Droplet Synthesis of Well-defined Block Copolymers Using Solvent-Resistant Microfluidic Device†

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Experimental

Materials and Chemicals

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques. The styrene, methyl methacrylate and methyl acrylate monomer were purchased from Aldrich Co. Ltd. and purified by distillation over CaH₂ under a reduced pressure. 2,2’-azobis-isobutyrylitrile (AIBN) was obtained from ACROS Organic and used as received. The RAFT agent, Pyrrole-1-carbodithioic acid benzyl ester (BPCD), was synthesized using the method described elsewhere [1]. Continuous flow copolymerization was carried out in a capillary microreactor with micromixers (MiChS-α mixer, MiChS Co., Ltd. Japan) connected to a stainless-steel tube reactor.

Synthesis of diblock copolymers in capillary microreactor and batch reactor

As shown in Figure S1, the MMA monomer (neat, 0.02 mol, flow rate 19.7-197 μL/min) and a solution of AIBN and RAFT (0.1 mmol & 0.05 mmol, respectively) agent in toluene (flow rate 19.7-197 μL/min) were introduced into micromixer M1 (MiChS-α mixer, MiChS Co., Ltd. Japan, stainless, channel size 200 μm). The resulting solution was passed through capillary microreactor R1 (stainless tube, i.d. 1000 μm, 50 cm) at 80°C (oil bath) to achieve the first block of copolymer, PMMA. The solution of PMMA and styrene monomer (neat, 0.02 mole, flow rate 19.7-197 μL/min) were introduced to micromixer M2 (MiChS-α mixer, MiChS Co., Ltd. Japan, stainless, channel size 200 μm) and the resulting solution was passed through capillary microreactor R2 (stainless tube, i.d. 1000 μm, 50 cm) heated to 80°C (oil bath), where copolymerization occurred. At the outlet of the capillary microreactor, the product was achieved by dilution in THF and precipitated by adding excess n-hexane. In
addition, bulk phase copolymerization was carried out by mixing the MMA monomer (0.02 mol), AIBN (0.1 mmol), identical RAFT agent (0.05 mmol) as used for both microreactions and 3 ml toluene in a 50 mL Schlenk flask [1]. The reaction mixture was immersed in an oil bath at 80°C for 16 h. After PMMA was achieved, the styrene monomer (0.02 mol) was continuously added and reacted at 80°C for 16 h to form the PMMA-b-PS block copolymer. Finally, the resulting PMMA-b-PS block copolymer was purified and characterized by H1-NMR and GPC. In the case of synthesis of alternative block copolymer PMA-b-PS, the synthesis procedure is the same as for PMMA-b-PS except MA (methyl acrylate) as a monomer.

Reference

**Fig. S1.** (A) Capillary reactor system for the polymerization of PMMA-b-PS. M1, M2: micromixer; R1, R2: capillary reactors, (B) the image of micromixer.

**Fig. S2.** Optical images of FP microchannel: (A) initial and after (B) 6 h, (C) 12 h, and (D) 24 h filled with toluene (solvent of copolymerization) at 80 °C. The scale bar is 200 µm.
Fig. S3. Particle size distribution of PMMA-\textit{b}-PS micelles 0.3 wt% concentration in an ethanol–water 80/20 wt% mixture. Micelles from PMMA-\textit{b}-PS synthesized by (A) droplet-based microreactor, (B) capillary microreactor, and (C) bulk reaction.

Fig. S4. TEM images of mesoporous silica obtained from PMMA-\textit{b}-PS template synthesized by (A) capillary reactor and (B) bulk reaction. The scale bar is 40 nm.