Droplet synthesis of well-defined block copolymers using solvent-resistant microfluidic device†

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Well-defined diblock copolymers were synthesized via an exothermic RAFT route by a droplet microfluidic process using a solvent-resistant and thermally stable fluoropolymer microreactor fabricated by a non-lithographic embedded template method. The resulting polymers were compared to products obtained from continuous flow capillary reactor and conventional bulk synthesis. The droplet based microreactor demonstrated superior molecular weight distribution control by synthesizing a higher molecular weight product with higher conversion and narrow polydispersity in a much shorter reaction time. The high quality of the as-synthesized block copolymer PMMA-b-PS led to a generation of micelles with a narrow size distribution that could be used as a template for well-ordered mesoporous silica with regular frameworks and high surface areas.

Introduction

The advent of new techniques, such as reversible addition fragmentation chain transfer (RAFT) polymerization, has revolutionized traditional free radical polymerization.1,2 RAFT polymerization with thiocarbonylthio compounds as reversible chain transfer agents allows better control of the macromolecular architecture and molecular weight of organic polymers than traditional processes. The particular advantages of this process lie in its flexible reaction conditions and the wide range of organic reactants possible.1,3 However, precise temperature control is essential for carrying out free radical copolymerization in a highly controlled manner, because free radical polymerization reactions are normally highly exothermic. Therefore, copolymerization reactions in conventional macroscale bath reactors often suffer from inefficient heat removal and an inhomogeneous reactor temperature, which results in inferior molecular weight distribution control.4

Recently, chemical processes using microreactors4–7 have attracted significant interest because they are expected to make innovative and revolutionary changes for chemical synthesis owing to their advantages such as effective mass transfer and heat transfer, rapid mixing and precise residence time control.4,8 Among these inherent advantages, efficient heat transfer appears to be one of the most important features for free radical copolymerization. Generally, the amount of heat generated in polymerization increases in proportion to the reactor volume; the heat removal capacity, decreasing with increased volume of bulk reactor, becomes a limiting factor. Therefore, the advantage of copolymerization in microreactors is obvious.4,5 In addition, continuous flow processes involving microreactors have been used in a range of polymer syntheses.9,10 These methods intrinsically offer the chance to produce high quality block copolymers, which has been attempted by connecting two capillary microreactor systems in series.11 With a complicated system composed of stainless capillary tubes and sophisticated micromixers, however, the obtained block copolymer had a broad polydispersity (>1.4) and not able to be used for further application. Very recently, droplet syntheses have been shown to offer superior mass transport due to the better mixing effect by chaotic advection on the nanolitre-scale. The enhanced homogeneity of the reaction media resulted in higher selectivity, as demonstrated in the syntheses of polymer beads and inorganic nanoparticles.12–18 In this regard, we hypothesized that droplet synthesis may further facilitate heat transfer and mixing between the reactants for radical polymerization. To date, there have been no reports on polymer syntheses from monomers in a droplet-based microreactor.

This paper reports the first demonstration of a droplet-based microfluidic synthesis for well controlled copolymerization of a solution phase through exothermic RAFT process. For comparison, syntheses were also carried out using capillary reactor and bulk synthesis methods. The assembly type microfluidic system was composed of a solvent resistant and thermally stable fluoropolymer (FP) lab-on-a-chip part for droplet generation and merging operation, and a capillary perfluoroalkoxyalkane tube (PFA, 30–120 cm, i.d. 508 µm) part for the extended reaction period at elevated temperatures. This simple and cost-effective FP device does not require any special and expensive photolithographic tools to fabricate with varying channel dimensions and thus it can be executed in a standard laboratory with minimal facilities. The droplet based microfluidic approach successfully produced well controlled diblock copolymers within a short reaction time with higher conversion and lower polydispersity than the alternative methods. Furthermore, application of the as-synthesized diblock copolymer for generation of spherical micelles with a homogenous size

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distribution created a template for well-ordered mesoporous silica with regular frameworks and high surface area, thus demonstrating the high quality of the block copolymer with superior molecular weight distribution control.

Materials and methods
Fabrication of microfluidic device and the solvent resistance

Solvent-resistant and thermally stable fluoropolymer (FP) microfluidic devices with varying channel sizes were fabricated using low molecular weight perfluoropolyether (low MW PFPE).19 The devices were made using a modified scaffold method without use of a photolithography master, as developed by our own group (Fig. 1).20 The template frameworks were assembled using commercially available tubes with different sizes and a metal bar. All the tubes were purchased from Upchurch Scientific. First, the perfluoroalkoxyalkane (PFA) tubing (o.d. ~1.5 mm, i.d. ~508 μm) was bound to the metal bar (Fig. 1(A)) to make a template to produce the PDMS mold. After curing the PDMS, the devices were cut carefully and the template tubing, metal bar were simply pulled out from the polymer matrix leaving the PDMS mold (Fig. 1(B)). Fig. 1(C) shows the scaffold made by connecting the PFA tubing with both ends of polyetherketone (PEEK) tubing with an outer diameter (o.d.) of ~510 μm. To create the perpendicular side channels for the injection, another PEEK tube (o.d. 360 μm, i.d. 100 μm or 50 μm) was glued with horizontal PEEK tubing. This scaffold was then placed on the PDMS mold, and a mixture of a pre-polymer of low MW PFPE and 1% 2-hydroxyl-2-methyl-propiophenone (photo-initiator, Aldrich, St. Louis, MO) was then poured over the scaffold and cured photo-chemically for 10 min. Finally, the template tubing was simply pulled out from the polymer matrix and the PDMS mold leaving the solvent-resistant fluoropolymer channel structures behind (Fig. 1(D)) within a short time and with minimal fabrication facilities.

To measure the solvent resistance, the FP microchannels were filled with different organic solvents, such as THF, n-hexane, chloroform, acetone, DMF, acetonitrile, DMSO, benzene, toluene, as well as bases and acids, and kept for several hours at 80 °C. Subsequently, the surface of the channel was checked and the degree of swelling of the FP microfluidic channels was calculated while the channels were in contact with various solvents based on the change in weight caused by absorption.

Synthesis of diblock copolymers

In this paper, two kinds of block copolymer PMMA-b-PS and PMA-b-PS were synthesized using the solvent-resistant microreactor. We assembled two microfluidic devices for continuous two steps copolymerization in the droplet-based microreactor. For PMMA-b-PS synthesis, the first block of copolymer, PMMA, was synthesized from methyl methacrylate (MMA), 2,2-azobis-isobutylronitrile (AIBN) initiator and the RAFT agent (pyrrole-1-carbodithioic acid benzyl ester, BPCD). As shown in Fig. 2 and Movie S1 in the ESI,† a monomer (neat, 0.02 mol, flow rate 1.75–17.5 μL min⁻¹) and a solution of AIBN + RAFT agent (0.1 mmol and 0.05 mmol, respectively) in toluene (flow rate 1.75–17.5 μL min⁻¹) were introduced separately into a double T-junction microfluidic device. The MMA monomer, and a solution of AIBN and the RAFT agent in toluene formed the dispersed phase. The continuous phase, fluorocarbon oil (FC oil, 3M) was injected from the horizontal inlet at a flow rate of Qc μL min⁻¹ (flow rate 7–70 μL min⁻¹) (Fig. 2). The MMA monomer
was forced into the continuous phase at the first T-junction of the channel at flow rate of Q_1 \mu \text{L min}^{-1} using a syringe pump (PHD 2000, Harvard Instruments) to initially form the first droplet. The solution of RAFT and AIBN in toluene was forced into a continuous phase at the second T-junction of the channel at a flow rate Q_2 \mu \text{L min}^{-1} to form the second droplet and merged immediately with the first droplet in the main horizontal channel to produce a larger droplet. Each resulting droplet contained the reaction mixture of monomer MMA, the initiator AIBN and RAFT agent, and is called a droplet microreactor. Each droplet reactor then flowed in the PFA tube (i.d. 508 \mu \text{m}), which was immersed in a silicon oil bath at 80 °C, with different delay loop lengths (30–120 cm) of the PFA tube. At the outlet of the first PFA tube, the resulting PMMA drop was continuously used as a macroinitiator to synthesize the PMMA-b-PS block copolymer through a reaction with the styrene monomer in the second step of a consecutive step-wise process. Similarly, the droplet of the mixed styrene monomer of a consecutive step-wise process. Similarly, the droplet of PMMA merged with the droplet of the mixed styrene monomer (neat, 0.02 mol) and AIBN initiator forced at flow rate of Q_1 \mu \text{L min}^{-1} (1.75–17.5 \mu \text{L min}^{-1}) in the microfluidic device and the resulting droplet flow in the PFA tube was maintained at 80 °C. The experiments were carried out at different flow rates of dispersed and continuous phases but the ratio of the flow rates between the dispersed and continuous phases was maintained at Q_1 : Q_2 : Q_3 : Q_4 = 1 : 1 : 1 : 4, which allowed easy control of the generation and merging of droplets. At the outlet of the PFA tube, the product was achieved by dilution in THF and precipitated by adding excess n-hexane.

In the case of synthesis of alternative block copolymer PMA-b-PS, the procedure is the same as for PMMA-b-PS except MA (methyl acrylate) is used as monomer. To compare with the droplet-based microreactor, continuous flow copolymerization in a capillary microreactor and bulk phase copolymerization were carried out (see Fig. S1, ESI†).

Applications of the synthesized PMMA-b-PS diblock copolymer

Firstly, PMMA-b-PS micelle nanoparticles were prepared as follows: 1.5 mg of as-synthesized PMMA-b-PS was dissolved in 0.5 mL toluene and then added to 3 mL of a mixed deionized water and ethanol solution under gentle stirring at room temperature. The solution was dialyzed directly against distilled water using a dialysis membrane (MWCO 1000 g mol\(^{-1}\)). The distilled water was exchanged every 3 h for 24 h in total to remove the organic solvent.\(^{26}\)

Secondly, ordered mesoporous silica was prepared from a mixture of diblock copolymer, 0.8 M HCl, H_2O and TEOS in a 1 : 24 : 4 : 5 weight ratio and 5% (w/w, compare to diblock copolymer) of pluronic F127 (BASF) surfactant as a structure-directing agent. The mixture was aged at 60 °C for 12 h and then kept at 95 °C for 24 h. Subsequently, the solid product was washed with deionized water and dried. To obtain the mesoporous silica materials, the samples were calcined at 550 °C in air for 6 h.\(^{12}\)

Characterization

\(^1\)H-nuclear magnetic resonance (NMR) was performed in CDCl\(_3\) on a Bruker DMX600 instrument with a 7788 Hz spectral width, a relaxation delay of 1.0 s, and a pulse width of 30°. The molecular weight distribution of the synthesized polymers was examined by gel permeation chromatography (GPC) using a Waters 515 HPLC isocratic pump equipped with a Waters 2414 Refractive Index detector and Waters styragel columns (HR 1, 2, 3, 4, 5E). THF (flow rate of 1.0 mL min\(^{-1}\)) was used as the solvent and polystyrene (Shodex standard) as a standard for universal calibration. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM 2100F, JEOL, Japan, operating at 200 kV. The scanning electron microscopy (SEM) was performed using a JSM-7000F, JEOL, Japan. The degree of polymerization was calculated from the NMR spectra using the signals of the vinyl group of the polymer and monomer. The particle size of the self-assembled nanoparticles in an aqueous medium was measured by dynamic light scattering (DLS) using a Part II laser particles analyzer (Photal Otsuka Electronic, Japan) at a concentration of 1 mg mL\(^{-1}\). The small-angle X-ray diffraction (SA-XRD) patterns were recorded on a MX Labo powder diffractometer using Cu-K\(_\alpha\) radiation (40 kV, 20 mA) at a scan rate of 1.0° min\(^{-1}\) over the range 0.5–7.0° (2θ). The pyrolyzed samples were crushed into fine particles and dispersed onto a thin holey-carbon support film. The surface area and N\(_2\) adsorption–desorption isotherms were measured at 77 K on a Micromeritics (ASAP 2010, USA) using the Brunauer–Emmett–Teller (BET) method.

Results and discussion

Fabrication and solvent resistance of FP microfluidic device

Fig. 1 shows a schematic diagram of the fabrication process, which was modified from the method developed by our own group. In this study, instead of the sophisticated masters fabricated by lithography techniques, a scaffold system composed of two tubings with different diameters was used, and could be performed in a standard laboratory with no special facilities. The viscous perfluoropolyether was poured into the framework, followed by photochemical curing for 10 min, as reported.\(^{20,27}\) The template was simply removed from the polymer matrix to obtain a flexible fluoropolymer (FP) microchannel with three different widths (Fig. 1(D)). The advantage of this method is the simple and cost-effective approach for the fabrication of a monolithic, microfluidic device with various channel dimensions through a single step using low surface energy templates that can be removed easily from the matrix. Moreover, it should be emphasized that two separate microfluidic devices can be readily connected by fixing the outlet ends of both channels with a piece of tube adaptor,\(^{21,22}\) which enables to instantly assemble the microfluidic system designed for specific use.

A FP microfluidic channel, which can resist most organic solvents, was used due to the easy swelling of PDMS in most organic solvents. To test the solvent resistance and thermal stability of the FP microchannel, the microchannel was filled with a range of solvents for several hours at elevated temperature 80 °C. There was no change in the channel diameter or defect formation on the channel surface caused by the solvents (see Fig. S2, ESI†). The swelling ratio was estimated based on the weight change caused by solvent absorption. The FP microchannel showed excellent resistance at 80 °C against strongly
swelling solvents, such as including toluene, benzene, THF, hexane and chloroform, as well as acids but not for alkali conditions.29

Copolymerizations in droplet based microreactor

The ‘double T-junction’ and single ‘T-junction’ geometry of microfluidic devices were used in this study. Fluorocarbon oil was used as a continuous phase because it wets the FP channel walls preferentially, and was immiscible with disperse phases. The assembly type of microfluidic system was designed using a combination of a lab-on-a-chip part to generate and merge the droplet and a capillary PFA tube (30–120 cm, i.d. 508 μm) to control the reaction time at elevated temperatures for consecutive step-wise process. The block copolymerization in the droplet-based microreactor was compared with the copolymerization in the bulk reaction and the continuous flow capillary reactor composed of micromixer and a stainless steel capillary. During operation within the above constraints of channel geometry, fluids and flow rates, we observed that the flow ratio of the oil to disperse phase influence the control of generation and merging of droplet.18 When the ratio was either Qc : Q1 : Q2 > 4 : 1 : 1 or Qc : Q1 : Q2 < 4 : 1 : 1, it was problematic with non-uniform merging of droplet or large size of droplet, leading to inhomogeneous polymerization with low conversion and high PDI. Therefore, we maintained Qc : Q1 : Q2 : Q3 = 4 : 1 : 1 : 1 for our synthesis experiments, which allowed easy control of the generation and merging of droplets and easy control of the flow of droplets in a stable, non-coalescing train downstream.

Firstly, homopolymers PMMA and PMA were synthesized from two different monomers using identical RAFT agent by a droplet microreactor, and compared to the products obtained from continuous flow capillary reactor and conventional bulk synthesis, as summarized in Table 1. Both polymerizations in a droplet-based microreactor showed the highest molecular weight and lowest PDI; the synthetic performance in the capillary reactor was also better than that in the bulk reaction. This feature is attributed to the confinement of the mixture of reactants in the droplet to the one nanolitre-scale, which is much smaller than that in a capillary microreactor, and the droplet is kept moving along the 60 cm long delay loop. In particular, chaotic advection within the droplet presumably exhibited a superior mixing effect to the micromixer in a capillary reactor, which reduces the layer thickness between the laminar fluids, as reported elsewhere.11,28 This may facilitate efficient heat transfer during exothermic polymerization and efficient mixing between the monomer, RAFT agent and initiator, resulting in the rapid consumption of the initial RAFT agent and fast equilibration of the dormant and active species.6,5 Therefore, fast polymerizations in a droplet-based microreactor produced higher molecular weight with a narrower dispersion. Typically, after a 10 min reaction time, the conversion of both MMA and MA monomers was almost complete (~99%), which is much faster than the capillary and bulk reaction.4,11 Moreover, it was found that PMA showed a higher molecular weight and lower PDI than PMMA in all three synthetic routes even under the use of identical RAFT agent (pyrrole-1-carboxylic acid benzyl ester, BPCD). It is believed that BPCD, with its anionic properties, is a more active RAFT agent for polymerization of MA monomer than MMA due to a higher transfer coefficient, which leads to a faster consumption rate of the transfer agent, resulting in a narrow polydispersity as reported in reference.3

Table 1 Comparative results of PMMA and PMA homopolymers synthesized by different reaction processes

<table>
<thead>
<tr>
<th>Polymer product</th>
<th>Reaction time/min</th>
<th>Flow rate, Qc μL min⁻¹</th>
<th>η a (%)</th>
<th>MW</th>
<th>PDI</th>
<th>Flow rate, Qc μL min⁻¹</th>
<th>η a (%)</th>
<th>MW</th>
<th>PDI</th>
<th>Bulk process for 16 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA 10</td>
<td>7</td>
<td>99.0</td>
<td>11445</td>
<td>1.22</td>
<td>19.7</td>
<td>89.1</td>
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<td>7542</td>
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<tr>
<td>5</td>
<td>14</td>
<td>97.5</td>
<td>9335</td>
<td>1.25</td>
<td>39.4</td>
<td>85.8</td>
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<tr>
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<td>19.7</td>
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<td>12216</td>
<td>1.17</td>
<td>73.8%</td>
<td></td>
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<tr>
<td>5</td>
<td>14</td>
<td>98.1</td>
<td>12121</td>
<td>1.15</td>
<td>39.4</td>
<td>86.6</td>
<td>10254</td>
<td>1.17</td>
<td></td>
<td>PDI: 1.18</td>
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Table 2 Comparative results of PMMA-b-PS and PMA-b-PS block copolymers synthesized by different reaction processes

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Total reaction time, min</th>
<th>Flow rate, Qc μL min⁻¹</th>
<th>η a (%)</th>
<th>MW</th>
<th>PDI</th>
<th>Flow rate, Qc μL min⁻¹</th>
<th>η a (%)</th>
<th>MW</th>
<th>PDI</th>
<th>Bulk process for 16 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-b-PS 20 (10)</td>
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<td>94.9</td>
<td>28462</td>
<td>1.20</td>
<td>19.7</td>
<td>89.1</td>
<td>17686</td>
<td>1.31</td>
<td>63.6%</td>
<td></td>
</tr>
<tr>
<td>15 (5)</td>
<td>14</td>
<td>93.5</td>
<td>22328</td>
<td>1.25</td>
<td>39.4</td>
<td>85.6</td>
<td>13953</td>
<td>1.34</td>
<td>12895</td>
<td>PDI: 1.40</td>
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<tr>
<td>11 (1)</td>
<td>70</td>
<td>85</td>
<td>19796</td>
<td>1.27</td>
<td>197</td>
<td>55.6</td>
<td>12174</td>
<td>1.35</td>
<td>14548</td>
<td></td>
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<tr>
<td>PMA-b-PS 20 (10)</td>
<td>7</td>
<td>95.2</td>
<td>25546</td>
<td>1.16</td>
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<td>19967</td>
<td>1.19</td>
<td>72.7%</td>
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<tr>
<td>15 (5)</td>
<td>14</td>
<td>94.0</td>
<td>22854</td>
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Table 2 Comparative results of PMMA-b-PS and PMA-b-PS block copolymers synthesized by different reaction processes

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Total reaction time, min</th>
<th>Flow rate, Qc μL min⁻¹</th>
<th>η a (%)</th>
<th>MW</th>
<th>PDI</th>
<th>Flow rate, Qc μL min⁻¹</th>
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<td>63.6%</td>
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<td>14</td>
<td>93.5</td>
<td>22328</td>
<td>1.25</td>
<td>39.4</td>
<td>85.6</td>
<td>13953</td>
<td>1.34</td>
<td>12895</td>
<td>PDI: 1.40</td>
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<td>55.6</td>
<td>12174</td>
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a Conversion of block copolymer syntheses, measured by 1H-NMR, () reaction time taken for synthesis of PMMA, PMA block.
Consequently the PMMA and PMA blocks obtained from a 10 min reaction were used for synthesis of block copolymers. As shown in Table 2, the synthetic performance of the obtained PMMA-b-PS and PMA-b-PS block copolymers was generally consistent with results of the homopolymers, which the highest conversion and molecular weight as well as the lowest PDI values were achieved from a droplet microreactor in comparison to the capillary and bulk reaction. Typically, the use of a PMMA block with high MW (11445) and low PDI (1.22) produced the highest quality PMMA-b-PS diblock copolymer with MW 28462 and PDI 1.20 by a droplet microreactor, presumably due to the enhanced homogeneous temperature distribution without hot spots and better homogenization of reactants in the nanolitre-scale droplet. Hence, it can be concluded that the droplet-based microreactor is a reliable, efficient method for synthesizing a better-defined block copolymer than the capillary or bulk reactions. 

In addition, comparative GPC curves of the PMMA-b-PS block copolymers obtained from the three synthetic routes assuredly demonstrated that the block copolymer obtained from the droplet-based microreactor showed a higher molecular weight with narrower molecular weight distribution compared to the other synthetic routes (Fig. 3). The shoulder in the plot for the capillary microreactor route was attributed to the presence of dead polymeric chains with high molecular weight that were formed via termination reactions by combination. It was reported that the change in flow rate affects not only the residence time but also other factors, such as the degree of mixing and nature of flow. We investigated the effect of flow rate on the conversion of copolymerization in the droplet microreactor with different PFA tube lengths (30–120 cm) to keep the same residence time under a fixed flow rate ratio Qc : Q1 : Q2 : Q3 = 4 : 1 : 1 : 1 between the dispersed and continuous phases. As shown in Fig. 4, for both cases of 15 and 20 min total reaction time, a higher Qc caused a higher level of copolymerization. The enhanced chaotic advection at higher flow rate promoted the mixing efficiency inside the droplet, resulting in a fast reaction and high conversion. In addition, longer residence times (20 min) produced higher conversion than shorter reaction time (15 min) as expected. However, the flow rates Qc was compromised to avoid negative effects such as broadened PDI, presumably due to cross-linking between confined diblock copolymer chains.

Applications of the synthesized PMMA-b-PS diblock copolymer

In order to demonstrate the high quality of well-defined block copolymers, the as-synthesized PMMA-b-PS block copolymer (MW: 28462 PDI: 1.20) from the droplet microreactor was used to generate micelles in an ethanol–water mixture. The self-assembly of well-defined block copolymers can be used to construct a range of nanostructures, including spherical micelles, worm-like micelles and vesicles, depending on the block lengths and ratios as well as the chemical composition. The self-assembly process can be controlled further by selecting a non-solvent and/or using solvent mixtures. Fig. 5 shows the presence of individual spherical micelles, indicating that the clustering is due to solvent evaporation. This evaporation also causes the collapse of the PMMA shell in the dry state, as illustrated by the radius of the PS core determined by TEM and SEM. The particle size distribution of the nanoparticles showed a narrow size distribution from 195 to 235 nm (see Fig. S3, ESI†), which is

![Fig. 3 Typical GPC curves of PMMA-b-PS obtained by (a) bulk reaction for 16 h; (b) capillary microreactor for 20 min. and (c) droplet-based microreactor for 20 min.](image)

![Fig. 4 Conversion plot, ηPMMA-b-PS vs. flow rate of the continuous phase, Qc, at an identical reaction time of PMMA-b-PS synthesis: (■) 20 min and (●) 15 min total reaction time in a droplet-based microreactor.](image)

![Fig. 5 (Left) SEM image of PMMA-b-PS (MW: 28462 PDI: 1.20) micelles obtained from the droplet microreactor, the scale bar is 500 nm. (Right) TEM image of PMMA-b-PS (MW: 28462 PDI: 1.20) micelles, the scale bar is 300 nm, at a 0.3 wt% concentration in an ethanol–water 80/20 wt% mixture.](image)
consistent with that observed in SEM and TEM images. Spherical micelles were also observed from polymers formed from the capillary microreactor and bulk phase polymerization routes. However, the size distribution of micelles was broader: 175–250 nm for the copolymer by capillary microreactor and 150–240 nm for the copolymer by bulk polymerization. This shows that the greater uniformity of spherical nanoparticles is due to the higher quality of PMMA-\(b\)-PS obtained from the droplet-based microreactor.

The PMMA-\(b\)-PS diblock copolymer (MW: 28462 PDI: 1.20) synthesized by a droplet microreactor was also used as a template for meso-structured silica in the presence of a F127 surfactant, as a structure-directing agent. The mesoporous silica materials calcined at 550 °C in air showed large domains of highly ordered hexagonally arranged structures with a consistent pore diameter of \(\sim 4.0\) nm, as shown by the TEM image in Fig. 6(A). Furthermore, small-angle X-ray diffraction patterns (SA-XRD) (Fig. 6(B)) of the mesoporous silica film showed a sharp peak at \(2\theta = 0.58\), and 1.04 indicating that a hexagonally packed cylindrical morphology had formed with a \(d\) spacing of 16.1 nm. This result is in excellent agreement with the results predicted from the phase diagram of PMMA-\(b\)-PS, as calculated by Leibler30 and Matsen.31

Brunauer–Emmett–Teller (BET) analysis confirmed the presence of a highly mesoporous structure with a pore volume close to 0.74 cm\(^3\) g\(^{-1}\), a high specific surface area of 822 m\(^2\) g\(^{-1}\), and a narrow pore size distribution of 3.9 nm (Fig. 6(C)), as determined by the BJH desorption pore distribution method, which was in good agreement with the TEM and SA-XRD results. The mesoporous silica with an open and continuous framework is comparable to the surface area and pore volume of the products prepared by other routes in the literature.32 However, diblock copolymers from both the capillary reactor and bulk phase reactor could not form an well-ordered silica structure (see Fig. S4, ESI\(^+\)) because the lower molecular weight and higher PDI could not meet the requirements for the self-assembly of uniform mesostructures.33 The observed results clearly show that a well defined PMMA-\(b\)-PS diblock copolymer produced using a droplet microreactor is a reliable route for preparing high quality block copolymers.

**Conclusion**

This work demonstrated the usefulness of an embedded template method to fabricate a monolithic solvent-resistant and thermally stable FP microfluidic device within a short timespan with minimal or no fabrication facilities. Further, the assembled droplet-based microreactor composed of a lab-on-a-chip type drop generator and capillary tube was for the first time used to synthesize polymers from monomers. In particular, PMMA-\(b\)-PS and PMA-\(b\)-PS diblock copolymers were synthesized by a consecutive step-wise process including the exothermic RAFT route to produce a well-defined product with higher conversion and narrower polydispersity in very short reaction time, compared to the products from a capillary or batch reactor. Moreover, in order to demonstrate the high quality of the as-synthesized diblock copolymer, micelles were generated in a water and alcohol mixture to form highly uniform spherical nanoparticles. Ordered mesoporous silica was then prepared using the block copolymer as a template. It is plausible that an attempt beyond this preliminary proof-of-concept result would be aimed at synthesizing alternative block copolymers with well-controlled molecular weight distributions by optimizing factors in a droplet-based microreactor.

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**Notes and references**