

Supporting Information

Control of Cross-Linking and Reactions in One-Step Dispersion Polymerization toward Particles with Combined Anisotropies

Yanan Liu, Kun Jiang, Yuhong Ma, Lianying Liu and Wantai Yang**

Beijing Engineering Research Center for the Synthesis and Applications of Waterborne
Polymers, College of Materials Science and Engineering, Beijing University of Chemical
Technology, Beijing 100029, China

EXPERIMENTAL SECTION

Monomer Conversion, Gel Content and Average Particle Size

Samples (0.5-1 ml, m_0) were taken at intervals during polymerization, rinsed extensively with methanol, dried in a vacuum oven to a constant weigh (m_1). The conversion of monomers was calculated from the expression: $\text{Conversion (\%)} = \frac{m_1}{m_0 \times 0.08} \times 100$

Dried particles (W_0) were immersed in THF (renewed 3 times) at room temperature for 24 h under stirring. After that, the particles were centrifuged at 10000 rpm for 15 min, washed 3 times with excess THF and 1 time with MeOH, dried at 40 °C overnight in a vacuum oven and weighed (W_1). Gel content of particles (the fraction of cross-linked polymers in particles), representing the cross-linking degree of particles, was determined by the formula:

$$\text{Gel content (\%)} = \frac{W_1}{W_0} \times 100.$$

Average size of particle includes average size (G , G') of growing particle domain (G domain), average size (N , N') of the newly formed domain (N domain), and average aspect ratio (L/G or N , L'/G') of particle before and after immersed in THF. The average size was evaluated statistically on the basis of counting at least 30 individual particles presented on SEM images using image processing software program Nano Measure 1.2. Particle monodispersity was represented by

coefficient of variation (CV_G %) of G domain size distribution, and coefficient of variation (CV_N %) of N domain size distribution. In our experiments, CV_G % is in the range of 3.0-3.5%, and CV_N % is in the range of 1.9-2.7%. When the value of $CV\%$ is less than 10%, particles are generally considered to be monodisperse (Horák D. *Acta Polym.*, 1996, **47**, 20-28).

GPC Analysis

Average molecular weights (M_n) and distributions (PDI) of polymers were determined by a Waters 515-2410 gel-permeation chromatography (GPC) instrument using THF as eluent. The result was calibrated using linear polystyrene with narrow molecular weight distribution as standard.

Attachment of Ag nanoparticles (NPs)

10 ml $AgNO_3$ solution (0.015 mol/l) was mixed with 0.01 g anisotropic particles (Poly (St-*co*-DMABP-*co*-MAA), Poly (St-*co*-DMABP-*co*-PMA)-SH, Poly (St-*co*-DMABP-*co*-PA)-SH, or Poly (St-*co*-DMABP)-SH) dispersed in 10 ml MeOH by sonication for 10 min. Then the mixture was exposed to UV light (375 W high-pressure mercury lamp, incident light intensity 12.5 W/m^2 , $\lambda=254 \text{ nm}$) for 30 min. The resultant particles were extensively washed with deionized water and MeOH by repetitive centrifugation and redispersion to remove the Ag NPs remained in medium. Finally, the particles were isolated and dried.

Coupling of protein

Particles (0.1 g) were suspended in 10 ml of phosphate buffered saline solution (PBS, 10 mM, pH = 7.4) with 0.02 ml of sodium dodecylsulfonate (SDS, 0.1 g/ml) aqueous solution and 5 ml of mouse IgG protein (1 $\mu\text{g/ml}$) added under stirring. Then reaction was continued for 12 h at 36 °C. Particles were separated by centrifugation, washed with PBS for three cycles and dried at room temperature.

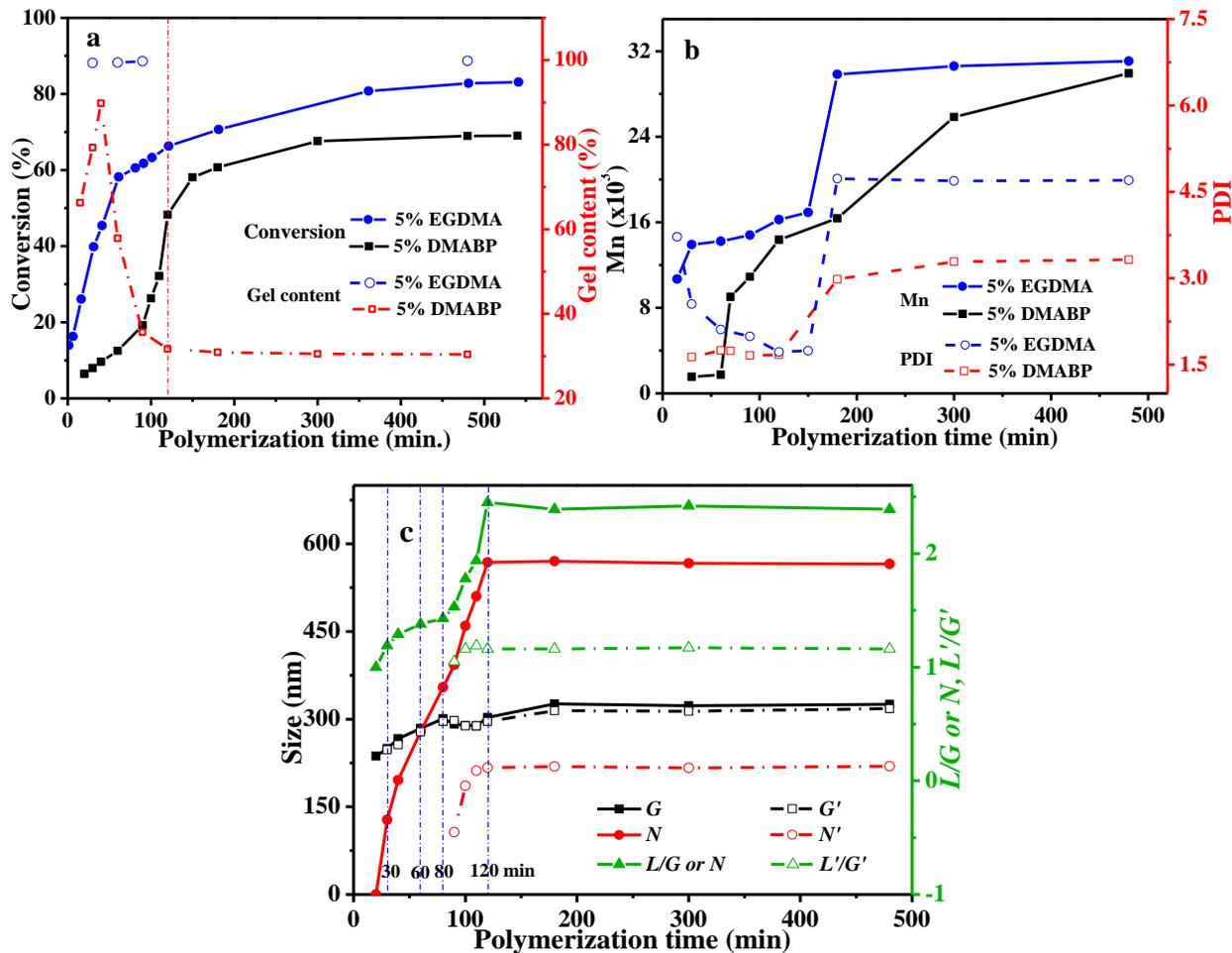


Fig. S1 (a) Monomers conversion, gel content of particle prepared during dispersion polymerization (Dis.P) with 5 % DMABP or 5 % EGDMA added at the beginning. (b) Molecular weight (Mn) and its distribution (PDI) of linear polymer contained in particle produced during Dis.P and dissolved in THF. (c) Average G domain size (G , G'), N domain size (N , N'), and aspect ratio (L/G or N , L'/G') of particles prepared during polymerization with 5 % DMABP added.

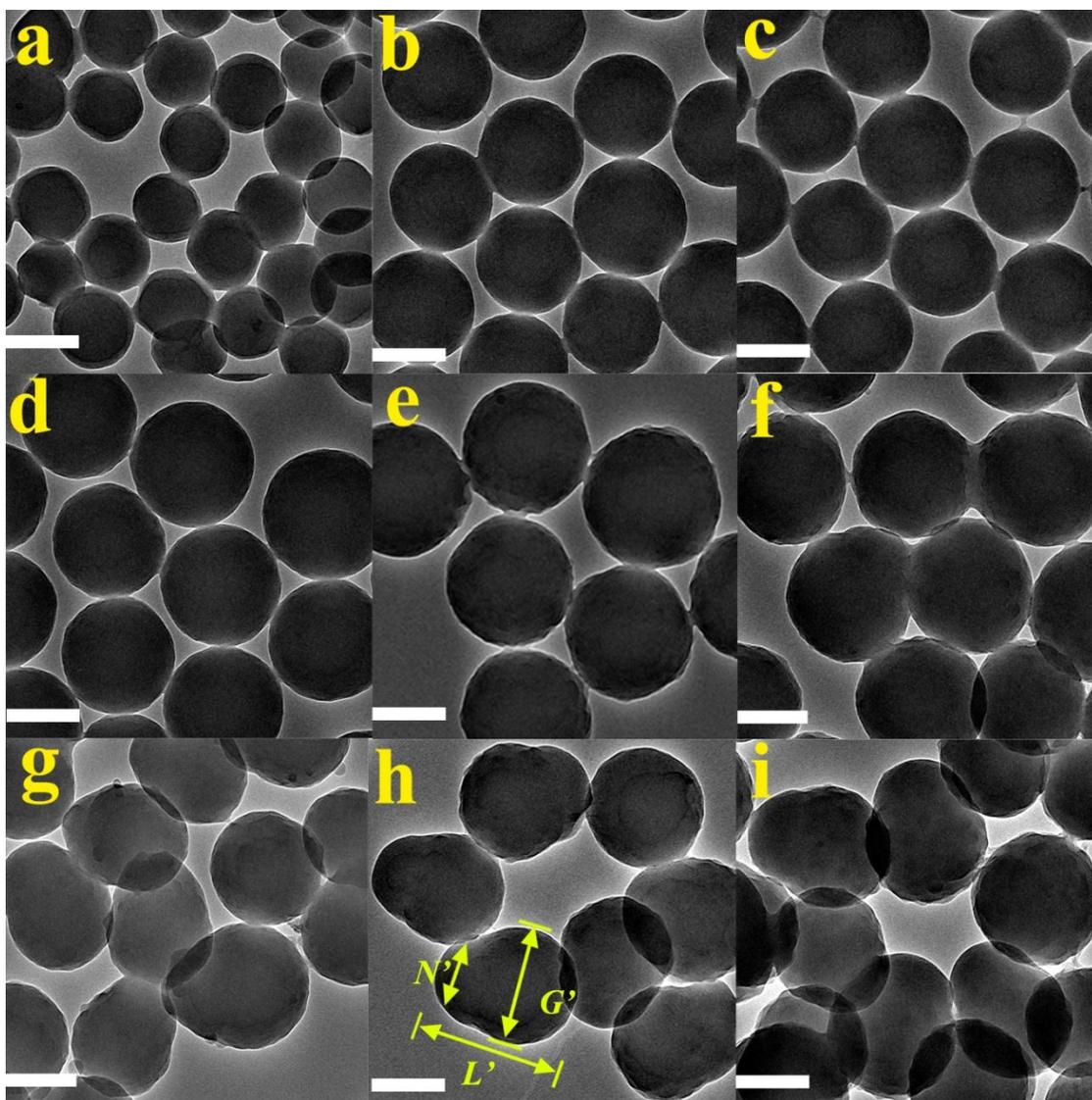


Fig. S2 TEM images (Scale bars: 200 nm) of particles produced during polymerization with 5% DMABP added initially, and immersed in THF. a-20, b-30, c-40, d-60, e-80, f-90, g-100, h-120, i-300 min.

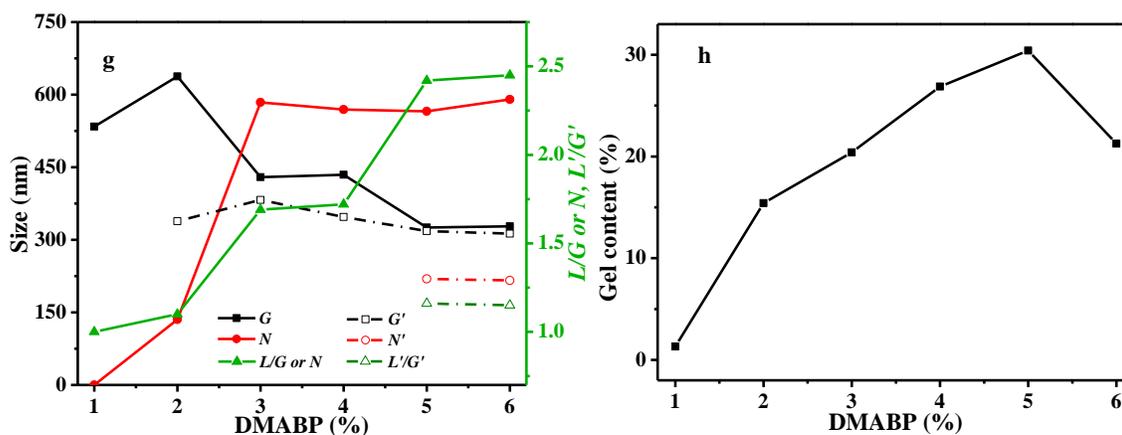
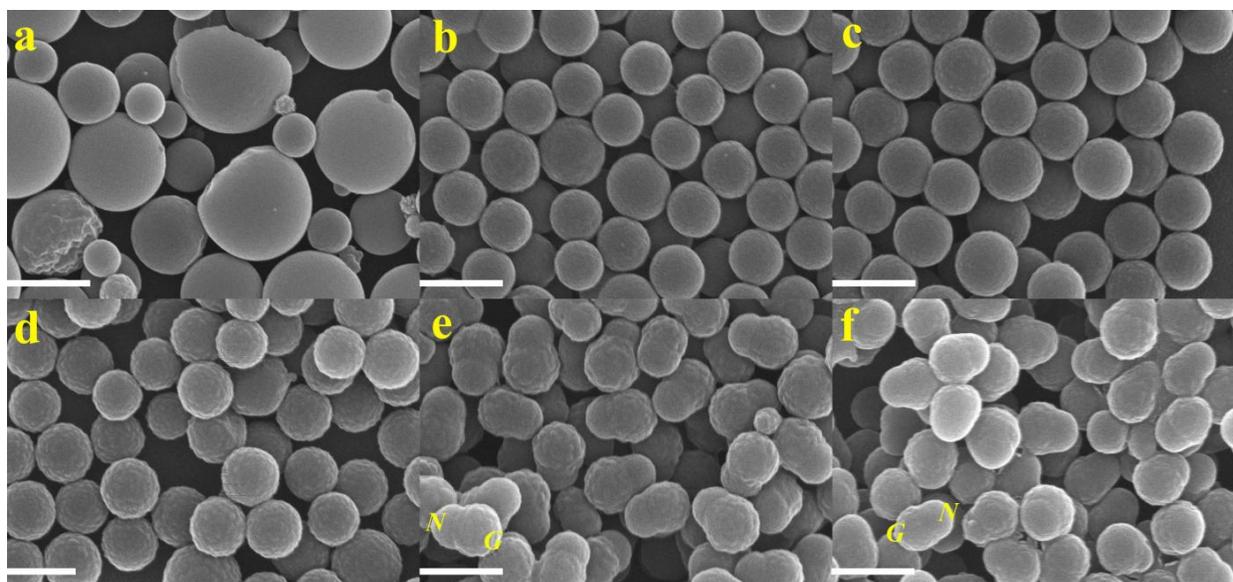


Fig. S3 SEM images (Scale bars: 500 nm) of particles produced with various contents of DMABP (a-1%, b-2%, c-3%, d-4%, e-5%, f-6%) and immersed in THF. g-Average G domain size (G , G'), N domain size (N , N'), and aspect ratio (L/G or N , L'/G') of resultant particles, h- Gel content of resultant particles.

In the following, Scare bars in SEM images are 500 nm, and in TEM images are 200 nm.

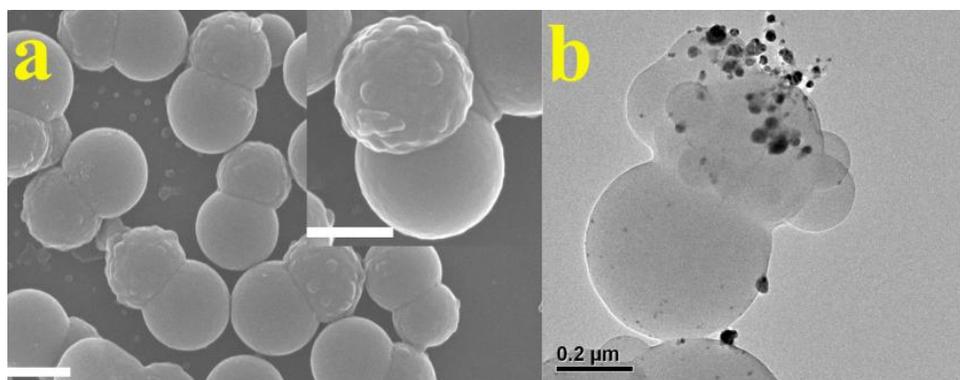


Fig. S4 (a) SEM images of Poly (St-co-DMABP-co-GMA) anisotropic particles coupled with mouse IgG protein, (b) TEM image of Poly (St-co-DMABP-co-MAA) anisotropic particles attached Ag NPs.

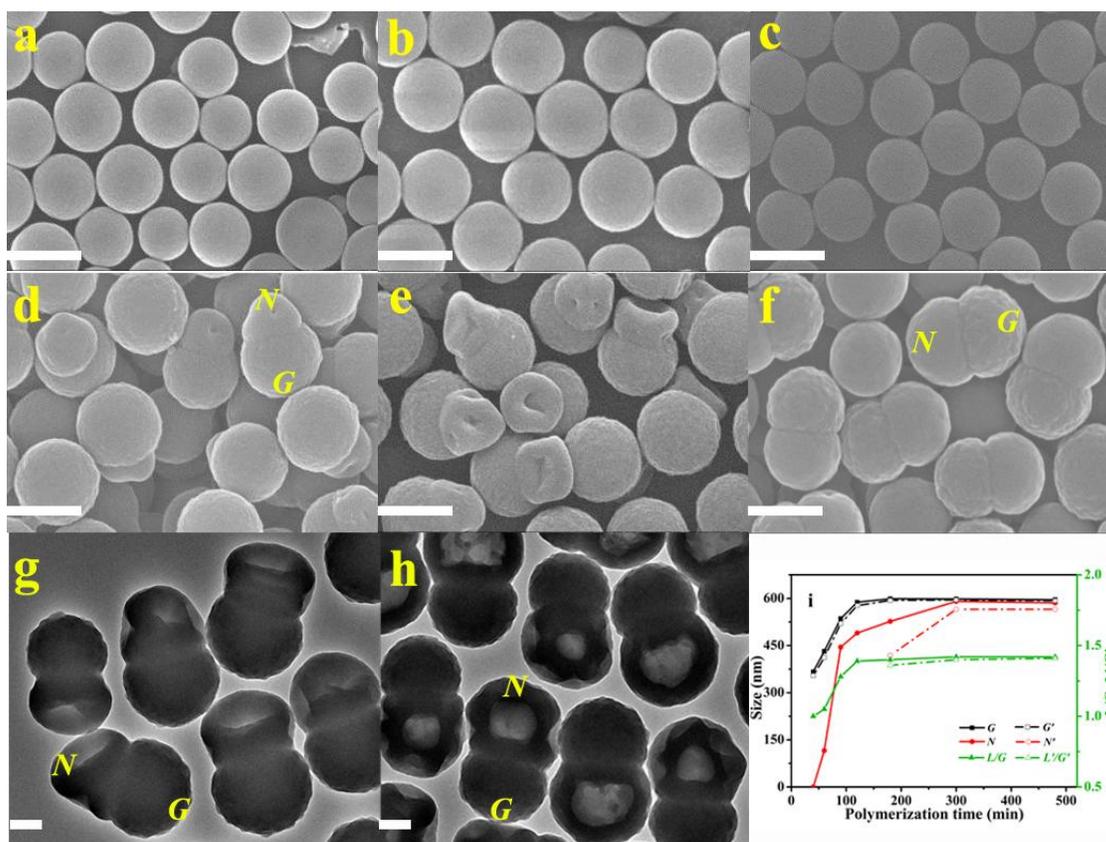


Fig. S5 SEM (a-f) and TEM (g, h) images of particles synthesized during polymerization with DMABP (4%) and PMA (4%) added initially, and immersed in THF. a- 40, b-60, c-80, d-120, e, g-180, f, h-480 min. i-Average G domain size (G , G'), N domain size (N , N'), and aspect ratio (L/G , L'/G') of resultant particles.

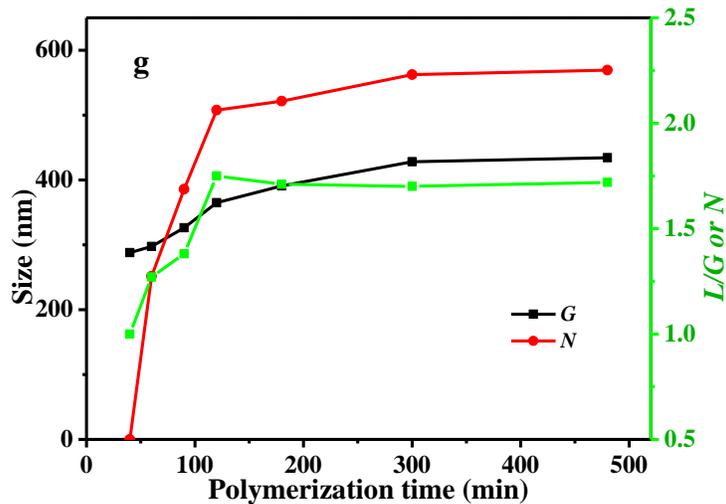
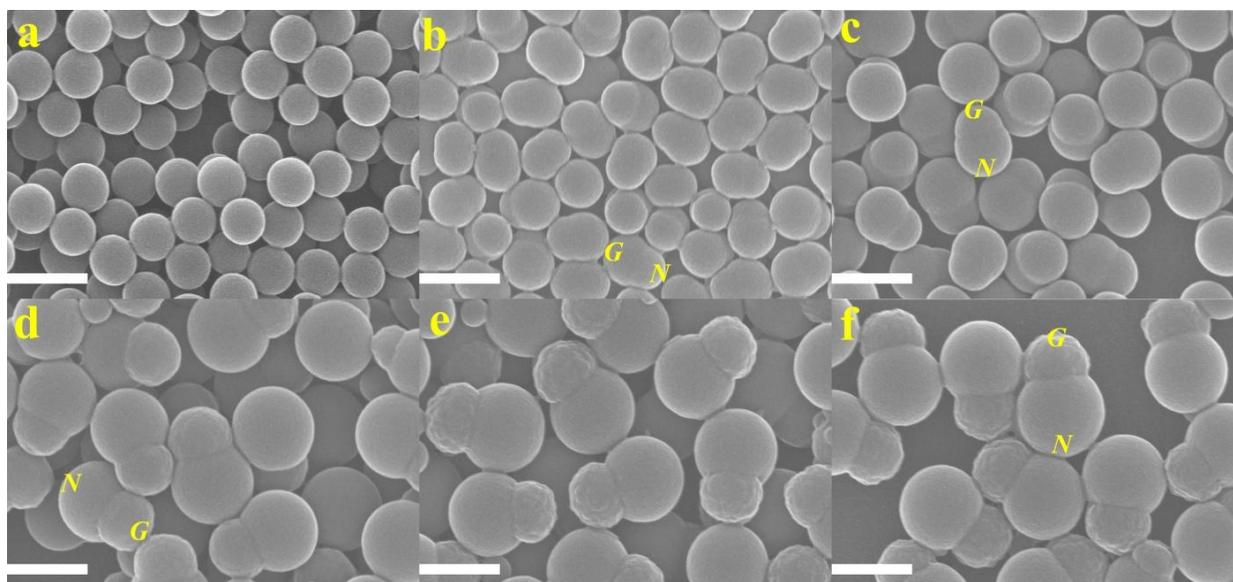


Fig. S6 Morphology evolution of particles produced during polymerization with only DMABP (4%) added initially. a-40, b-60, c-90, d-120, e-180, f-300 min. g-Average G domain size (G), N domain size (N), and aspect ratio (L/G or N) of particles prepared with DMABP (4%) added.

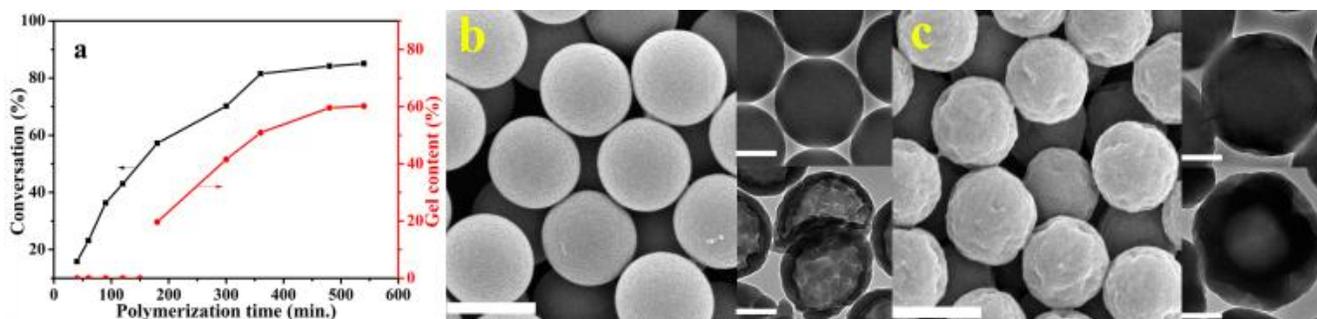


Fig. S7 Monomer conversion, gel content of particles prepared during polymerization with only 4% PMA added (a). SEM and TEM images of particles prepared at 180 min (b), or at the end of polymerization (c). The upper and lower right inserted are TEM images of particles before and after immersed in THF.

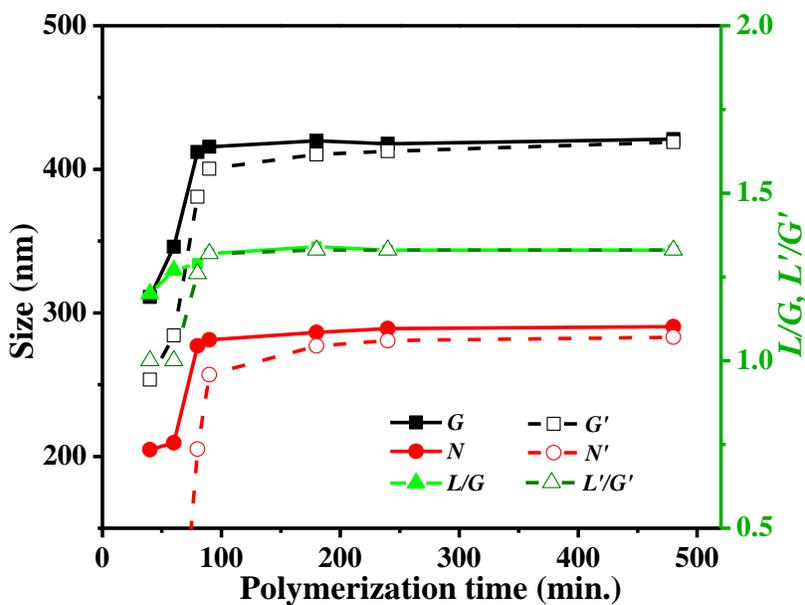


Fig. S8 Evolutions of average G domain size (G, G'), N domain size (N, N'), and aspect ratio ($L/G, L'/G'$) of particles prepared during polymerization with DMABP (4%) and PA (4%) added.

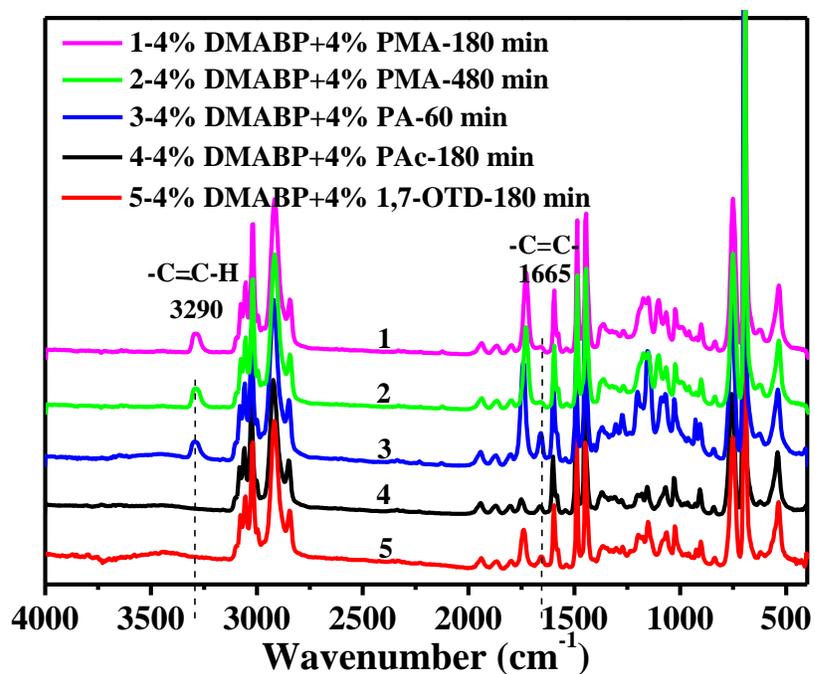


Fig. S9 FTIR spectra of particles produced at 180 min and 480 min (spectrum 1, 2) when DMABP and PMA were used, or of particles produced at 60 min with DMABP and PA used (spectrum 3), or of particles produced at 180 min when DMABP and PAc, or DMABP and 1,7-OTD were added initially.

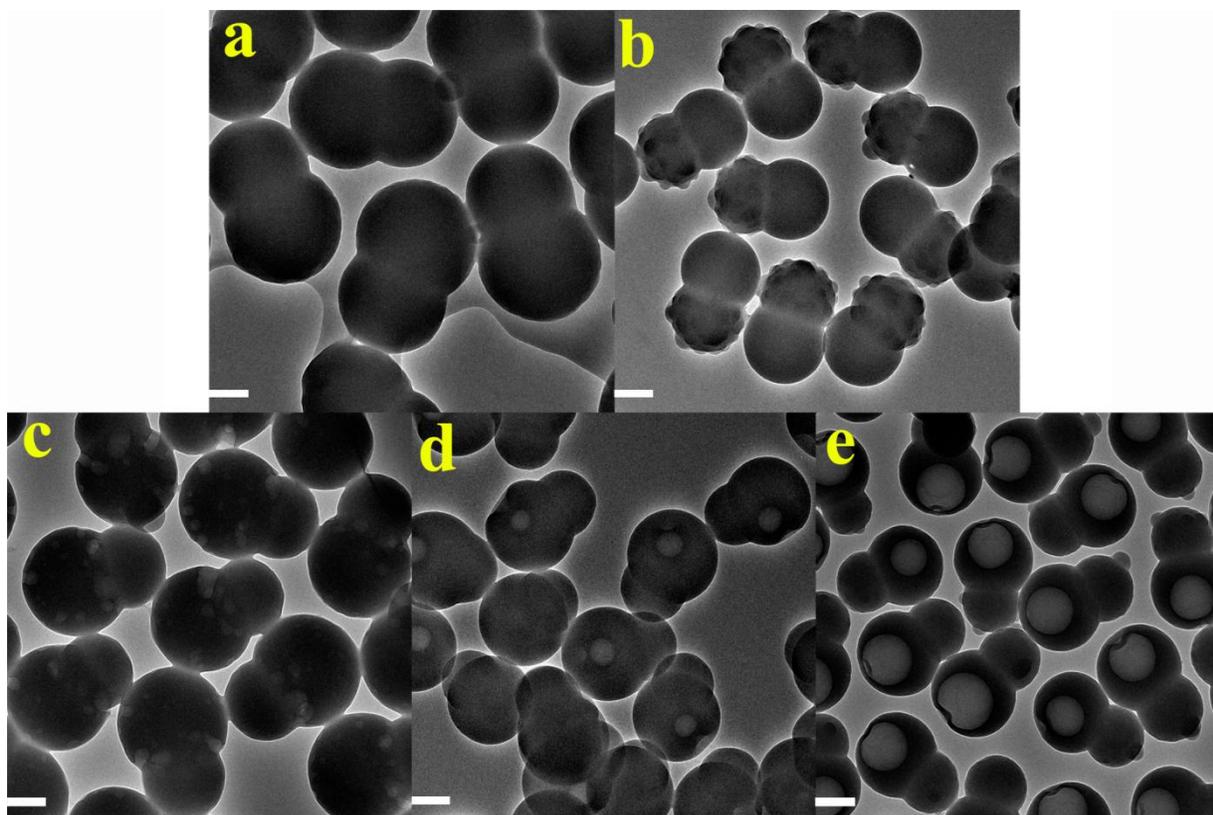


Fig. S10 TEM images of particles produced by initially adding 4% DMABP and a-4% PMA (4% BDMT added at 180 min), or b-4% PA (4% TMPTMP added at 60 min), c-4% PAc (4% BDMT added at 180 min), d-4% 1,7-OTD (4% BDMT added at 180 min), e-2% MAA and 4% 1,7-OTD (4% PFDT added at 180 min).

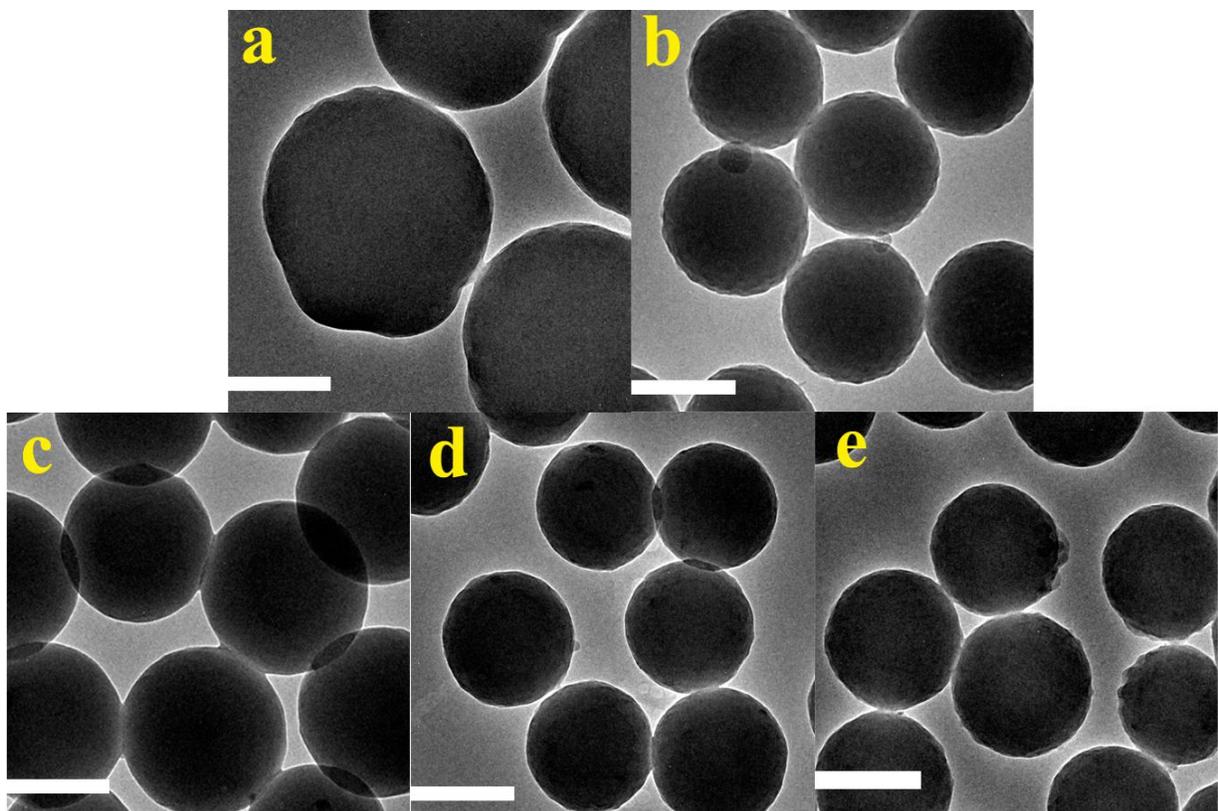


Fig. S11 TEM images of particles produced by initially adding 4% DMABP and a-4% PMA (4% BDMT added at 180 min), or b-4% PA (4% TMPTMP added at 60 min), c-4% PAc (4% BDMT added at 180 min), d-4% 1,7-OTD (4% BDMT added at 180 min), e-2% MAA and 4% 1,7-OTD (4% PFDT added at 180 min), and immersed in THF.

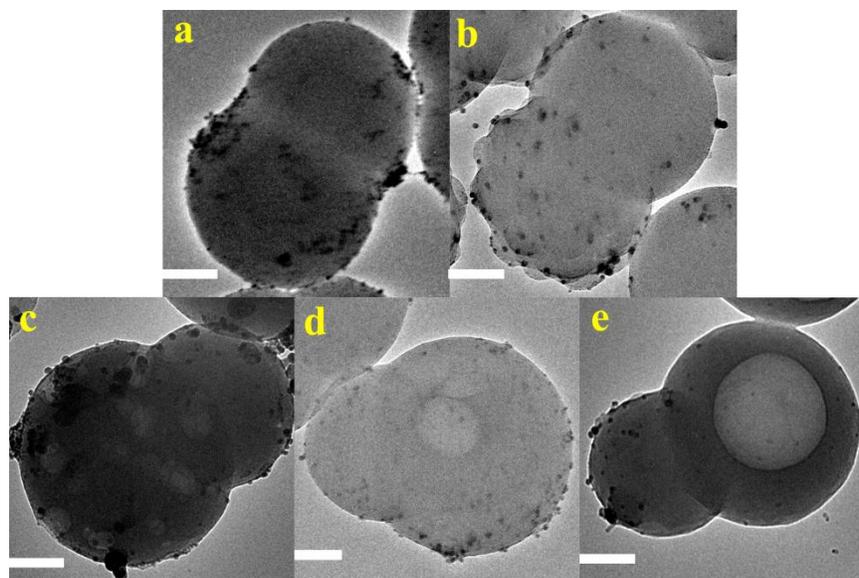


Fig. S12 TEM images of a-Poly(St-co-DMABP-co-PMA)-SH, b-Poly(St-co-DMABP-co-PA)-SH, c-Poly(St-co-DMABP)-PAC-SH, d-Poly(St-co-DMABP)-OTD-SH and e-Poly(St-co-DMABP-co-MAA)-OTD-CF₃ anisotropic particles attached Ag NPs.

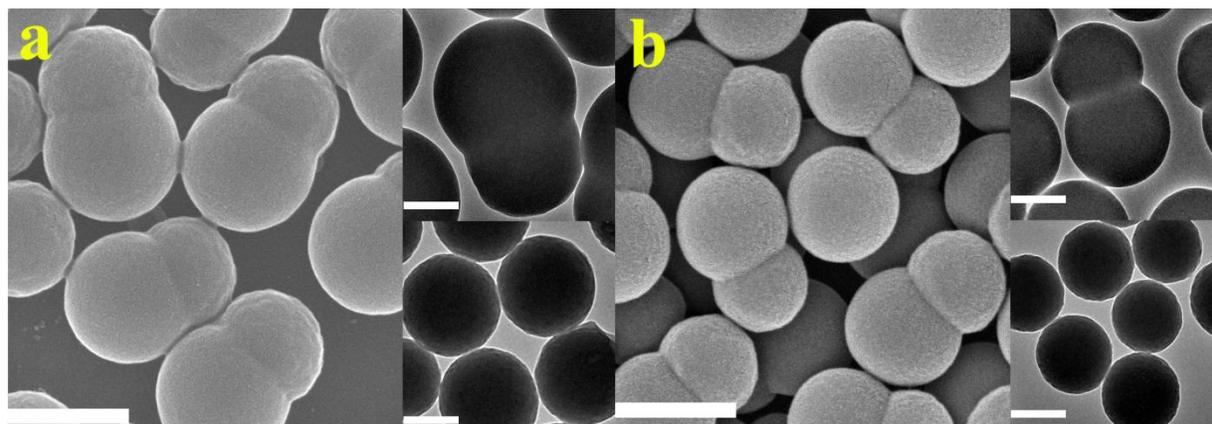


Fig. S13 (a-b) SEM and TEM images of particles produced by initially adding 4% DMABP and 4% PAc (a), or 4% 1, 7-OTD (b). The upper and lower right inserted are TEM images of particles before and after immersed in THF.