

## Supporting Information

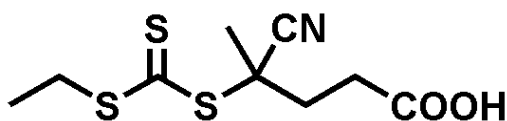
### Seeded dispersion RAFT polymerization and synthesis of well-defined ABA triblock copolymer flowerlike nanoparticles

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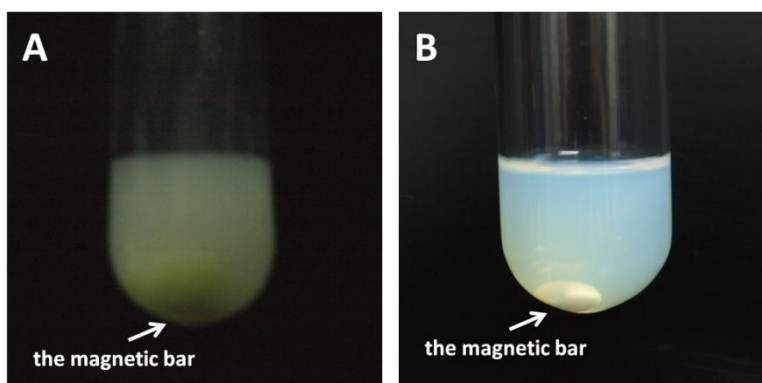
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#### 1. The chemical structure of ECT



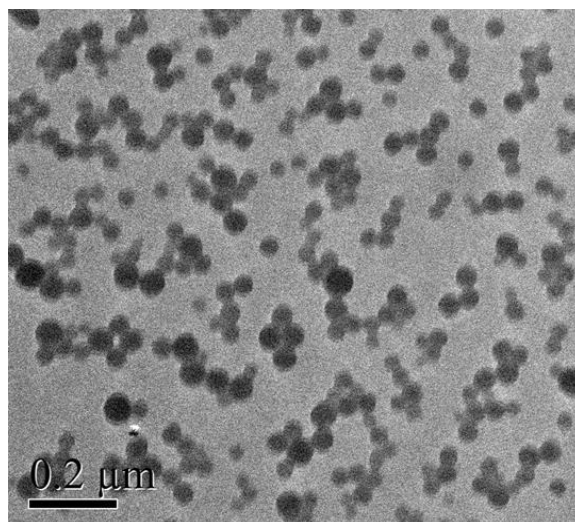
Scheme S1. The chemical structure of ECT

#### 2. Optical photos of the PS<sub>186</sub>-*b*-PDMA<sub>58</sub>-TTC diblock copolymer dispersed in the ethanol/water solvent mixture and the ternary styrene/ethanol/water mixture



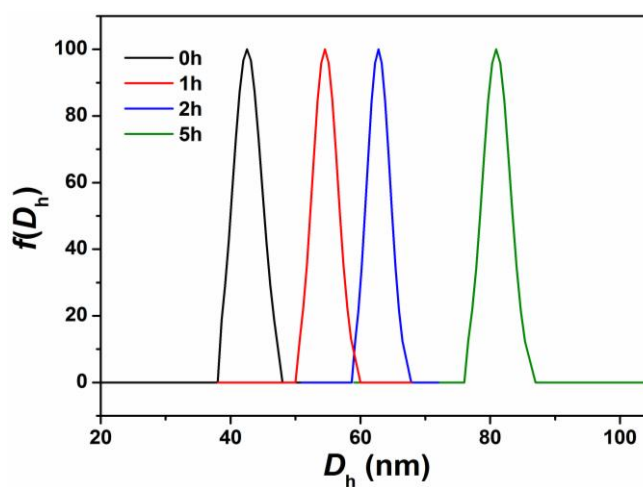
**Figure S1.** The dispersion of the 2.0 wt% PS<sub>186</sub>-*b*-PDMA<sub>58</sub>-TTC diblock copolymer in the ethanol/water solvent mixture (80:20 by weight) (A), and the 6.0 wt% PS<sub>186</sub>-*b*-PDMA<sub>58</sub>-TTC in the ternary styrene/ethanol/water mixture (11:80:20 by weight) (B).

### 3. The TEM image of the PS<sub>186</sub>-*b*-PDMA<sub>58</sub> nanoparticles prepared by self-assembly strategy



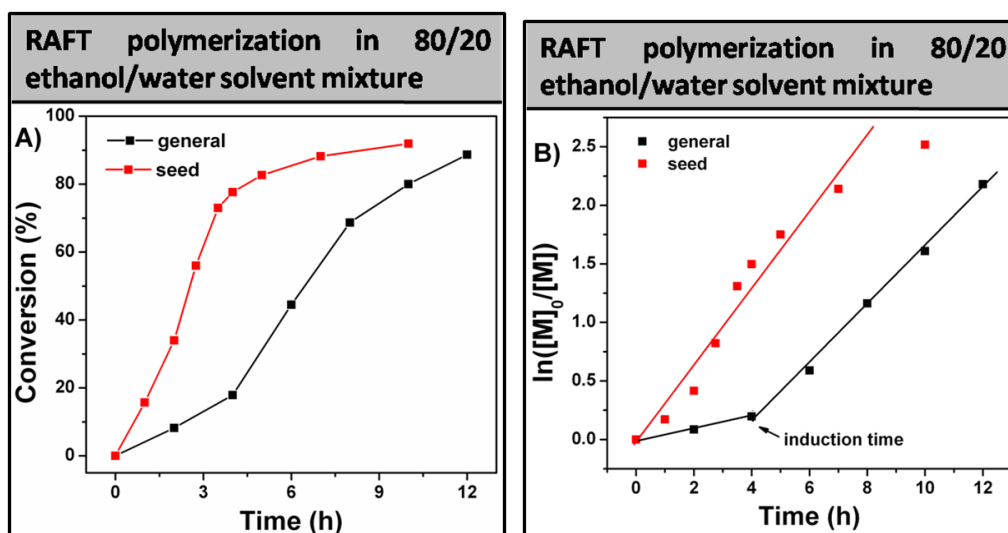
**Figure S2.** The TEM image of the nanoparticles of PS<sub>186</sub>-*b*-PDMA<sub>58</sub>-TTC diblock copolymer prepared by dialysis of the 2.0 wt% PS<sub>186</sub>-*b*-PDMA<sub>58</sub>-TTC diblock copolymer DMF solution against the ethanol/water mixture (80/20 by weight).

### 4. The hydrodynamic diameter distribution of the PS<sub>186</sub>-*b*-PDMA<sub>58</sub> seed-nanoparticles and the PS-*b*-PDMA-*b*-PS triblock copolymer flowerlike nanoparticles



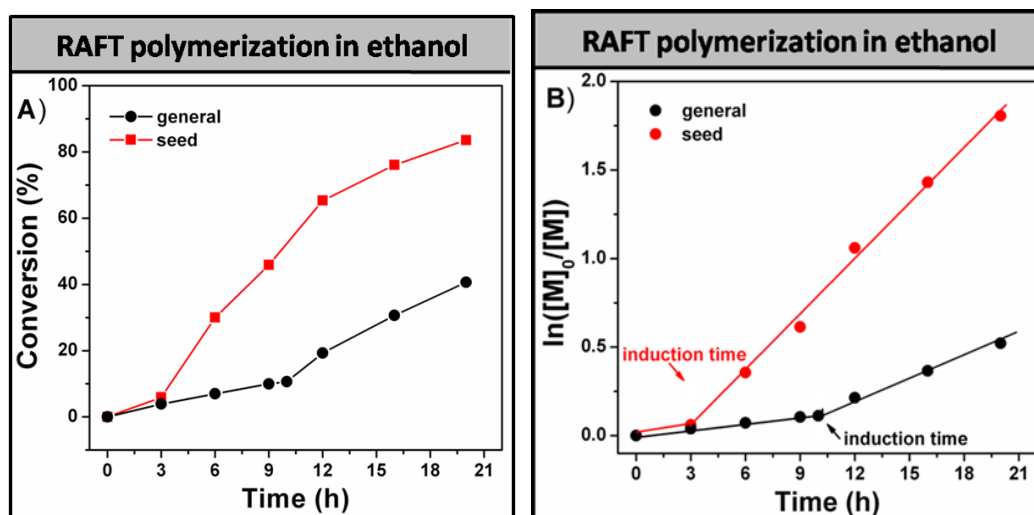
**Figure S3.** The hydrodynamic diameter ( $D_h$ ) distribution of the PS<sub>186</sub>-*b*-PDMA<sub>58</sub> seed-nanoparticles (0 h) and the PS-*b*-PDMA-*b*-PS flowerlike nanoparticles prepared at the different polymerization times. Polymerization conditions can be found in the caption of Figure 4.

### 5. Kinetics of the PDMA<sub>59</sub>-TTC mediated dispersion RAFT polymerization and the seeded dispersion RAFT polymerization in the 80/20 ethanol/water.



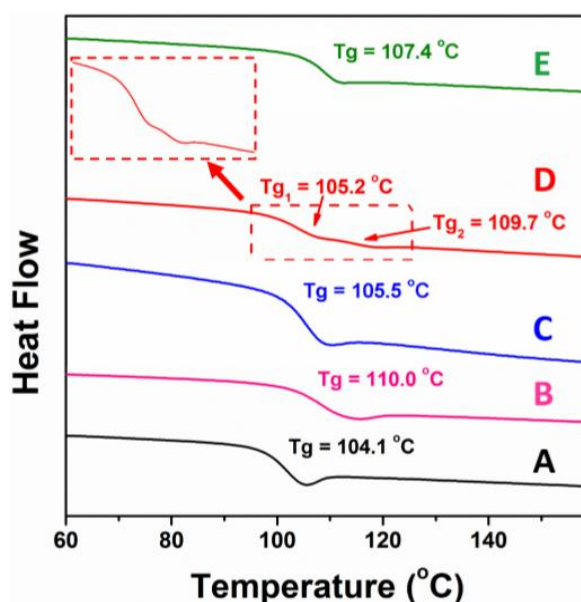
**Figure S4.** The conversion-time plots (A) and the  $\ln([M]_0/[M])$ -time plots (B) of the PDMA<sub>59</sub>-TTC mediated dispersion polymerization (black dot-line) and the seeded dispersion polymerization (red dot-line). Polymerization conditions for the PDMA<sub>59</sub>-TTC mediated dispersion polymerization: the dispersion RAFT polymerization of styrene was performed in the ethanol/water mixture (80/20 by weight) 70 °C under  $[St]_0:[m-R]_0:[AIBN]_0 = 900:3:1$ , in which the weight content of the feeding monomer plus PDMA<sub>59</sub>-TTC is 15 wt%; polymerization conditions for the seeded dispersion RAFT polymerization can be found in Figure 4.

### 6. Kinetics of the PDMA<sub>59</sub>-TTC mediated dispersion RAFT polymerization and the seeded dispersion RAFT polymerization in pure ethanol.



**Figure S5.** The conversion-time plots (A) and the  $\ln[M]_0/[M]$ -time plots (B) of the PDMA<sub>59</sub>-TTC mediated dispersion polymerization (black dot-line) and the seeded dispersion polymerization (red dot-line). Polymerization conditions for the PDMA<sub>59</sub>-TTC mediated dispersion polymerization: the dispersion RAFT polymerization of styrene was performed in ethanol at 70 °C under  $[St]_0:[m-R]_0:[AIBN]_0 = 1200:3:1$ , in which the weight content of the feeding monomer plus the PDMA<sub>59</sub>-TTC or PS<sub>186</sub>-*b*-PDMA<sub>58</sub> macro-RAFT agent is 15 wt%.

## 7. The DSC analysis



**Figure S5** DSC thermograms of PS<sub>186</sub>-TTC (A), PDMA<sub>50</sub>-TTC (B), PS<sub>186</sub>-*b*-PDMA<sub>58</sub>-TTC (C), PS<sub>57</sub>-*b*-PDMA<sub>54</sub>-*b*-PS<sub>57</sub> (D), and PS<sub>186</sub>-*b*-PDMA<sub>58</sub>-*b*-PS<sub>225</sub> (E).