

**Colloidal crystal of monodisperse fluoro-nanoparticles by aqueous polymerization-induced self-assembly**

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## Experimental section

### 1. Material

Poly(ethylene glycol) methyl ether (mPEG<sub>45</sub>-OH,  $M_n = 2000$  g/mol, J&K), randomly methylated- $\beta$ -cyclodextrin (MCD,  $M_n = 1206$  g/mol, D-chem), 2,2'-Azobis(2-methylpropionamide) dihydrochloride (VA-056; J&K), oxalyl chloride (Adamas), 4-dimethylaminopyridine (DMAP, Adamas), dicyclohexylcarbodiimide (DCC, Meryer), 2,3,4,5,6-pentafluorobenzyl bromide (Meryer), 2,3,4,5,6-pentafluorostyrene (PFS; Energy Chemical), methacrylic acid (Sigma-Aldrich) and 2,6-di-*tert*-butyl-4-methylphenol (Adamas) were used as received. Azobisisobutyronitrile (AIBN, TCI) was used after recrystallization. 2-Methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl] propanoic acid (TTC) and 4-cyano-4-pentanoic acid dithiobenzoate (CPADB) were synthesized according to the previously published procedures.<sup>1,2</sup>

### 2. Characterization

**2.1 <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR):** <sup>1</sup>H NMR spectra were recorded using both JEOL JNM-EA 400 spectrometer and JEOL JNM-ECZ400S spectrometer at 400 MHz (CDCl<sub>3</sub>, and D<sub>2</sub>O as solvent).

**2.2 <sup>19</sup>F Nuclear Magnetic Resonance (<sup>19</sup>F NMR):** <sup>19</sup>F NMR spectra were recorded using JEOL JNM-ECZ400S spectrometer at 376 MHz (CDCl<sub>3</sub> as solvent).

**2.3 Size-Exclusion Chromatography (SEC):** The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and polydispersity ( $D$ ) were characterized by a Waters 1515 Gel permeation chromatography (GPC) instrument, using THF with a flow rate of 1.0 mL/min as eluent at 35 °C. The samples of block copolymers were freeze-dried and dissolved in THF. A series of narrow distribution linear polystyrene ( $M_p$  from 580 to 2580000 g/mol) was used for calibration.

**2.4 Dynamic Light Scattering (DLS):** DLS measurements were recorded using Malvern Zetasizer Nano ZS90 at 25 °C with a He-Ne laser (633 nm), and the scattering light at 90° was detected. All the dispersions were diluted for the DLS measurements. All the DLS tests were repeated 3 times.

**2.5 Transmission Electron Microscope (TEM):** The morphologies of samples were characterized using Hitachi H-7650B transmission electron microscope at the accelerating voltage of 80 kV. The dispersions were dialysis against water for 3 days to remove MCD. Then the dispersions were all diluted. As a typical example of the sample preparation, the diluted dispersion (10  $\mu$ L) was dropped onto a carbon-coated copper grid. After 1 min, the excess dispersion was removed, and the sample onto the copper grid were dried at room temperature for 24 h.

**2.6 Scanning Electron Microscope (SEM):** The SEM images were collected using a Hitachi SU-8010 scanning electron microscope at the accelerating voltage of 10 kV. The dispersions were dialysis against water for 3 days to remove MCD. Then the dispersions were all diluted. The diluted dispersion was dropped onto a clean silicon wafer and dried at room temperature. The surfaces are sprayed platinum for 180 s.

### 3. Synthesis

#### 3.1 Synthesis of macro chain transfer agents

**a)** The synthesis of PEG<sub>45</sub>-TTC:<sup>3</sup> Oxalyl chloride (0.645 mL, 7.5 mmol), TTC (1.8 g, 5 mmol),

and dichloromethane (DCM, 25 mL) were added into a dry round-bottom flask under argon atmosphere. The reaction was stopped when the gas did not generate. The DCM and excess oxalyl chloride were removed via rotary evaporation. Then mPEG<sub>45</sub>-OH (2.5 g, 1.5 mmol) and DCM (25 mL) were added under argon atmosphere, and the mixture was stirred at room temperature for 24 h. After concentration, the mixture was precipitated in diethyl ether. The product was collected after filtration and dried in vacuum oven at room temperature.

**b)** The synthesis of PEG<sub>45</sub>-CPADB:<sup>4</sup> CPADB (2.79g, 10 mmol), mPEG<sub>45</sub>-OH (4.0 g, 2 mmol), DMAP (0.122 g, 1 mmol) and DCM (75 mL) were added into a dry round-bottom flask. Then the solution of DCC (2.472 g, 12 mmol) in DCM (30 mL) was dropwise added into the above mixture. The reaction was performed for 3 d at room temperature. After removing the salt, the product was precipitated in diethyl ether, collected by filtration, and dried in vacuum oven at room temperature.

### 3.2 Synthesis of PFBMA

The synthesis of PFBMA:<sup>5</sup> Anhydrous potassium carbonate (6.89 g, 0.05 mol), methacrylic acid (1.27 mL, 0.015 mol), 2,3,4,5,6-pentafluorobenzyl bromide (1.50 mL, 0.01 mol), acetone (64 mL) and the 2,6-di-*tert*-butyl-4-methylphenol (a few crystals) were added into a dry round-bottom flask. After refluxing for 3 h, the salt and excess solvent was removed by filtration and rotary evaporation, respectively. The residual mixture was then dissolved in diethyl ether and extracted with water, solution of sodium bicarbonate, and water again, in order. The organic phase was dried by magnesium sulfate overnight, and was filtered through basic aluminum oxide. The excess solvent was removed by rotary evaporation, and the product was stored at -20 °C.

### 3.3 Polymerization of PEG-*b*-PPFS

**a)** The aqueous polymerization of PEG-*b*-PPFS: In a typical experiment, PFS (0.194 g, 1 mmol), PEG<sub>45</sub>-TTC (23.6 mg, 0.01 mmol), MCD (3.62 g, 3 mmol), and VA-056 (0.84 mg, 0.003 mmol) were weighted into a certain amount of water (5.00 g, 5.00 mL) in a 25 mL Schlenk flask. After 30 min of deoxygenation by argon and stirring process, the polymerization was started at 60 °C. The polymerization was typically run for 18 h to achieve the quantitative monomer conversion. The samples were undergoing dialysis and freeze-dried, then were analysis by <sup>1</sup>H\ <sup>19</sup>F NMR spectroscopy and THF SEC. The feed of PFS was depend on the target degree of polymerization.

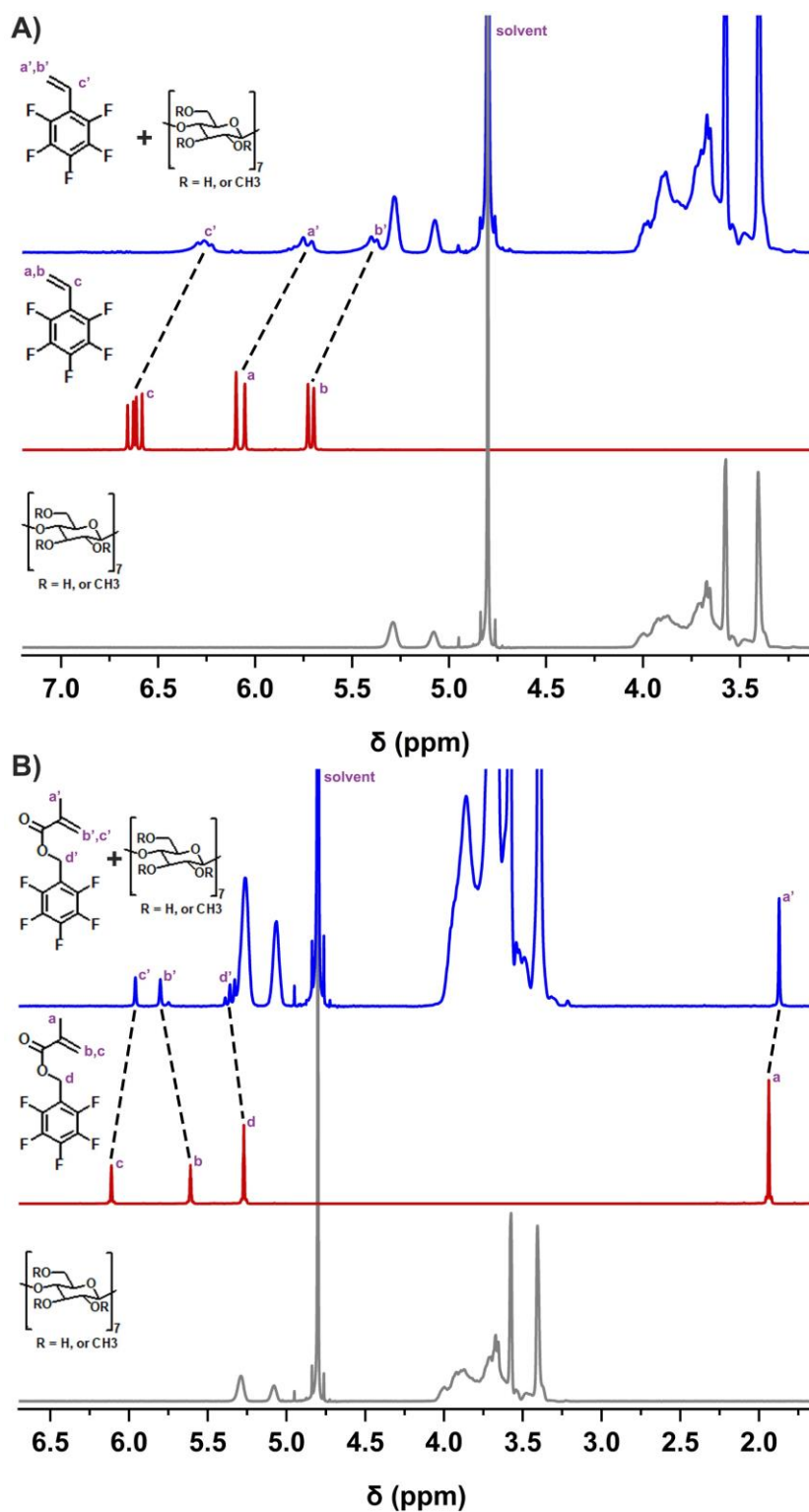
**b)** We also tried the polymerization of PEG-*b*-PPFS in 1,4-dioxane to prove the well RAFT control of PEG-TTC to PFS. In a typical experiment, PFS (1.94 g, 10 mmol), PEG<sub>45</sub>-TTC (0.236 g, 0.1 mmol), and AIBN (4.93 mg, 0.03 mmol) were weighted into a certain amount of 1,4-dioxane (2.1 mL, 2.18 g) in a 25 mL Schlenk flask. After 30 min of deoxygenation by argon and stirring process, the polymerization was started at 60 °C. The polymerization was typically run for 50 h to achieve the quantitative monomer conversion. The polymer was precipitated in water and then re-dissolved in 1,4-dioxane. Then product was precipitated in hexane and was collected for further characterization.

### 3.4 Polymerization of PEG-*b*-PPFBMA

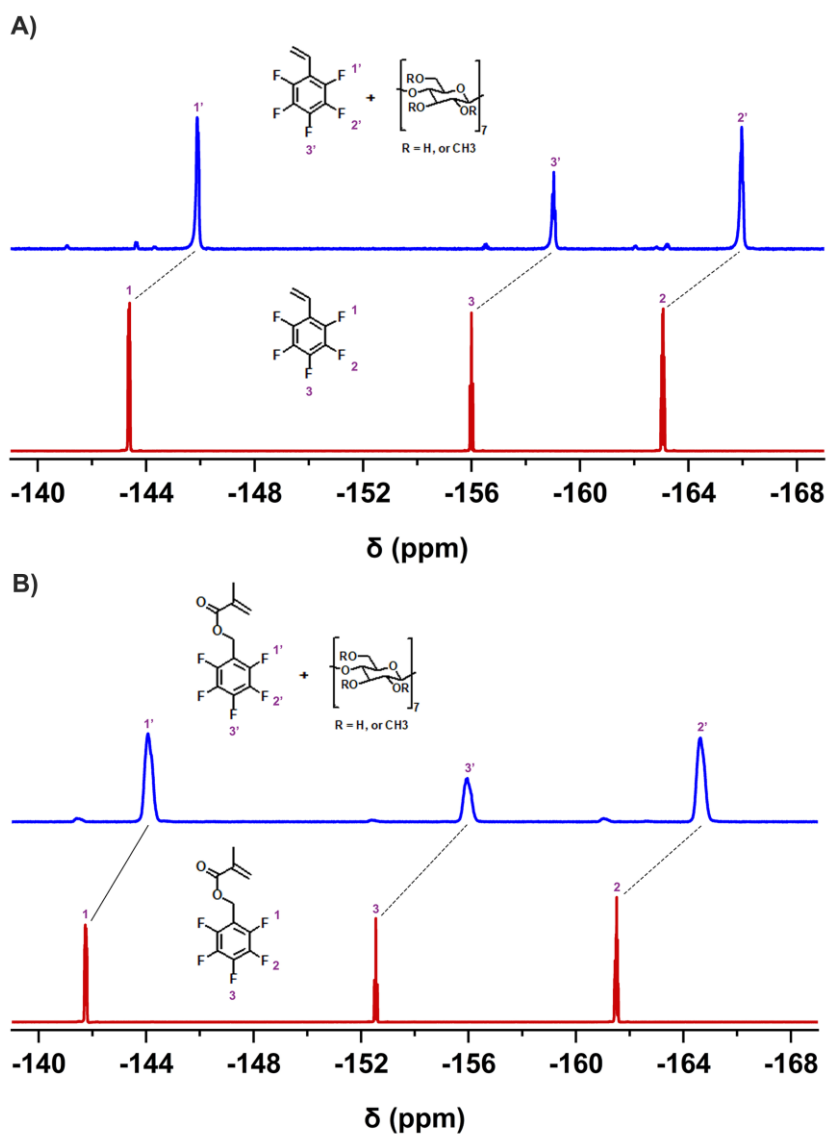
The polymerization of PEG-*b*-PPFS: In a typical experiment, PFBMA (0.266 g, 1 mmol), PEG<sub>45</sub>-CPADB (23.6 mg, 0.01 mmol), MCD (3.62 g, 3 mmol), and VA-056 (0.84 mg, 0.003 mmol) were weighted into a certain amount of water (5.00 g, 5.00 mL) in a 25 mL Schlenk

flask. After 30 min of deoxygenation by argon and stirring process, the polymerization was started at 60 °C. The polymerization was typically run for 18 h to achieve the quantitative monomer conversion. The samples were undergoing dialysis and freeze-dried, then were analysis by  $^1\text{H}/^{19}\text{F}$  NMR spectroscopy and THF SEC.

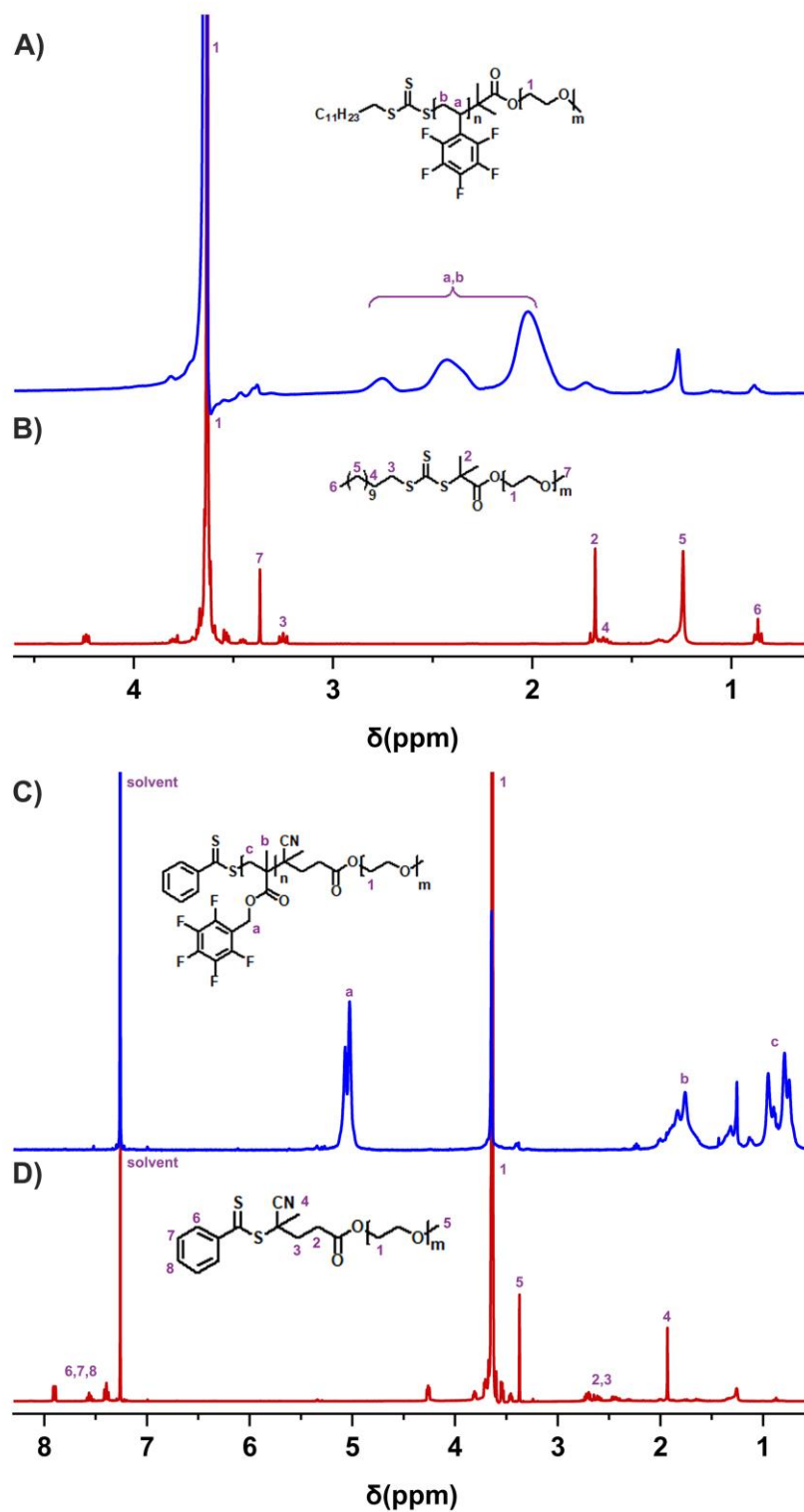
## Additional results



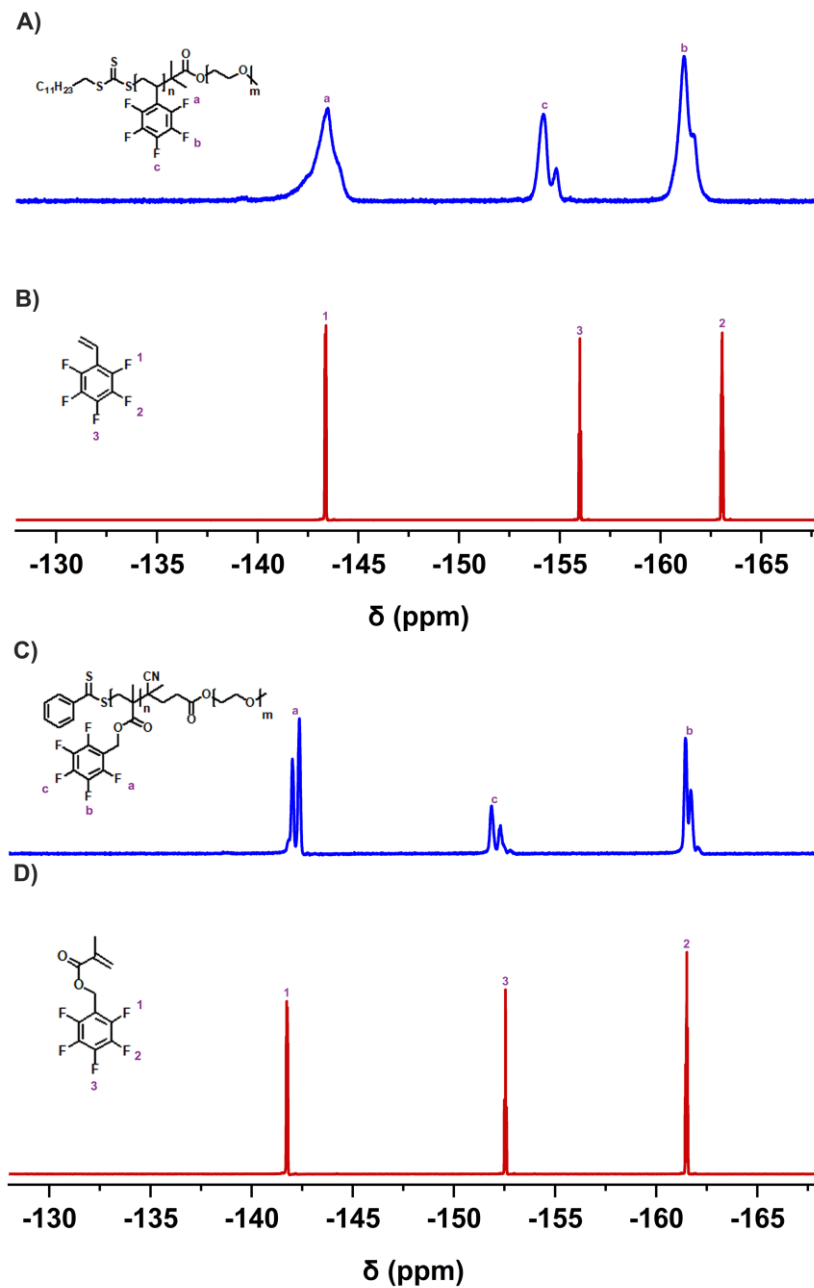
**Fig. S1.** A)  $^1\text{H}$  NMR spectra of MCD (grey, solvent:  $\text{D}_2\text{O}$ ), PFS (red, solvent:  $\text{CDCl}_3$ ), and PFS/MCD complex (blue, solvent:  $\text{D}_2\text{O}$ ), and B)  $^1\text{H}$  NMR spectra of MCD (grey, solvent:  $\text{D}_2\text{O}$ ), PFBMA (red, solvent:  $\text{CDCl}_3$ ), and PFBMA/MCD complex (blue, solvent:  $\text{D}_2\text{O}$ ).



**Fig. S2.** A)  $^{19}\text{F}$  NMR spectra of PFS (red, solvent:  $\text{CDCl}_3$ ), and PFS/MCD complex (blue, solvent:  $\text{D}_2\text{O}$ ), and B)  $^{19}\text{F}$  NMR spectra of PFBMA (red, solvent:  $\text{CDCl}_3$ ), and PFBMA/MCD complex (blue, solvent:  $\text{D}_2\text{O}$ ).

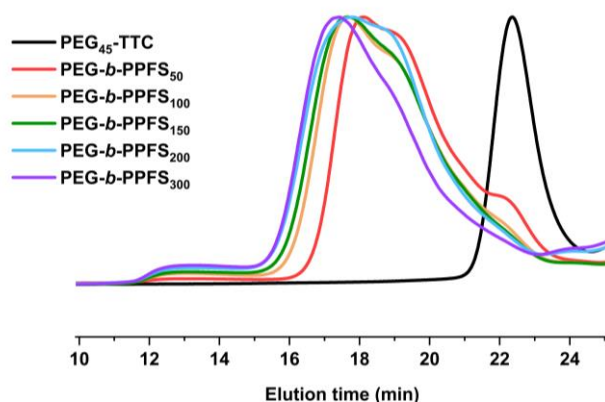


**Fig. S3.** Represent of  $^1\text{H}$  NMR spectra of A) PEG-*b*-PPFS, B) PEG-TTC, C) PEG-*b*-PPFBMA, and D) PEG-CPADB. (Solvent:  $\text{CDCl}_3$ )



**Fig. S4.** Represent of  $^{19}\text{F}$  NMR spectra of A) PEG-*b*-PPFS, B) PFS, C) PEG-*b*-PPFBMA, and D) PFBMA. (Solvent:  $\text{CDCl}_3$ )



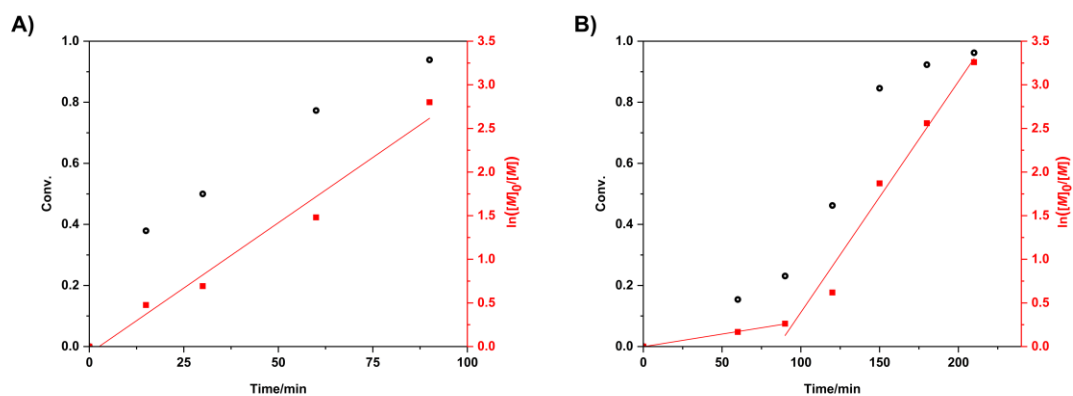


**Fig. S5.** SEC curves of PEG-TTC and PEG-*b*-PPFS

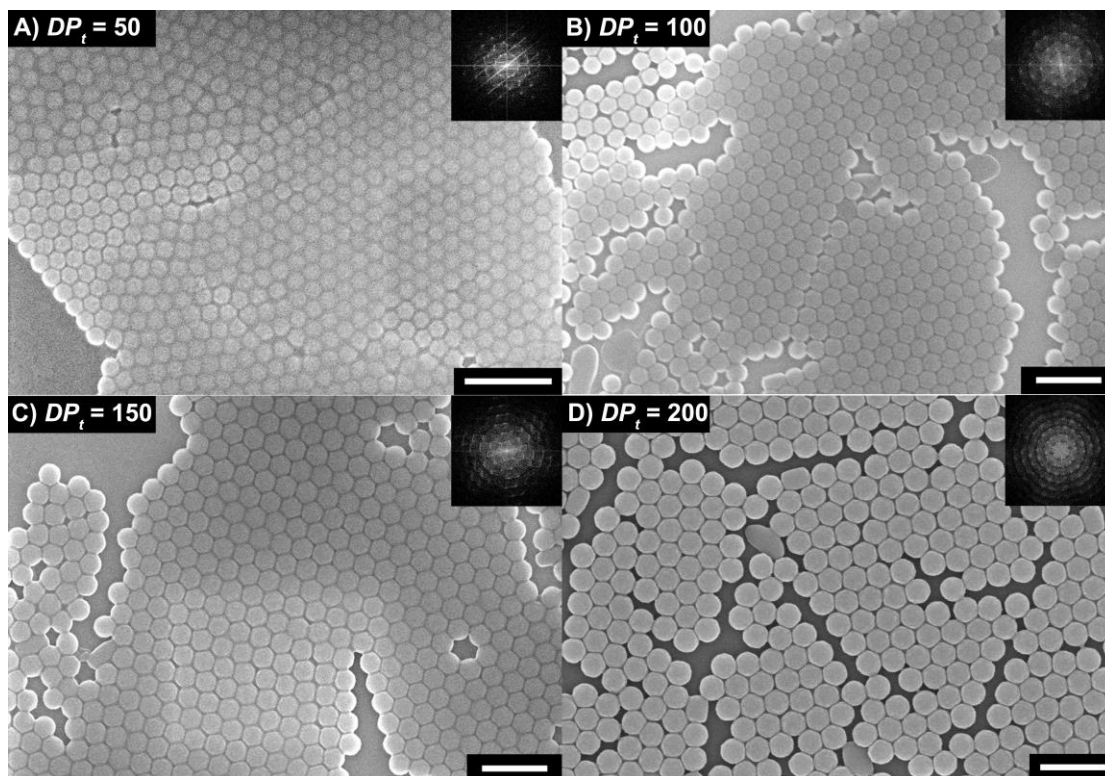
**Table S1.** SEC results of PEG-*b*-PPFS

| No.            | $DP_t$ | SEC               |                   |               |
|----------------|--------|-------------------|-------------------|---------------|
|                |        | $M_n$             | $M_w$             | $\mathcal{D}$ |
| 1              | 50     | $1.44 \cdot 10^4$ | $3.82 \cdot 10^4$ | 2.66          |
| 2              | 100    | $1.94 \cdot 10^4$ | $5.76 \cdot 10^4$ | 2.97          |
| 3              | 150    | $2.14 \cdot 10^4$ | $6.51 \cdot 10^4$ | 3.04          |
| 4              | 200    | $2.54 \cdot 10^4$ | $7.48 \cdot 10^4$ | 2.94          |
| 5              | 300    | $3.07 \cdot 10^4$ | $8.67 \cdot 10^4$ | 2.83          |
| 6 <sup>a</sup> | 100    | $9.76 \cdot 10^3$ | $1.23 \cdot 10^4$ | 1.26          |

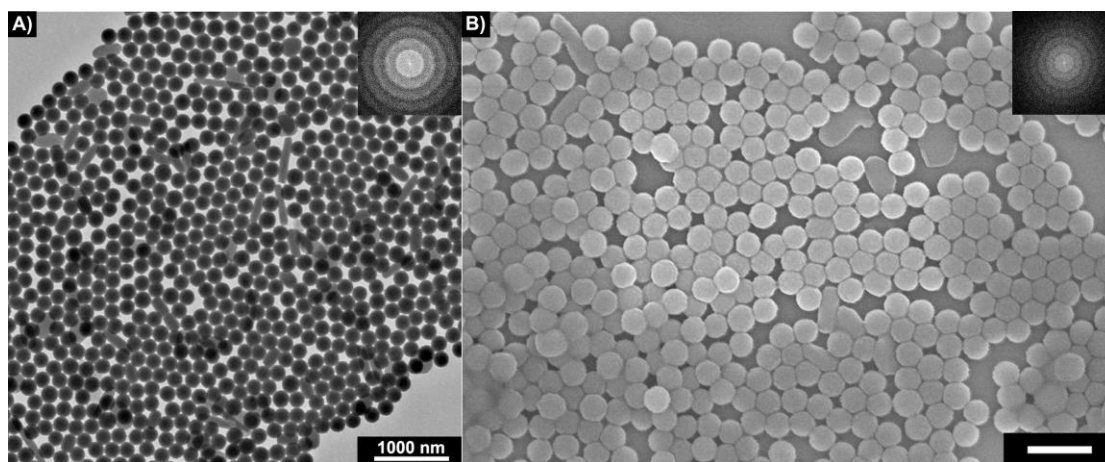
<sup>a</sup> This polymerization was performed in 1,4-dioxane, as described in section 3.3 b) of Experimental section.



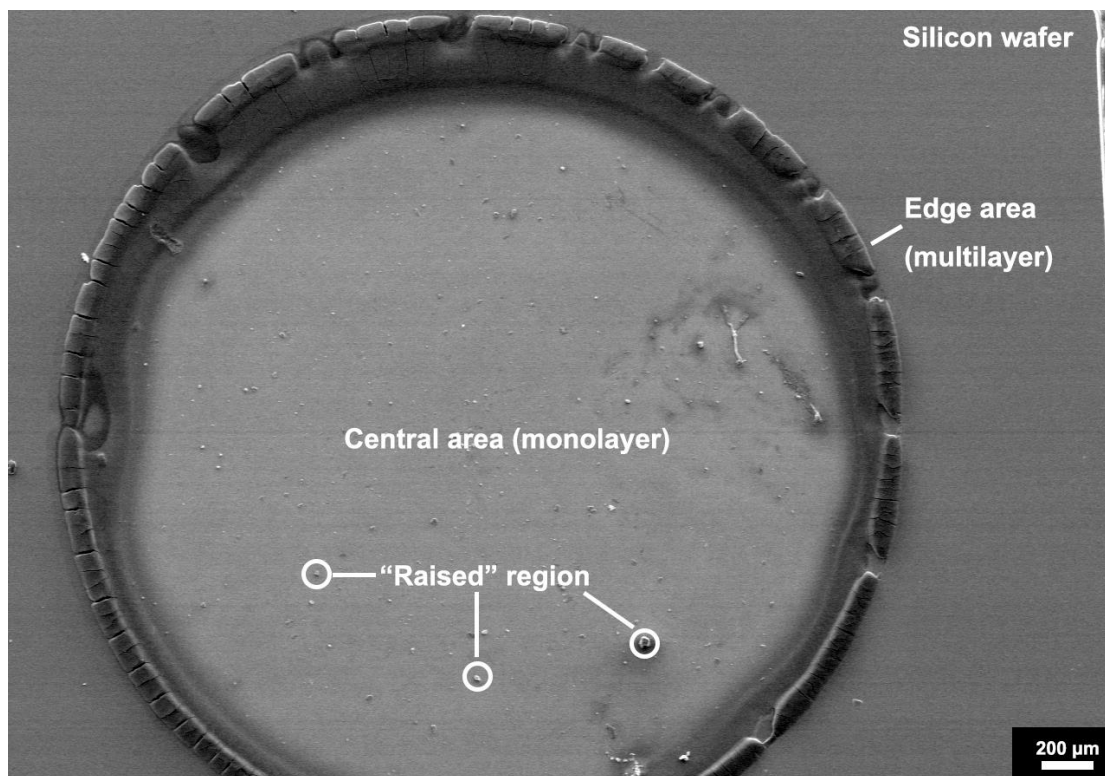
**Fig. S6.** Conversion and  $\ln([M]_0/[M])$  versus time of the aqueous host-guest mediated polymerization of A) PFS, and B) PFBMA, both judged by  $^1\text{H NMR}$ .  $DP_t = 300$ .



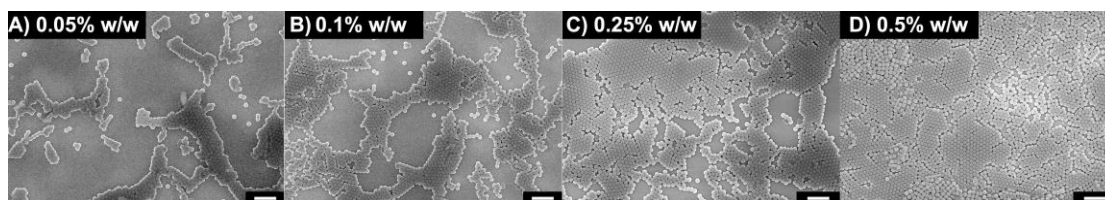
**Fig. S7.** SEM images of PEG-*b*-PPFS of different  $DP_t$ : A) PEG<sub>45</sub>-*b*-PPFS<sub>50</sub>, B) PEG<sub>45</sub>-*b*-PPFS<sub>100</sub>, C) PEG<sub>45</sub>-*b*-PPFS<sub>150</sub>, and D) PEG<sub>45</sub>-*b*-PPFS<sub>200</sub> (Scale bar = 500 nm). The insert images show the corresponding FFT patterns.



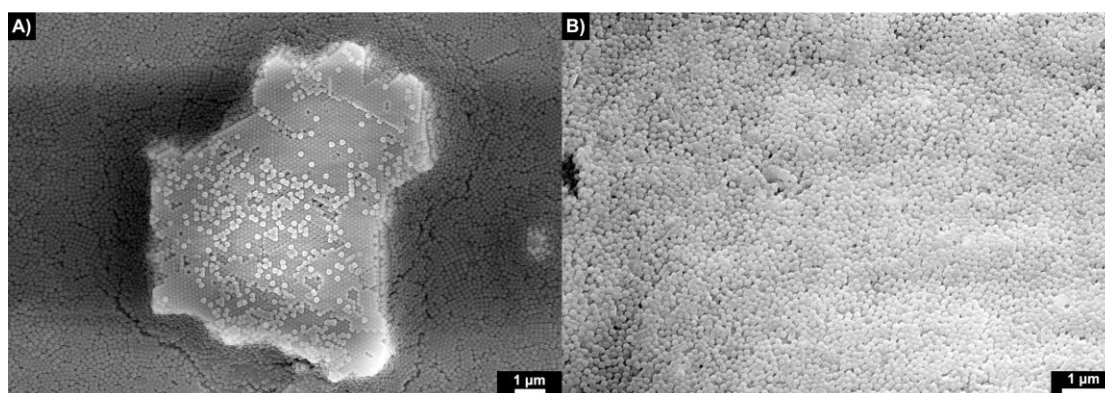
**Fig. S8.** A) TEM image, and B) SEM image of PEG<sub>45</sub>-*b*-PPFS<sub>300</sub>. The insert images show the corresponding FFT patterns.



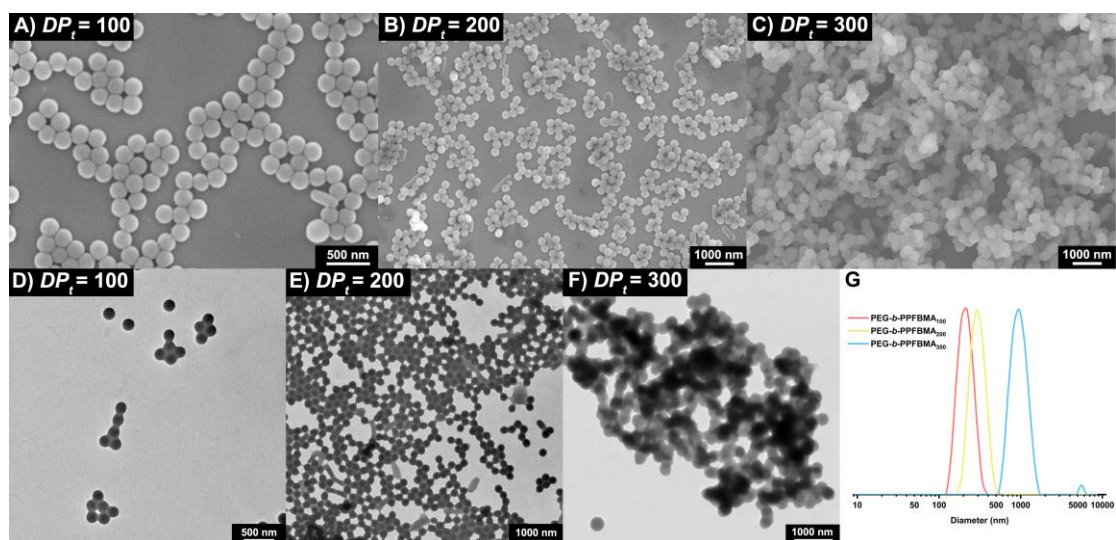
**Fig. S9.** SEM image of the “coffee-ring” pattern of the evaporated droplet. ( $DP_t = 100$ , 0.5% w/w)



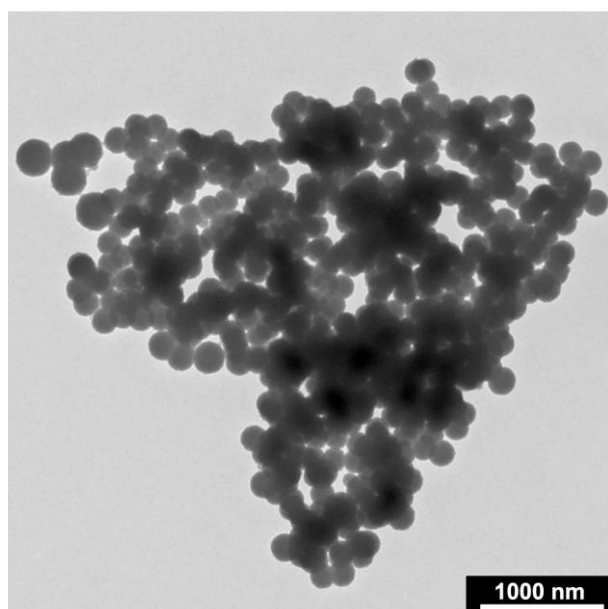
**Fig. S10.** SEM images of 2D colloidal crystal of PEG<sub>45</sub>-*b*-PPFS<sub>150</sub> (Scale bar = 1 μm). A) 0.05% w/w, B) 0.1% w/w, C) 0.25% w/w, D) 0.5% w/w.



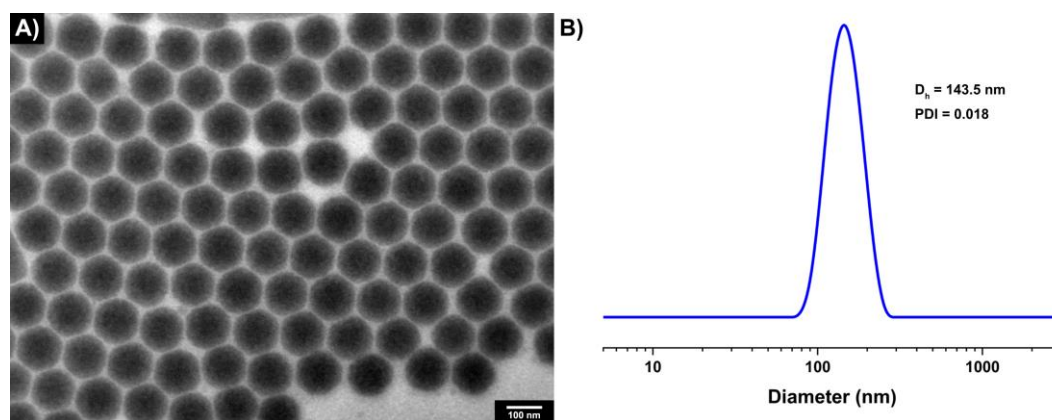
**Fig. S11.** SEM images of A) “raised” region, and B) random deposited structure in edge area.



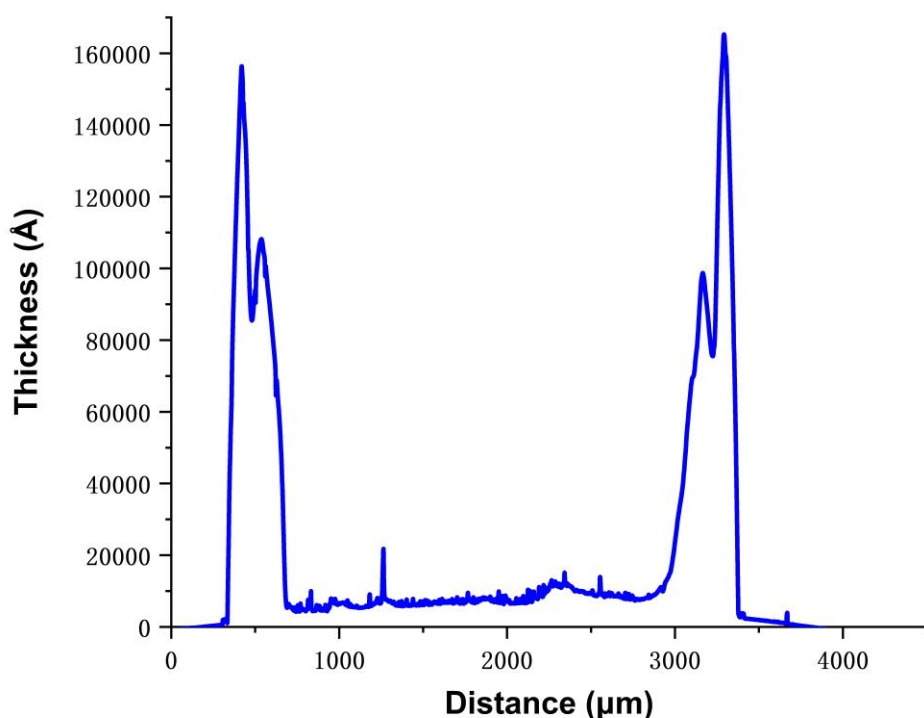
**Fig. S12.** A-C) SEM images, D-F) TEM images and G) DLS curve of  $PEG_{45}\text{-}b\text{-PPFBMA}_y$ ,  $y = 100, 200$ , and  $300$ .



**Fig. S13.** The TEM image of  $PEG_{45}\text{-}b\text{-PPFS}_{400}$ .



**Fig. S14.** A) TEM image and B) DLS result of  $PEG_{45}\text{-}b\text{-PPFS}_{100}$  before dialysis.



**Fig. S15.** The characterization of the thickness of the “coffee-ring” pattern. The two peaks in the image correspond to the thicknesses recorded as the probe “enters” and “leaves” the colloidal crystal pattern (the path is not along the diameter), i.e., the thickness of the structure shown in Fig. 3. Characterized by Bruker DektakXT stylus profilometer.

## References

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