}$). In view of this, the value of U_c was in the range of 1.668–2.33 cm/s. The values of R_{e_1} We, and Ca were respectively 14.8, 33, and 3.5 without the surfactant considering $U_c \approx 1.668$ cm/s. In the presence of a 5 wt % surfactant, the interfacial tension reduced to 1.6 mN/m. The corresponding values of Re, We, and Ca were respectively 14.8, 79, and 8.9. It is noted that as per eq 5, the value of the capillary number increased in the presence of surfactants due to the reduction in the interfacial tension. The values of the capillary number in this work were much greater than what was considered in the work of Christafakis and Tsangaris, Ca \approx $0.1{-}1.0.^{58}$ Consequently, the deformation observed in this work was much higher (Table 2), and much longer gel droplets were produced.

To assess the effects of the surfactant indicated above, the values of Q_D and Q_C were kept at 0.01 and 0.5 mL/min, respectively, and the concentration of Pluronic F127 was increased from 0.0 to 5.0 wt %. The resulting gel and aerogel microparticle length distributions are presented in Figure 4,



Figure 5. (a) IR spectra and (b) TGA traces of aerogel microparticles produced with Pluronic F127. The onset of degradation is marked at 5% weight loss.

and the mean values of the length and diameter of pill-shaped particles are summarized in Table 2.

The data presented in Figure 4 and Table 2 reveal the following trends. First, the gel microparticle length increased from 1403 \pm 59 μ m to 2105 \pm 89 μ m as the concentration of Pluronic F127 was increased from 0.0 to 5.0 wt %. A corresponding increase in the gel microparticle diameter from 244 \pm 11 μ m to 371 \pm 22 μ m was also observed. The shrinkage data reveal higher shrinkage values in the particle length in aerogel specimens obtained with surfactants, e.g., 5.3% with no surfactant to 15.3% in the presence of a 5 wt % surfactant. The distributions of particle length and diameter of aerogel specimens produced with and without surfactants diverged from that of gel specimens at a high surfactant concentration as revealed in Figure 4. These are clearly apparent in Figure 4d,h. These observations led us to believe that there were two different mechanisms at work, both attributed to the introduction of Pluronic F127 into the system.

First, it was noted earlier that Pluronic F127 served as both a viscosity modifier and as a surfactant. In its presence, the room temperature viscosity of polyimide sol increased from 0.85 mPa·s for DMF to 1.15 mPa·s at 1 wt % and 2.1 mPa·s at 5 wt % surfactant loading,²² and the interfacial tension between polyimide sol and silicone oil reduced from 4.0 to 1.6 mN/ m.²⁹ The increase in viscosity and reduction in interfacial tension both delayed the breakup rate of the liquid jet of polyimide sol from the tip of the 27G needle. Consequently, the liquid jet stretched further from the needle tip before the droplet breakoff occurred,²⁹ and larger droplets were formed in the droplet generator. The increase in the viscosity of the droplet phase with the addition of a surfactant also reduces the deformability of the droplets for a given continuous phase flow rate in the contraction region. This resulted in an increase in the gel microparticle diameter.

We now discuss higher values of shrinkage in Table 2 in the presence of surfactants. We attribute the higher shrinkage to the residual Pluronic F127 surfactant in the gel particles. Pluronic F127 is traditionally used as a surfactant due to the presence of both nonpolar polypropylene oxide and polar polyethylene oxide groups.^{59,60} In particular, the polyethylene oxide groups tend to retain polar solvents such as DMF and acetone. Accordingly, in the supercritical drying step, the presence of trace amounts of DMF and acetone in the gel

produced nonzero capillary stress and caused shrinkage due to the collapse of the pores.

The aerogel specimens were analyzed using IR and TGA to verify the presence of the residual surfactant in the system. Such results are presented in Figure 5. Figure 5a shows that Pluronic F127 was still present in the aerogel microparticles, as evident from the Pluronic F127 alkane groups at 2880 cm⁻¹. The other bands at 1716, 1776, and 1365 cm⁻¹ show the symmetrical and asymmetrical stretching of C=O and C-N respectively of the polyimide functional group. The absence of COOH (2926 cm⁻¹) and CONH (3272 cm⁻¹) bands also signifies the successful chemical imidization of polyamic acid. The presence of Pluronic F127 was corroborated by the TGA curves in Figure 5b.Pluronic F127 was found to start degrading at a lower temperature of 390 °C and left no char at 700 °C, while neat polyimide started degradation at 504 $^\circ\mathrm{C}.$ The reduction in the char residue from 61 to 41 wt % with an increase in the Pluronic F127 concentration from 0.0 to 5.0 wt % indicated that the final aerogels did retain Pluronic F127 even after the solvent exchange steps and supercritical drying. This residual surfactant retained polar solvents DMF and acetone in the gel, which in turn caused an increase in shrinkage values as seen in Table 2.

ADSORPTION OF MB BY POLYIMIDE GEL MICROPARTICLES

As indicated in the Experimental section, an ensemble of 12 mg of spherical and pill-shaped water-filled polyimide gel microparticles was used to study the adsorption behavior of MB. Figure 6 presents a comparison of the adsorption behavior of MB by polyimide gel microparticles observed over a period of 3 weeks. We do not claim that the values reported in Figure 6 are indicative of maximum MB adsorption capacities by the polyimide microparticles. It is apparent from Figure 6 that the initial rate of adsorption was high and can be attributed to the high surface area of gel microparticles. Figure 6 also shows that spherical and pill-shaped particles had similar initial adsorption rate, although the extent of adsorption was slightly higher for the pill-shaped particles, e.g., 26.6 mg/g at 30 000 min than the spherical particles with 24.6 mg/g at 30 000 min.

We recall that the volumes of representative ensembles of pill-shaped and spherical particles in 12 mg of DI water-filled gel specimen were the same, as the particles originated from the same droplet generation process and that the contraction

Pill-shaped gel microparticles Spherical gel microparticles Spherical gel microparticles 15 10 10 5 0 5000 10000 15000 20000 25000 30000 35000 Time (mins)

Figure 6. Adsorption of MB by spherical and pill-shaped polyimide gel microparticles.

zone was not used when spherical particles were intended. Accordingly, the dye adsorption experiments accommodated the inherent effect of particle size distributions included in 12 mg of ensemble of DI water-filled gel particles. In view of this, repeated measurements with different ensembles of particles produced under the same condition were not conducted. We also noted that absorbance measurements of the control MB solution using UV—vis spectrophotometry were reproducible.

A slightly higher adsorption in the case of pill-shaped particles can be attributed to the higher surface area-to-volume ratio compared to spherical particles. It is noted that the weight of the spherical microparticles was controlled in this work by the flow rates of the dispersed and continuous phase flow rates in the droplet generator (Figure 1a). It is also noted that the pill-shaped particles were formed by passing the spherical droplets through a contraction flow. In view of this, the pill-shaped and spherical particles should ideally have the same weight. We attribute the MB adsorption on the polyimide surface in gel microparticles to π - π interactions between the aromatic rings of the MB molecule and the polyimide chain. A quantification of these interactions was beyond the scope of this work and will be a part of our future report.

CONCLUSIONS

The results presented in this paper established that pill-shaped polyimide aerogel microparticles can be successfully fabricated using a co-flow microfluidic setup without the use of surfactants. This was achieved by introducing a downstream contraction flow region to deform the spherical droplets generated in an upstream microfluidic droplet generator operating in the jetting regime. The heating of the pill-shaped microparticles at 80 °C expedited the sol-gel transition and fixed the pill-shaped geometry. This work also showed that the microparticle length can be controlled by varying the ratio of the flow rates of polyimide sol and silicone oil. The triblock copolymer surfactant that dissolved in the polyimide sol increased the length and diameter of pill-shaped particles by delaying the breakup in the droplet generator.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c05424.

Gel and aerogel microparticle length distributions at several dispersed and continuous phase flow rates (PDF)

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Notes

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