Fabrication of Hollow, Spherical Polymeric "Micropillows" Using a Dual Layer Spinneret

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ABSTRACT: Hollow, spherical, millimeter diameter scale polymer "micropillows" (MPs) were fabricated via nonsolvent-induced phase separation/extraction, using a dual layer spinneret extrusion system. Wall thicknesses in the 45–350-μm range were achieved via the extraction of the *n*-methyl-2-pyrrolidone (NMP) polymer solvent into a high-molecular weight poly(propylene glycol) nonsolvent. Introduction of heptane into the core of the particles and vaporization of that heptane at elevated temperatures enabled moderate particle expansion and avoided particle collapse after extraction of the NMP solvent. For the most dilute polymer solution feed, the final product was an imidized MP particle with a diameter of about 1.5 mm, a wall thickness of about 45 μm, and a geometric compression ratio of about 6.0. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2835–2842, 2011

Key words: polyimides; phase separation; microencapsulation; hollow microsphere; reversible collapse

INTRODUCTION

For many decades, nonsolvent-induced phase separation has been used to produce hollow fibers for high selectivity, high-flux molecular separations.[1] Such fibers are now very successful items of commerce in a variety of gas separation applications. From our laboratory experience with this technology and our observations during *unsuccessful* fiber-spinning experiments, we believed that it would be possible to use the same technology for the production of hollow polymer spheres of controlled size and polymer wall thickness. The aim of the current work is the fabrication of such an object, which we will refer to as a micropillow (MP). These MPs could have a number of interesting technological applications in controlled release of drugs and chemicals, variable density fluids and solids, and light weight materials.[2–6] Especially, polyimide MPs have a number of beneficial attributes in these applications such as high temperature, and chemical resistance, flame resistance, and high mechanical properties.[7–10] Based on gas transport, mechanical properties, and density-versus-pressure considerations, a polyimide (Upilex®) was chosen as the shell material for a MP with the following targeted structural properties:

diameter of about 1.5 mm and wall thickness less than 100 μm to yield a geometric compression ratio greater than 3.0. The so-called geometric compression ratio is the limiting value for initial versus final pressure ratios and is just the ratio of the initial volume of the MP to the volume of the polymer shell. MPs with these physical and gas transport properties are ideal for the production of high-pressure density control materials where MPs collapse reversibly to yield higher densities, which is proportional to the external pressure. For example, during oil and gas well-boring applications, it is required to control the density of the drilling fluid based on the depth of the well or the external pressure. In such application, the mechanically strong impermeable shell of MPs can collapse reversibly while retaining internally compressed gas without any damage to the MP in response to the external pressure. As a result, MPs with targeted structural properties such as wall thickness enhance the ability to control the density precisely while enabling more pressurize/depressurize application cycles during service life time of MPs.

Initial, first generation, experiments were carried out following so-called dry-wet solution-processing techniques using a water quench bath.[11] This technique enabled us to make MPs with about 1-μm dense wall supported by a mesoporous structure of about 300-μm thickness and with a mostly open coarse macroporous core (see Fig. 1). To achieve higher dense wall thicknesses, the water quench bath was replaced by high-molecular weight minimally invasive nonsolvent, poly(propylene glycol) (PPG). With this improved solvent-extraction
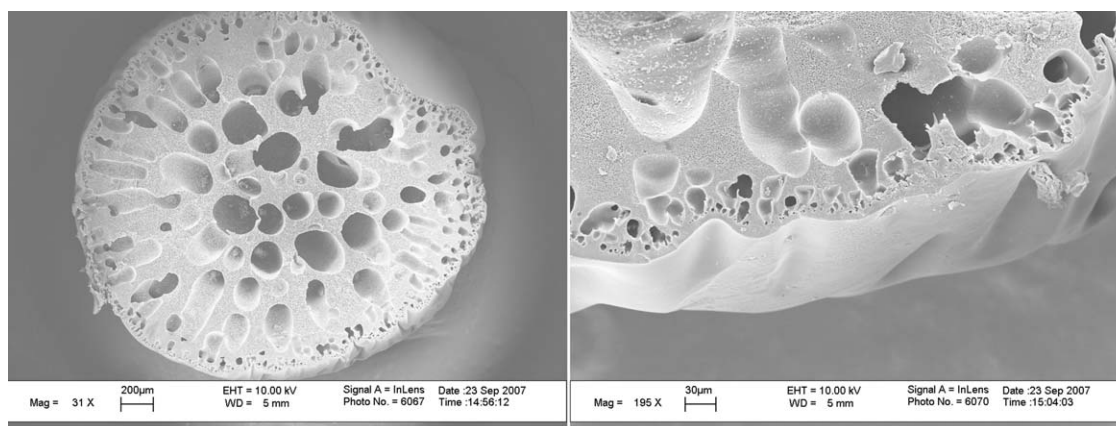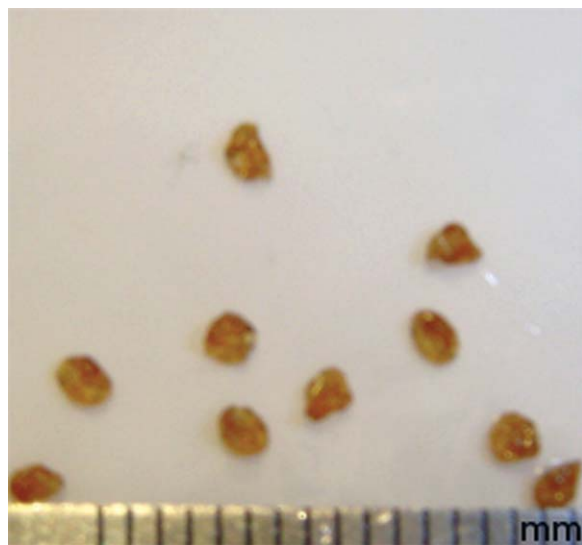
Figure 1 SEM images of first generation nonimidized MPs prepared by solution processing with a water quench bath: (left) cross section of a bisected MP and (right) higher magnification image of wall area showing dense outer skin.

technique, we were able to achieve dense wall thicknesses in the 200–350 μm range. During ambient temperature extraction of the residual solvent, the MPs usually collapsed in an irreversible manner due to the pressure gradient being formed across the nonvitrified sheath of the MPs as the core fluid contents were removed to create a hollow shell (see Fig. 2). Avoidance of this collapse is the challenge addressed herein. We accomplish this goal by the introduction of a volatile nonsolvent (heptane) into the core of the particles, a process enabled by the dual layer spinneret system described herein.

EXPERIMENTAL

Materials

Because of excellent mechanical and barrier properties (3.1×10^{-4} Barrer for oxygen at 30°C),[12] U-Varnish-S®,

Figure 2 Optical image of first generation, nonimidized MPs, showing collapsed structures formed after solvent extraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the nonimidized polyamic acid (PAA) form of Upilex-S was chosen for the fabrication of MPs. The chemical structures of nonimidized and imidized forms of the polymer are shown in Figure 3. Based on published mechanical properties, a hollow imidized Upilex-S sphere of 0.15 cm diameter and 50-μm wall thickness should be able to withstand over 10,000 psi of internal pressure.[13] Also, our own measurements of nitrogen transport in polymer films show that such a structure would maintain 90% of initial pressurization for several months.[14] The overall plan involved the following steps: fabrication of the MPs in the PAA form, infusion of pressurized N_2 into the core, and imidization of the wall to trap the N_2 in the core. All the experiments were carried out using two 20 wt % U-Varnish-S solutions with different molecular weights and correspondingly different solution viscosities, 50 and 1000 Poise at 25°C. The chemical structure of PAA form of Upilex-S (Fig. 3) consists of equal amounts of amide and acid groups in the polymer backbone. The amide groups react with acid groups, eliminating H_2O, and forming rings during the thermal imidization process to give the final product, Upilex-S. The repeating units have molecular weights of 392 and 356 g/mol, yielding a 9.2% weight loss on imidization. The reported glass transition temperature of this polymer is >300°C; the density of the polyimide form is 1.47 g/cc.[15] (*n*-Methyl-2-pyrrolidone) (NMP) was used to dilute the original 1000 Poise U-Varnish-S solutions to reduce the viscosity into the range required for our MP extrusion system (generally around 50 Poise at 25°C).

Heptane was chosen as the core nonsolvent for two reasons: its boiling point is in an accessible range (100°C), and it is expected to have low permeability in the PAA form of the polymer. PPG with $M_n = 725$ was selected as the nonsolvent for the extraction of NMP due to its expected lack of inward diffusion during solvent extraction, strong
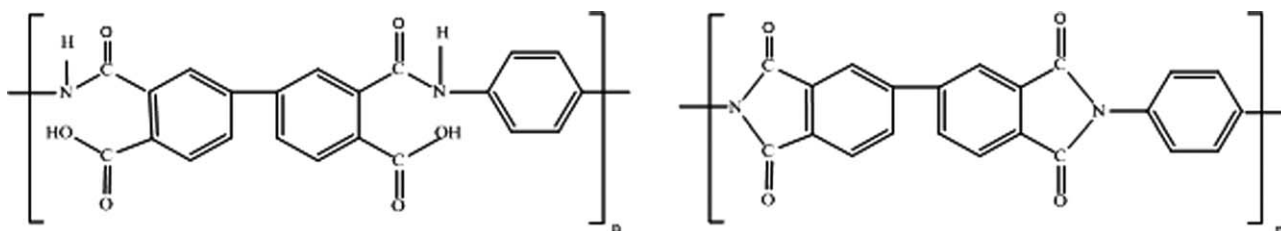
Figure 3 Chemical structures of (left) the nonimidized polyamic acid, U-Varnish-S®, and (right) the imidized polymer, Upilex-S®.

solubility for NMP, and ability to withstand high temperatures. Also, PPG is an environmentally safe solvent-extraction medium to facilitate efficient solvent extraction during MP formation. We carried out density measurements for two PPG samples, one at 425 M_n and the other at 725 M_n. The PPG density is about 1.00 g/cm^3 at 25°C with a temperature coefficient of -8×10^{-4}/C and little variation with molecular weight. All the solvents and nonsolvents, namely NMP, PPG, and heptane, were purchased from Aldrich and were either anhydrous or reagent grade.

### Micropillow fabrication process

Material preparation

Hollow MPs are fabricated from a 10 wt % PAA in NMP solution with an appropriate small amount of volatile component, heptane, in the core. The 10 wt % PAA was prepared by diluting the original 1000 Poise PAA solution with NMP at room temperature followed by mixing on a roller at room temperature for 24 h. Once the dilution process of PAA in NMP was confirmed by visual inspection, the solution was transferred into a syringe pump (Teledyne ISCO, Lincoln, NE) and kept undisturbed at room temperature for another 24 h to degas the polymer solution. The core material, heptane, was also loaded to another syringe pump and kept undisturbed at room temperature for 24 h to degas. The amount of heptane is determined as the amount needed to provide one atmospheric internal vapor pressure at 100°C, assuming no loss from the central solution into the PAA surrounding layer, and the eventual total vaporization at 1 atm to form the hollow MP core. This heptane amount was in a ratio of roughly 1 : 100 relative to the extrusion fluid on a volume basis.

Hollow MP fabrication

Our approach involved the use of a unique triple orifice, dual-layer spinneret that departs in important ways from more traditional triple orifice spinnerets.[16] The new spinneret design, ideal for MPs,

places the smallest annulus (137-μm opening) around the bore needle (Fig. 4, top), while dry nitrogen gas was used as the coaxial flow in the larger annular opening (614.7 μm) to "pluck" formed liquid drops at the end of the core needle. The core-needle dimensions were set by the lower tolerances of machining and proved to be sufficient for the
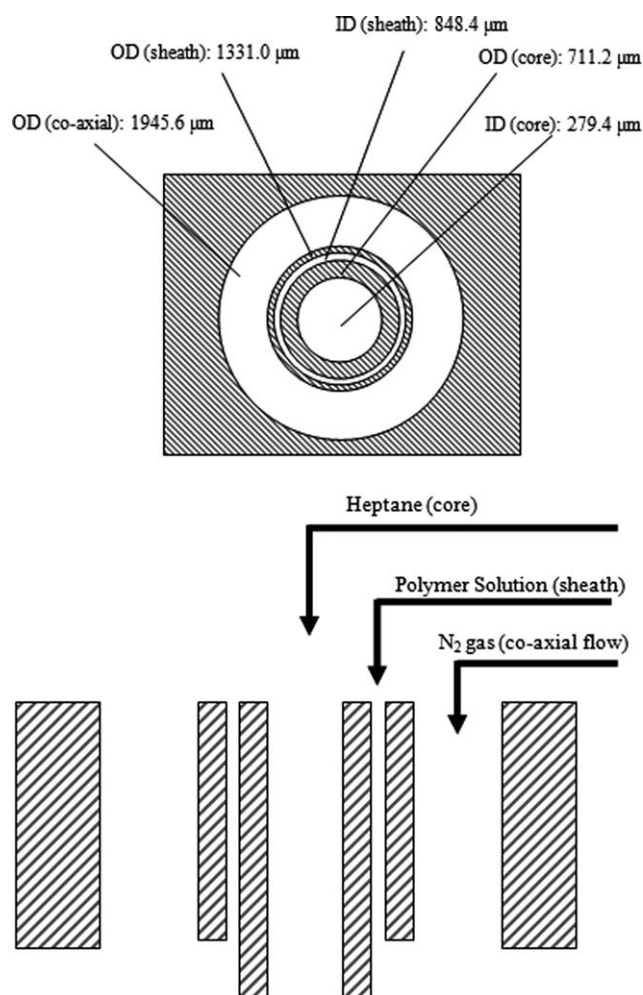
Figure 4 Top: Annular dimensions of the spinneret used for the creation of MPs. Bottom: Schematic representation of "triple orifice" annular spinneret and material feed lines for MP fabrication. Heptane, polymer solution, and N$_2$ gas were injected through core, sheath, and coaxial feed lines, respectively.

fabrication of MPs, though smaller core needles may lead to more efficient MP fabrication. Initial experiments involving traditional triple orifice spinnerets resulted in the creation of irregularly shaped MPs, while the new spinneret resulted in regularly spherical and smaller diameter MPs. This is most likely due to the fact that in traditional triple orifice annular spinnerets, the polymer is extruded through the larger annular opening, while the N_2 gas passes through the smaller annular opening, resulting effectively in a larger extrudate that is more difficult for the gas to "pluck" away from the annulus.

As can be seen in Figure 4 (bottom), the spinneret is designed to use a small amount of volatile nonsolvent, heptane as the core material for the fabrication of hollow MPs. The core material, heptane, and sheath material, 10 wt % PAA, were injected through core and sheath feed lines, respectively. Syringe pumps were used to control the core and sheath fluid flow rates during extrusion through the spinneret. The flow rate of the sheath polymer solution was varied between 5 and 20 mL/h. At lower sheath flow rates, liquid drops were large, and, as a result, irregular spheres were generated. A continuous production was achieved at sheath flow rate around10 mL/h. The temperature of the spinneret and extraction column was controlled using temperature controllers (Model: CN9111A, Omega Engineering, Stamford, CT) and heating tapes (McMaster-Carr, GA). Nitrogen gas flow rates were adjusted with flow meters (Model: Sho-rate 1355, Brooks Instruments, Hatfield, PA) to control drop formation and size. Optimum MP production was observed at 1200 ccm/min of coaxial nitrogen gas flow rate and hence flow rate was maintained at 1200 ccm/min throughout all experiments. At lower coaxial gas flow rates, larger liquid drops were formed and tend to wet the bottom surface of the spinneret, resulting in the disruption of the MP production. This can be attributed to the lack of sufficient force of the coaxial gas to pluck the formed liquid drops at the end of spinneret annulus. At higher coaxial flow rates, sheath polymer solution was sprayed into small polymer droplets. Viscosity of the polymer solution also played an important role during MP fabrication. During MP fabrication, it was observed that PAA solutions with viscosity less than 50 Poise yielded spherical MPs at room temperature. However, all the experiments were carried out with diluted polymer solutions to avoid complications with viscosity effects and to control the wall thickness. Although it required some optimization of flow rates of materials and coaxial gas, and concentration of the sheath polymer solution, once it was set, the system was quite stable and reproducible nascent MP drops could be formed at a good rate, typically 20 per minute.
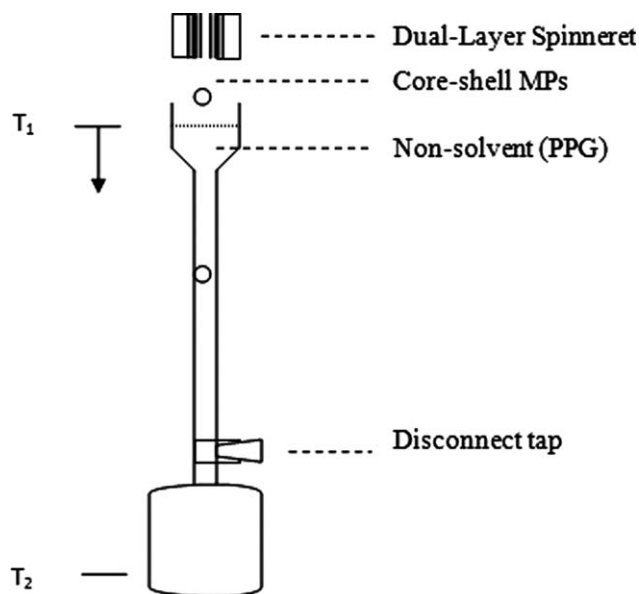
Figure 5 Schematic of temperature programmable narrow solvent extraction column for high-molecular weight nonsolvent, PPG. T_1 and T_2 ($\sim$ 55 and $\sim$ 65°C, respectively) are controlled temperature areas to maintain a temperature profile along the extraction column.

A 100-cm long glass tube (inner diameter = 16 mm), fitted with a 100-mL round-bottomed flask at one end was used as the solvent extraction column. The other end of the glass tube was modified to have a "conical" shape to facilitate liquid drop capture as illustrated in Figure 5. The lower one-third of the glass tube was wrapped with heating tape followed by insulating material to maintain a temperature profile along the NMP extraction column filled with PPG (M_n = 725) in such a way that MPs enter into a high temperature zone where enough heptane vaporizes to prevent MP collapse. The surface temperature of the PPG was maintained between 55 and 60°C by regulating the heating tapes wrapped around the glass tube and was varied for optimum results. Two thermocouples attached to the bottom and upper parts of the solvent extraction column were used to monitor the temperature.

When the liquid drop reaches the surface of the PPG, it enters the fluid and sinks, because its density (about 1.05 g/cc) is greater than that of the PPG (about 0.972 g/cc). As the liquid drop travels down the warm PPG extraction column, NMP extraction into the PPG occurs. As a result, a thin vitrified layer is formed around the surface of the liquid drop, and this is the initial stage of MP formation. When the MP reaches the higher temperature zone, some heptane evaporates to fill the space inside the MP as illustrated in Figure 6. Because the volatile material is not soluble in the sheath, the externally vitrified layer will trap the evaporated heptane vapor, reducing the effective density of the MP while holding the
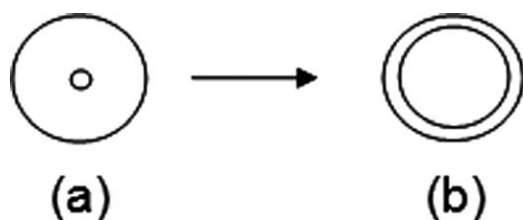
Figure 6 Schematic of a MP. (a) Initial state: sheath with mostly poly(amic acid)/NMP and nonvaporized heptane in core; (b) intermediate state: partially vitrified/imidized sheath with vaporized heptane in core.

spherical shape of the MP. The buoyancy effect of PPG forces the lower density MPs to move up the column for collection at the PPG surface with a plastic pipette. Currents due to thermal gradients also play a role in bringing the MPs back to the surface. Defective MPs, that is, those without an intact low-permeability skin, sink to the bottom of the apparatus for later collection and postmortem analysis.

Removing residual solvents

The residual NMP solvent remaining in the MP can plasticize the vitrified polymer wall causing shape deformation. Therefore, harvested MPs were collected on to a filter paper and immediately transferred to a vacuum oven (VWR, 49 Torr) at 100°C. The high temperature of the oven vaporized the internal heptane at essentially one atmosphere to help maintain the shape (or perhaps expand the particle somewhat) while the vacuum and elevated temperature facilitated rapid removal of the residual NMP from the MP. The filter paper caused a small distortion in the particle shape at times; however, no better surface was identified, and the effect was small.

Post-treatment procedure

MPs with vitrified walls are capable of maintaining their shape at normal atmospheric condition for at least several hours. However, they do not posses sufficient mechanical strength to be used in high pressure applications where MPs are supposed to collapse reversibly due to external pressure and easily can be cut-in-half by using a regular blade. Therefore, some of these MPs were imidized using the recommended UBE thermal program [programmed staging up to 450°C in a high temperature oven or in a thermal gravimetric analysis (TGA)]. The imidized MPs show better mechanical properties and did not have any detectable change in shape during regular handling for weeks. Apparently, the mechanical properties of these imidized MPs are similar to that of commercially available Upilex-S films with robust tensile strength of 520 MPa at 25°C.[13]

MP characterization

Scanning electron microscopy

Both nonimidized and imidized MP cross sections were examined under a high-resolution Scanning Electron Microscope (LEO 1530, Cambridge, UK) to determine the wall thickness and porosity. The SEM samples were prepared by cutting MPs wrapped in a polyethylene bag in-half with a stainless steel blade. Without using this approach, the tough vitrified MPs could not be cleanly cut even at cryogenic temperatures. Even with the specialized method noted earlier, some distortion in shape from the cutting process was always present. Successfully bisected halves were mounted on SEM sample holders and sputter coated with gold before they were examined.

Thermal gravimetric analysis

Thermal gravimetric analysis (TGA, Natzsh Luxx 409 PC) was carried out on MPs to determine the amount of residual NMP and degree of imidization. The data reveals the loss of NMP and water from MP as a function of both time and temperature. Although, the general features of the TGA graph can be reproduced, the *absolute* value of the weight loss showed poor reproducibility due to poor signal/noise with such small 0.4 mg samples. Nevertheless, the trend in all cases was reproducible, and the results were generally consistent in terms of expected weight losses (e.g., for imidization).

RESULTS AND DISCUSSION

Hollow MPs were made using solvent-extraction processing techniques both in the air gap and extraction column. First, heptane as the core material and PAA solution as the sheath material were extruded through the dual-layer spinneret into the air gap and then into the solvent extraction column.

During fall through the air gap, liquid drops lose a small amount of NMP, thereby driving the outer surface composition toward the vitrification and formation of a thin skin layer.[11] Once the liquid drop enters the solvent-extraction column at elevated temperatures, a rapid NMP extraction occurs due to high solubility of NMP in PPG. The outflow of the solvent drives the composition of the region below the skin layer towards vitrification, thereby increasing the wall thickness and its modulus. The temperature profile along the extraction column was controlled in such a way to cause the MP to enter the hot region after the wall thickness grows sufficiently to trap the internal pressure generated by the vaporized heptane without failing. Vaporized heptane helps to maintain the spherical shape of the MP
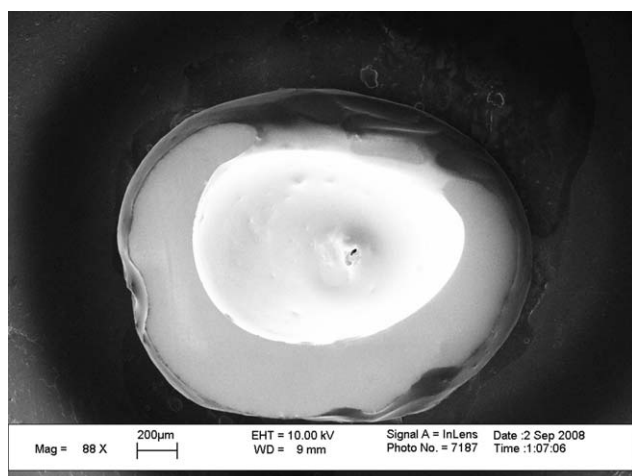
Figure 7 SEM image of nonimidized spherical MP with a dense wall fabricated with 20 wt % PAA.

while allowing further NMP extraction. First-generation MPs were kept in hot PPG for about 30 min and later stored in PPG at room temperature. The final wall thickness of these nonimidized first-generation MPs was about 300 µm as shown in the SEM image displayed in Figure 7. It is significant, however, that the porous form was eliminated in this generation, as opposed to that displayed Figure 1.

First-generation MP particle fabrication was carried out using original 20 wt % PAA (50 Poise at 25°C) as the sheath material. To reduce the wall thickness, diluted 1000 Poise PAA was used as the sheath material while lowering the fabrication temperature to maintain the required fluidic properties such as viscosity. In this series of experiments, the original PAA solution was diluted with NMP at room temperature to obtain the desired concentrations. Corresponding wall thicknesses were measured using SEM images of bisected nonimidized MPs. With the reduction of PAA concentration in
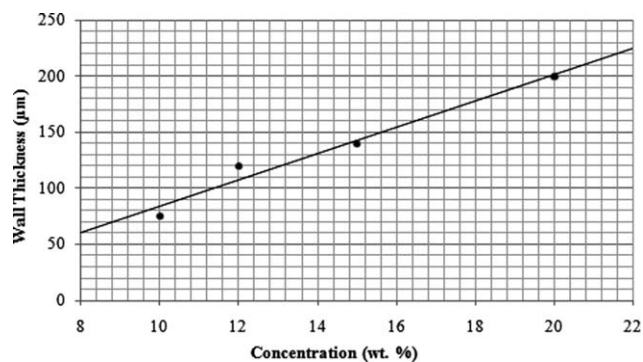

Figure 8 Wall thickness of MPs versus polyamic acid concentration in NMP. Solid line is regression line ($t = 11.7C - 33.5$).

NMP, it was observed that wall thickness decreases in a linear fashion as shown in Figure 8. The calculated wall thickness based on the amount of PAA present in the original liquid drops is in good agreement with these measured values.

With the reduction of the amount of polymeric materials in MPs, the observed buoyancy effects were substantially changed. These observed changes were effectively exploited for efficient self-removal of MPs prepared with 10 wt % PAA and will be discussed in detail in the following sections. Optical images of MPs prepared with 10 wt % PAA are shown in Figure 9 before and after imidization.

MPs prepared with low concentrations of polymer material in NMP show distinct buoyancy effects. With 10 wt % PAA, all earlier observations made with MP fabrications are valid up to the point where MP reaches the temperature zone where some heptane evaporates to fill the space inside the MP as illustrated in Figure 6. As explained earlier, the volatile material is not soluble in the sheath, and so the externally vitrified layer will trap the evaporated vapor reducing effective density of the MP while
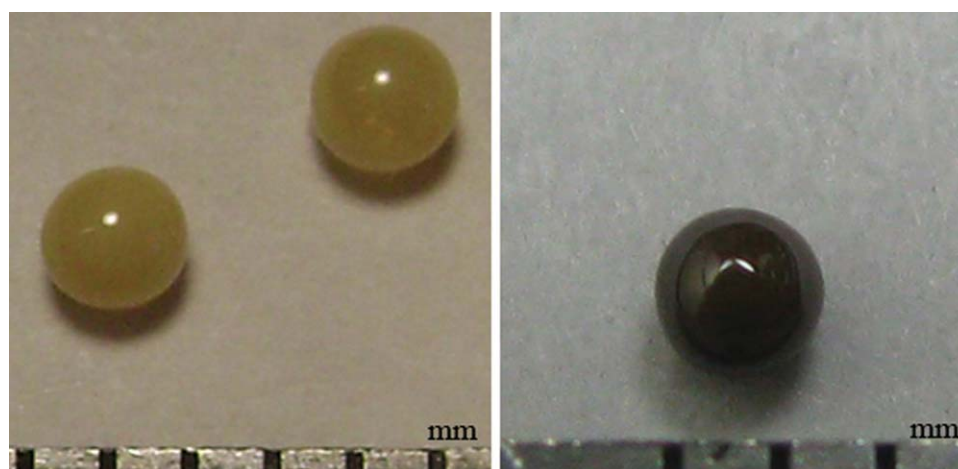
Figure 9 Optical images of nonimidized (left) and imidized (right) MPs fabricated with 10 wt % PAA solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
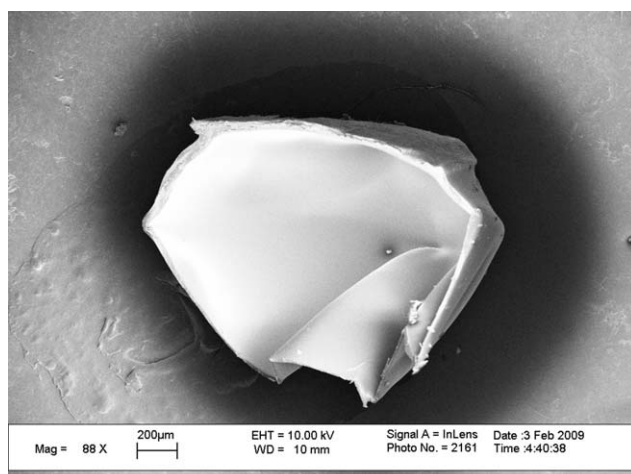
Figure 10 SEM image of bisected, imidized MP. The original diameter before bisection and the induced distortions was 1.5 mm.

holding the spherical shape of the MP. However, because these MPs have less polymer material in the wall (and, therefore, lower overall density), the buoyancy effect of PPG is strong enough to force low density MPs to move up the column for collection at the PPG surface with a plastic pipette. Collected MPs were immediately transferred to a vacuum oven at 100°C. After several minutes, clear visible nuclei were formed at the center of MPs under vacuum (49 Torr) due to heptane vaporization. A SEM image of imidized, bisected MP is shown in Figure 10. With the thinner wall, some distortion in the particle shape was inevitable during bisection, as can be seen in the figure.

The expected wall thickness for these MPs was around 75 μm based on no volume expansion relative to the as extruded central core containing heptane (see Fig. 8). However, the measured wall thickness using SEM images is actually about 45 μm. We believe that, with the reduction of polymer concentration, the thickness of the wall decreased, thereby facilitating more expansion or "puffing" of the particle under vacuum at 100°C, further reducing the wall thickness. Therefore, the sharp decrease in wall thickness can be attributed to the extra volume expansion of the MP at 100°C under vacuum, and this measured value is in good agreement with calculated wall thickness based on the original amount of polymer material. Furthermore, measured wall thickness and diameter values of MPs were used to calculate the geometric compression ratio of fabricated MPs, and it was found that the geometric compression ratio of fabricated MPs is about 6.0, exceeding the minimum targeted value of 3.0. Therefore, these MPs enable one to change the density of fluids in a wider range than expected or produce low density composite materials with higher compression ratios.

The original liquid particle weight was 4.63 ± 0.005 mg including heptane (average weight of 10 liquid drops). After 24 h in vacuum, the MP weight was reduced to 0.668 mg, which corresponds to 95% removal of NMP. Because a 10 wt % PAA solution was used to fabricate these MPs, the expected MP weight after imidization was about 0.421 mg after correcting for heptane content. To confirm these results further, TGA analysis was carried out on MPs. The expected value for the final weight of the MP after imidization is the original polymer weight (10% of 4.63 mg) corrected for the 9% weight loss during imidization. The measured final weight of imidized MP was 0.416 mg, which is very close to the expected value of 0.421 mg after imidization.

Different techniques have been developed for the fabrication of polyimide forms over the decades; however, little attention has been paid to the manufacture of hollow polymer microspheres.[17,18] There are few reported techniques for the fabrication of microspheres such as vapor deposition polymerization, electrohydrodynamic atomization, and thermal treatment of polymer resin mixed with a blowing agent.[18–20] Both former techniques yielded microspheres with highly defective walls.[18,19] Therefore, those techniques cannot be used to fabricate MPs, which can retain high-internal gas pressure for extended period of time. In the latter technique, powdered forms of poly(amicacid) precursors were considered as the starting materials by other researchers due to primarily ease of processing.[20–22] However, the technique is less productive for the fabrication of MPs as explained below. Our work involved the fabrication of polyimide hollow MPs with targeted structural properties such as highly impermeable dense wall, controlled wall thickness using a dual layer spinneret. As a result, the fabrication technique and the properties of MPs discussed here are quite novel compared to the work noted in earlier reports. For example, the starting materials for this work were selected in such a way to avoid any chemical or physical mixing during fabrication and were kept in physically separate syringe pumps and injected directly to respective annulus of the spinneret to form the liquid drops. As a result, every liquid drop has almost identical weight, shape, and composition yielding MPs with a very narrow size distribution. Furthermore, it enables one to control the diameter of MPs by changing the polymer solution flow rate or coaxial gas flow rate. For example, larger flow rates of coaxial gas enabled smaller droplets. Also, wall thickness can be controlled by changing the concentration of the polymer solution.

Earlier researchers used a dried solid containing PAA and tetrahydrofuran as the starting material.

This earlier technique involved crushing of the solid followed by sieving to obtain different particle sizes ranging from 75 to 300 μm.[21,22] From the experimental discussion of published data, it is evident that small solvent-saturated particles containing "macro void" were heated slowly enough to allow them to nucleate into a multiwall foam, whose internal walls collapse to leave hollow microspheres. The technique has limited or no control over fabricating microspheres with targeted structural properties such as wall thickness and diameter. Another major disadvantage of this technique is that individual particles should have a locked single macroscopic void to form a hollow sphere upon heating. This lowers the potential number of particles available to produce hollow microspheres. Therefore, the earlier technique cannot be considered as efficient to produce MPs with targeted properties in industrial scale. On the other hand, our fabrication technique enables hollow MPs from each liquid drop, which is formed at the tip of the spinneret annulus. However, due to the slow production rate that takes place one MP at a time and involvement of precisely controlled multiple steps, the cost of production of MPs with this technique may be higher compared to other techniques.

Also, fabrication of defect free MPs is extremely important for high pressure applications. Our technique puts measured amount of hexane at the core of the liquid drop using a core annulus during liquid drop formation, whereby effectively avoiding sheath and core materials. As a result, the technique enables to produce spherical smooth physically separate individual hollow MPs with defect free wall. In other techniques, blowing agent is mixed with the sheath material causing the formation of defective wall.[21,22] Another advantage of the technique is that application of noninvasive nonsolvent extraction column of PPG enabled formation of a dense wall. As a result, the MPs demonstrated gas transport properties similar to that of dense films. So, by controlling the polymer concentration, MPs with controlled wall thickness, hence targeted transport properties can be achieved.

CONCLUSION

We have demonstrated that hollow polymeric spheres with targeted geometric properties can be produced by a combination of nonsolvent-induced phase separation and solvent extraction in a fabrication system using a dual layer spinneret. Defect-free hollow-polymer MPs of 0.15-cm diameter were fabricated successfully with wall thickness of 45 μm, thus yielding a geometric compression ratio of about 6.

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