

Supporting Information

Combined Chain- and Step-Growth Dispersion Polymerization toward PSt Particles with Soft, Clickable Patches

Kun Jiang, Yanan Liu, Yaping Yan, Shengliu Wang, 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

Conversion of Monomers and Content of click polymers in PPs

Conversion of all monomers added was determined gravimetrically. Samples (1 ml, m_0) were taken at intervals during polymerization, washed three times with MeOH and dried in a vacuum oven to a constant weigh (m_1). Monomer proportion (φ) was estimated by the expression:

$\varphi = \frac{m_{\text{st}} + m_{\text{click}}}{m_{\text{total}} + m_{\text{click}}}$, where m_{st} represents mass of St, m_{click} stands for mass of click monomers (thiol

and ene), m_{total} is total mass of reagents added initially. Conversion of monomers was calculated by

the expression: Conversion (%) = $\frac{m_1}{m_0 \times \varphi} \times 100$.

Content of click polymers in PPs was evaluated by gravimetrically measuring gel contained in PPs, or by FT-IR analyzing characteristic absorptions of click polymers in patchy particles (PPs).

Gel content. Dried particles (W_0) were immersed in THF (renewed 4 times) at room temperature for 24 h under stirring. After that, the particles were washed 3 times with excess THF and 1 time with MeOH by centrifuging at 10000 rpm for 5 min, then dried at 40 °C for 24 h in a vacuum oven and weighed (W_1). Gel content of particles (fraction of cross-linked click polymers) was determined

by the formula: Gel content (%) = $\frac{W_1}{W_0} \times 100$.

Average particle size estimation. Average size of body, dimples or bulges and average numbers of dimples or bulges presented on body were 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. Monodispersity of body, dimples or bulges was represented by polydispersity index (PDI).

FT-IR analysis. Characteristic absorption of ester carbonyl groups ($-\text{O}-\text{C}=\text{O}$) at around 1735 cm^{-1} from thiols such as TMPMP, PETMP, or enes such as TMPTA, DTPTA, and absorption of carbonyl groups ($-\text{C}=\text{O}$) at 1690 cm^{-1} from TTT on FT-IR spectra were selected. An internal reference peak at 540 cm^{-1} was used. Their peak area (A_{1735} , A_{1690} , A_0) was integrated, and peak area ratios (N_{1735} , N_{1690}) were calculated to quantitatively determine the incorporation of thiol or/and ene segments (click polymers) in PPs: $N_{1735} = \frac{A_{1735} \times 1.35}{A_0}$, $N_{1690} = \frac{A_{1690}}{A_0}$. 1.35 was the ratio of peak area at about 1735 cm^{-1} to that at about 1690 cm^{-1} on FT-IR spectrum of equimolar mixture of thiol (such as TMPMP) and ene (such as TTT).

Degradation of PPs.

0.1 g PPs were dispersed in 20 ml NaOH (1.25 mol. l^{-1}) solution in MeOH, then the dispersion was stirred magnetically for 24 h at room temperature to allow click polymers to be degraded completely. The resultant particles were washed with MeOH by repetitive centrifugation till pH value of the medium was near 7.

Attachment of Fe_3O_4 nanoparticles (NPs) to PPs.

0.1 g FeCl_3 , 0.11 g FeSO_4 and 0.1 g PPs were dispersed in 20 ml MeOH. The mixture was stirred for 8 h at room temperature to ensure the complexation of Fe^{3+} and Fe^{2+} with $-\text{SO}_3^-$ fully. Subsequently, PPs were recovered through centrifugation to remove superfluous Fe^{3+} and Fe^{2+} and redispersed in 30 ml H_2O . The dispersion was transferred to a 100 ml three-neck round-bottom flask equipped with a mechanical stirrer, and heated to $70\text{ }^\circ\text{C}$ in a water bath. After bubbling nitrogen for 30 min and 3 ml $\text{NH}_3\cdot\text{H}_2\text{O}$ was added to the flask when temperature came to $70\text{ }^\circ\text{C}$.

The reaction was maintained at 70 °C for 2 h. The resultant particles were washed with H₂O by repetitive centrifugation to remove residual Fe₃O₄ NPs in medium.

Attachment of Ag NPs

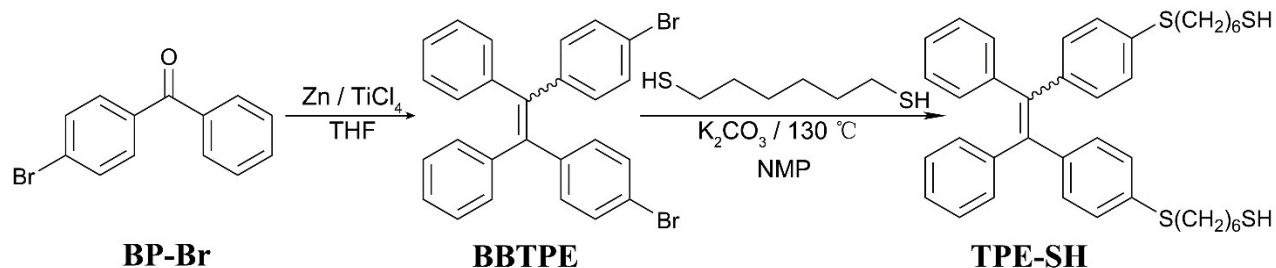
0.01 g AgNO₃, 0.05 g PPs were dispersed in 10 ml MeOH, and then the mixture was stirred in darkness for 8 h at room temperature to ensure the coordination of Ag⁺ with thiol sufficiently. Subsequently, PPs were recovered through centrifugation to remove superfluous Ag⁺ and redispersed in 20 ml MeOH. The dispersion was exposed to UV light (375 W high-pressure mercury lamp, incident light intensity, 12.5 W/m², λ=254 nm) for 10 min. The resultant particles were washed with MeOH by repetitive centrifugation to remove the residual Ag NPs in medium.

Post-functionalization of PPs.

0.1 g PPs, 0.05 g functional monomer (PFOA, OT, GSH) or 0.001 g TPE-SH were dispersed in 20 ml MeOH. Then, the dispersions were homogenized using magnetic stirring in a quartz vial for 30 min, and exposed to UV light (375 W, 12.5 W/m², λ=254 nm) for 2 h. The resultant particles were washed with MeOH by repetitive centrifugation to remove the superfluous monomer in medium.

Synthesis of 1, 2-bis (4-(6-mercaptohexylthio) phenyl)-1, 2-diphenylethene (TPE-SH).

TPE-SH was synthesized according to the following route:



Firstly, 1, 2-bis(4-bromophenyl)-1,2-diphenylethene (BBTPE) was synthesized according to literature (X. F. Duan, J. Zeng, J. W. Lü and Z. B. Zhang, *J. Org. Chem.*, 2006, **71**, 9873-9876). Briefly, zinc powder (1.6 g, 24 mmol) and 40 mL THF were added to a four-necked flask equipped

with a magnetic stirrer and a reflux condenser under an Ar atmosphere. The mixture was cooled to -5 to 0 °C, and TiCl_4 (1.3 mL, 12 mmol) was slowly added by a syringe with temperature kept under 10 °C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heated at reflux for 2.5 h. The solution of 4-bromobenzophenone (BP-Br, 2.4 mmol) in 15 mL THF was added slowly. After addition, the reaction mixture was heated at reflux until BP-Br was consumed. Then the mixture was quenched with 10% K_2CO_3 aqueous solution and taken up with CH_2Cl_2 . The organic layer was collected and concentrated. The crude material was purified by flash chromatography to give desired products.

Subsequently, according to literature (H. Matsushima, S. Hait, Q. Li, H. Zhou, M. Shirai and C. E. Hoyle, *Eur. Polym. J.*, 2010, **46**, 1278-1287), TPE-SH was synthesized. BBTPE (1 g, 2 mmol), and 1, 6-hexanedithiol (3.6 g, 24 mmol) were dissolved in 1-methyl-2-pyrrolidone (NMP, 20 mL). K_2CO_3 (1.5 g) was added and the reaction mixture was stirred and heated at 130 °C under nitrogen for 12 h. The mixture was cooled down to room temperature and washed by hexane three times to remove excess 1, 6-hexanedithiol. After concentration of the mixture, the residue was purified by column chromatography (SiO_2 , eluent 40% ethyl acetate in hexane) to give TPE-SH as a light green wax: ^1H NMR (CDCl_3) δ 7.15-6.82 (m, 18 H), 2.67 (t, 8 H), 1.47-1.23 (m, 18 H).

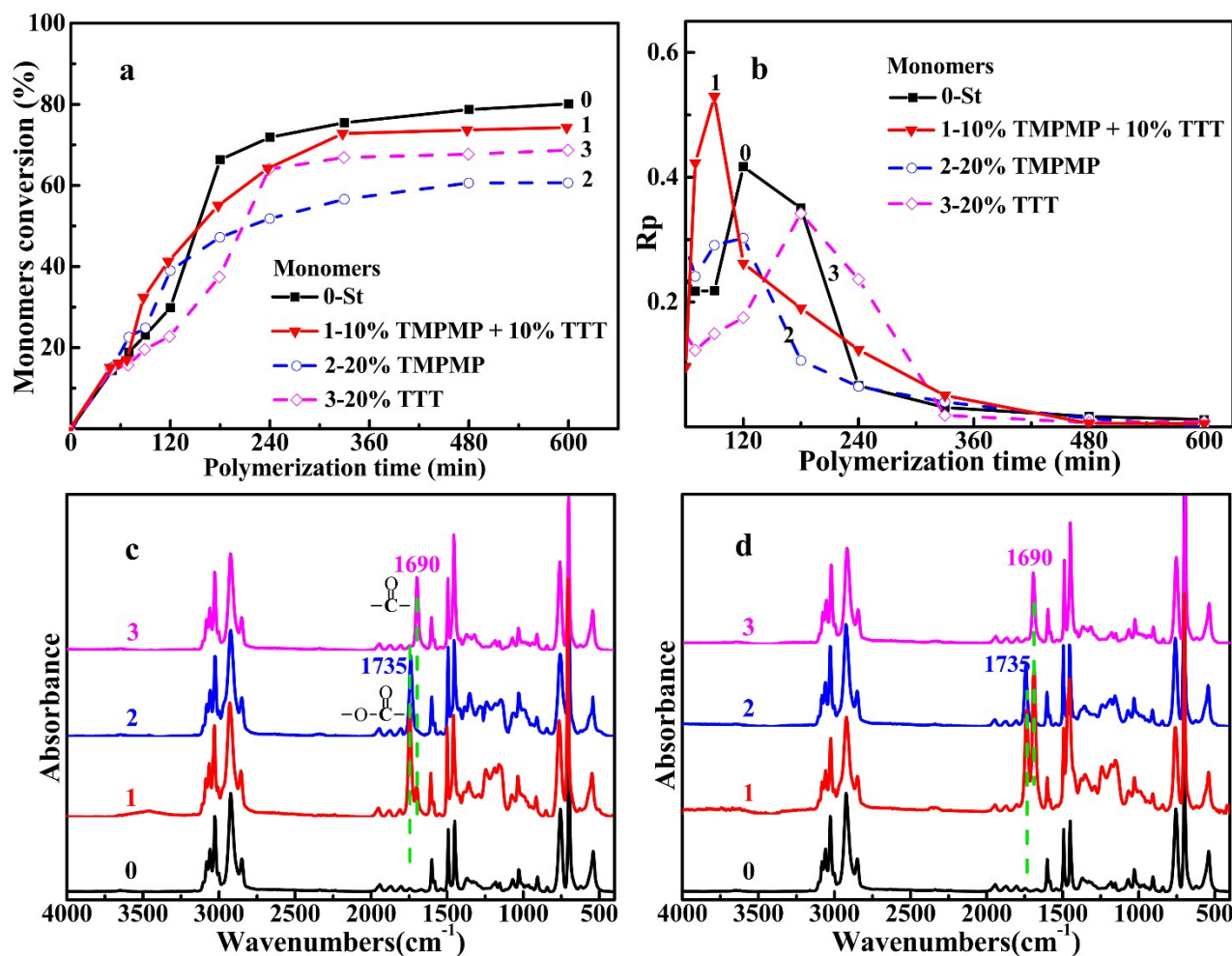


Fig. S1 (a) Monomers conversion, (b) reaction rate (R_p , differentiation of monomers conversion at various times) obtained during dispersion polymerization (Dis.P), in which thiol or/and ene were added at 50 min. (c, d) FTIR spectra of plain PSt particle (spectrum 0), PSt particles containing polymers of TMPMP and TTT (spectrum 1), polymers of TMPMP (spectrum 2), or polymers of TTT (spectrum 3). PSt particles containing polymers of TMPMP and/or TTT were prepared by adding TMPMP and/or TTT at 50 min (c) or at 330 min (d).

Table S1 The average size of body, dimples or bulges, PDI values and average numbers of dimple or bulge on PPs in Fig.1

Particles (Body Size, nm/PDI - Dimples or Bulges Size, nm/PDI) - Average Dimple or Bulge Numbers			
a1 (497/0.022- /)	a2 (434/0.019- /)	a3 (479/0.020-)	a4 (444/0.043-)
b1 (558/0.035- /)	b2 (660/0.018-131/0.037)-2.9	b3 (666/0.024-308/0.117)-1.2	b4 (664/0.014-213/0.073)-3.5
c1 (573/0.018- /)	c2 (653/0.021-130/0.030)-10.8	c3 (655/0.024-219/0.035)-11.4	c4 (693/0.030-320/0.042)-6.1
d1 (564/0.018-70/0.022)-4.2	d2 (640/0.028-186/0.040)-11.8	d3 (641/0.021-178/0.028)-12.0	d4 (643/0.028-183/0.032)-9.4

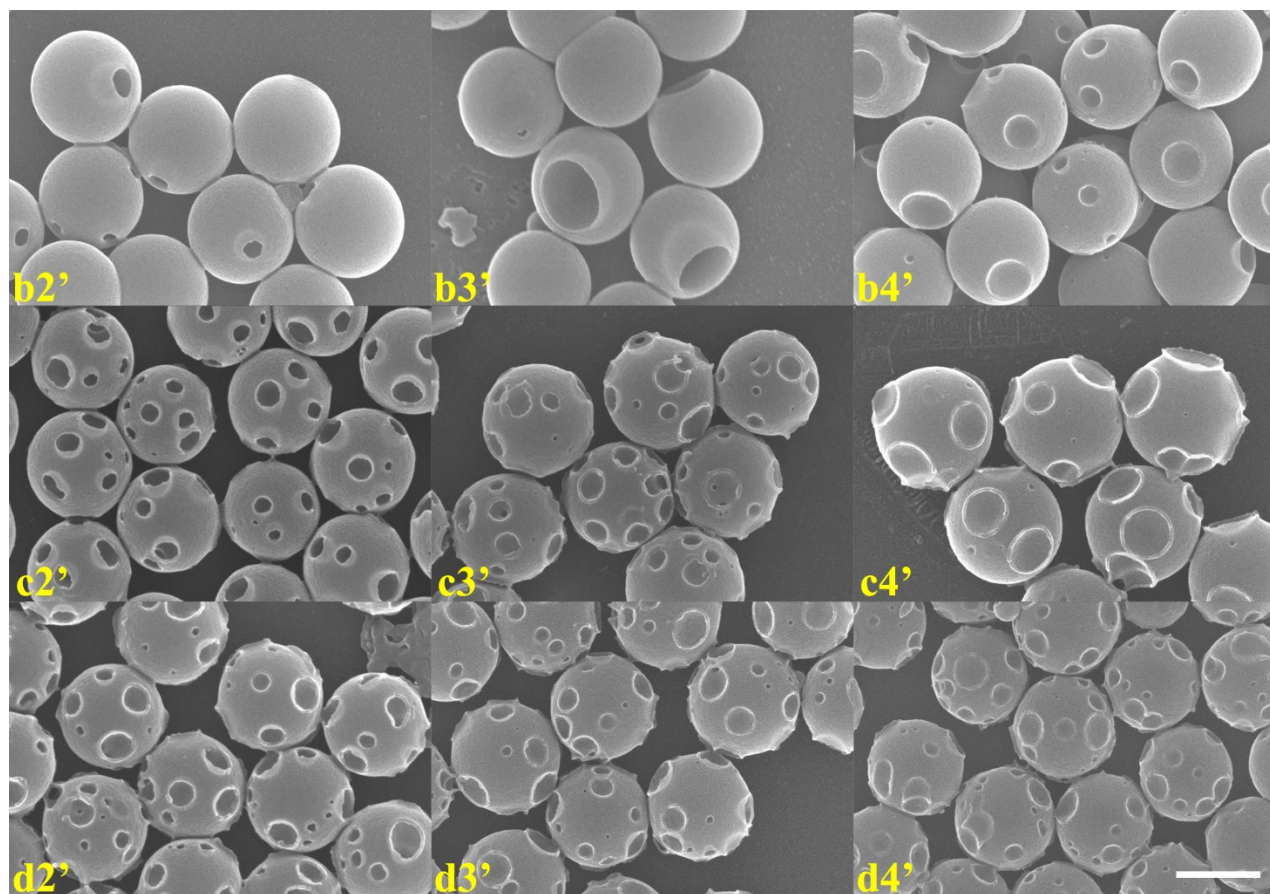


Fig. S2 SEM images of particles prepared when various amounts of TMPMP (8, 10, 15 %) and TTT (8, 10, 15 %) were added at 270 min (b2' - b4'), 330 min (c2' - c4'), 420 min (d2' - d4'), respectively, during polymerization of St, and then subjected to degradation in NaOH solution. Mole ratio of -C=C/-SH=1/1. Scale bars are 500 nm.

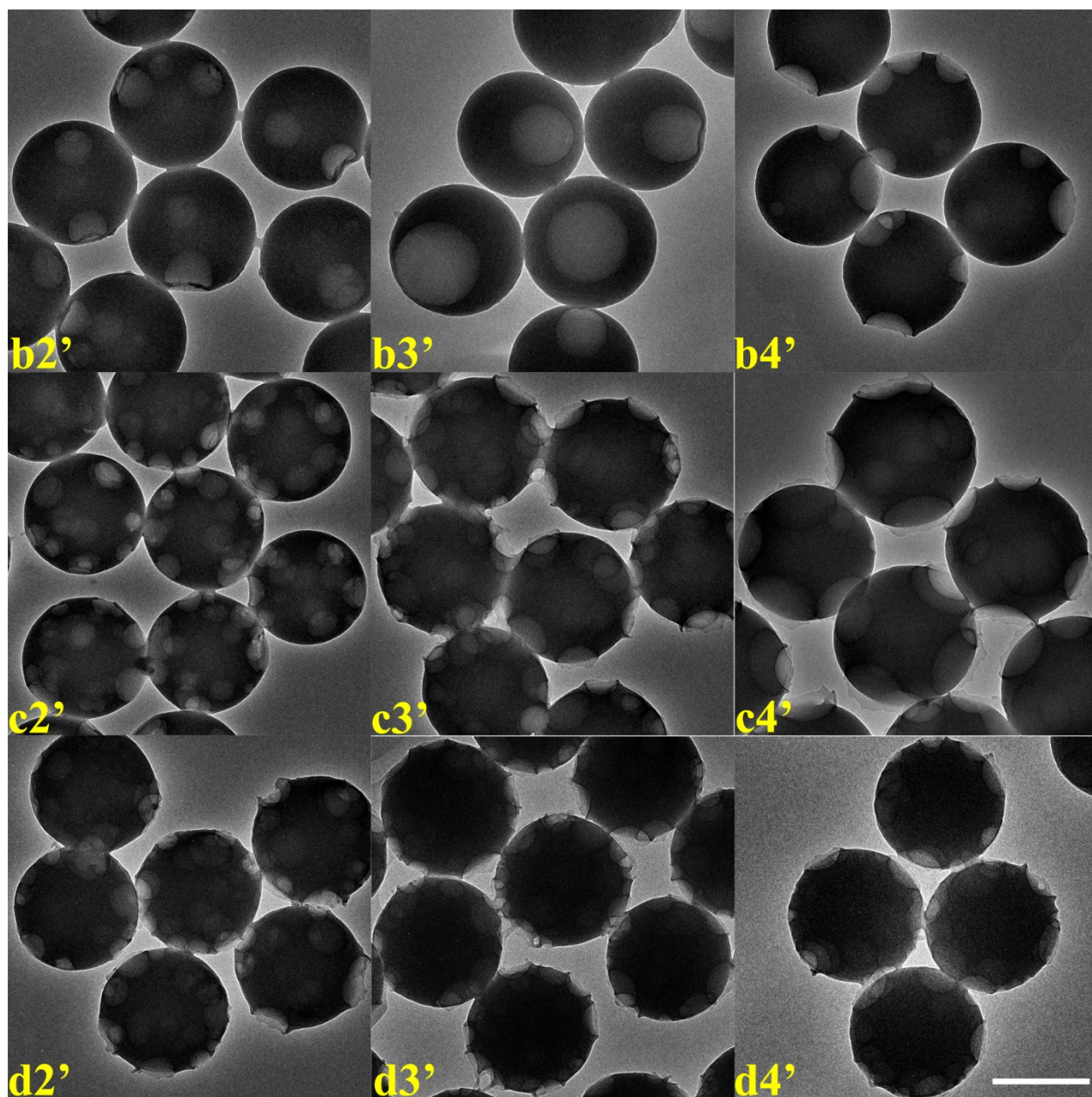


Fig. S3 TEM images of particles prepared when various amounts of TMPMP (8, 10, 15 %) and TTT (8, 10, 15 %) were added at 270 min (b2' - b4'), 330 min (c2' - c4'), 420 min (d2' - d4'), respectively, during polymerization of St, and then subjected to degradation in NaOH solution. Mole ratio of $-C=C-/-SH=1/1$. Scale bars are 500 nm.

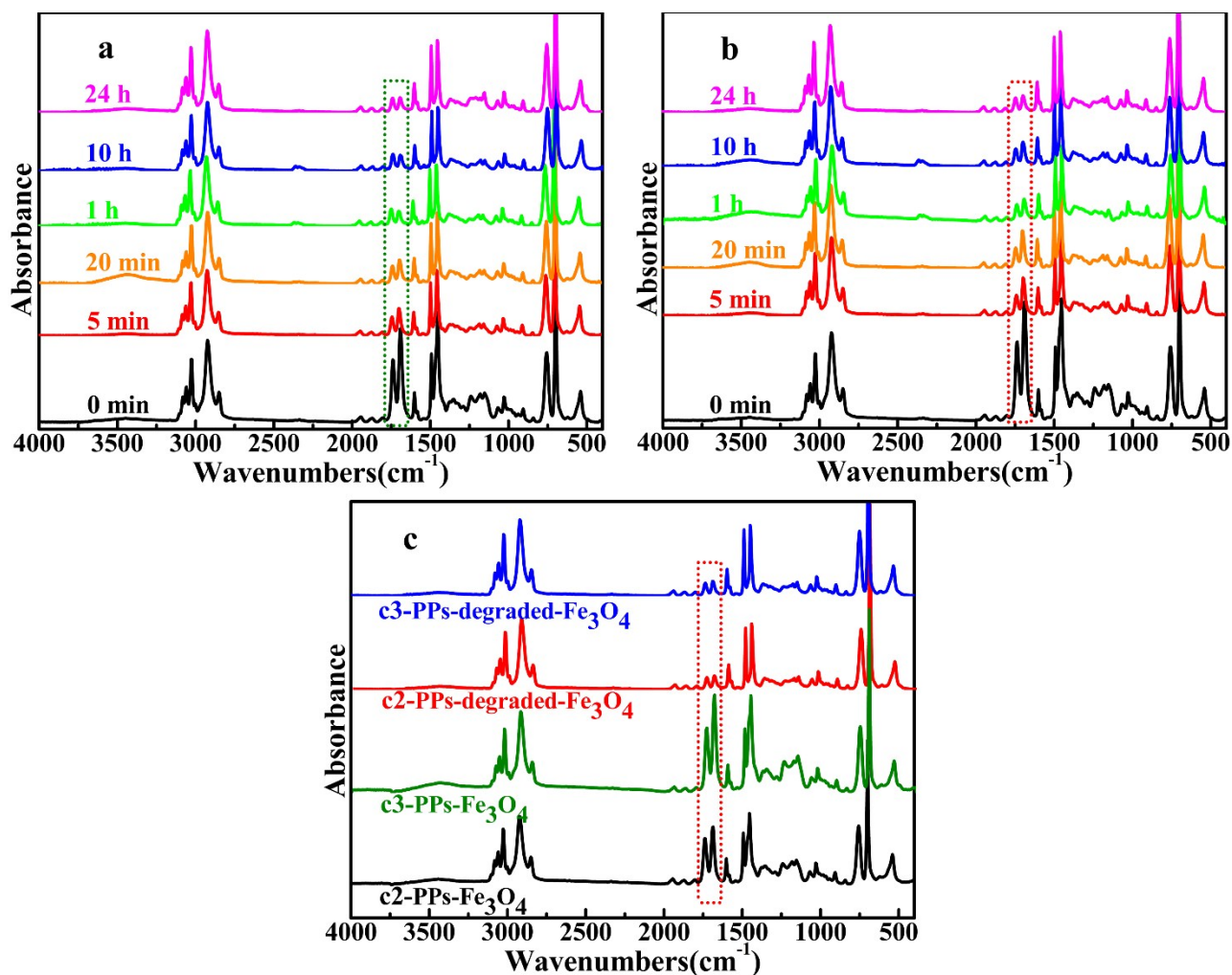


Fig. S4 FTIR spectra of PPs (a- PPs in Fig. 1 c2, b- PPs in Fig. 1 c3) obtained during degradation in NaOH solution. (c) FTIR spectra of PPs (c2- PPs in Fig. 1 c2, c3- PPs in Fig. 1 c3) attached with Fe_3O_4 NPs, or subjected to degradation in NaOH solution at first and then attached with Fe_3O_4 NPs.

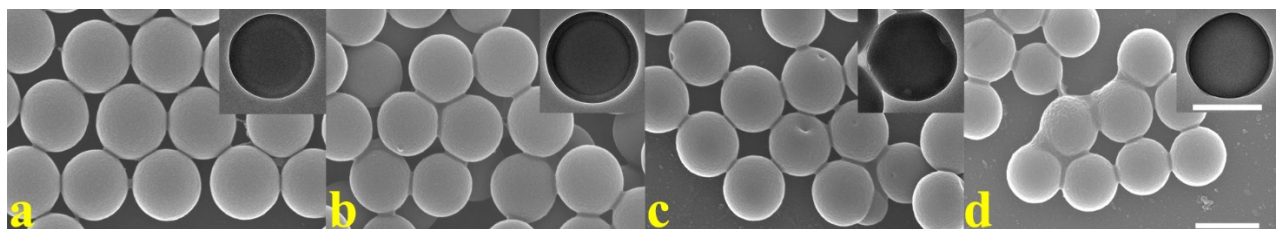


Fig. S5 SEM and TEM images of particles prepared when various amounts of TMPMP (a-4, b-8, c-10, d-15 %) and TTT (a-4, b-8, c-10, d-15 %) were added at 150 min during polymerization of St. Scale bars are 500 nm.

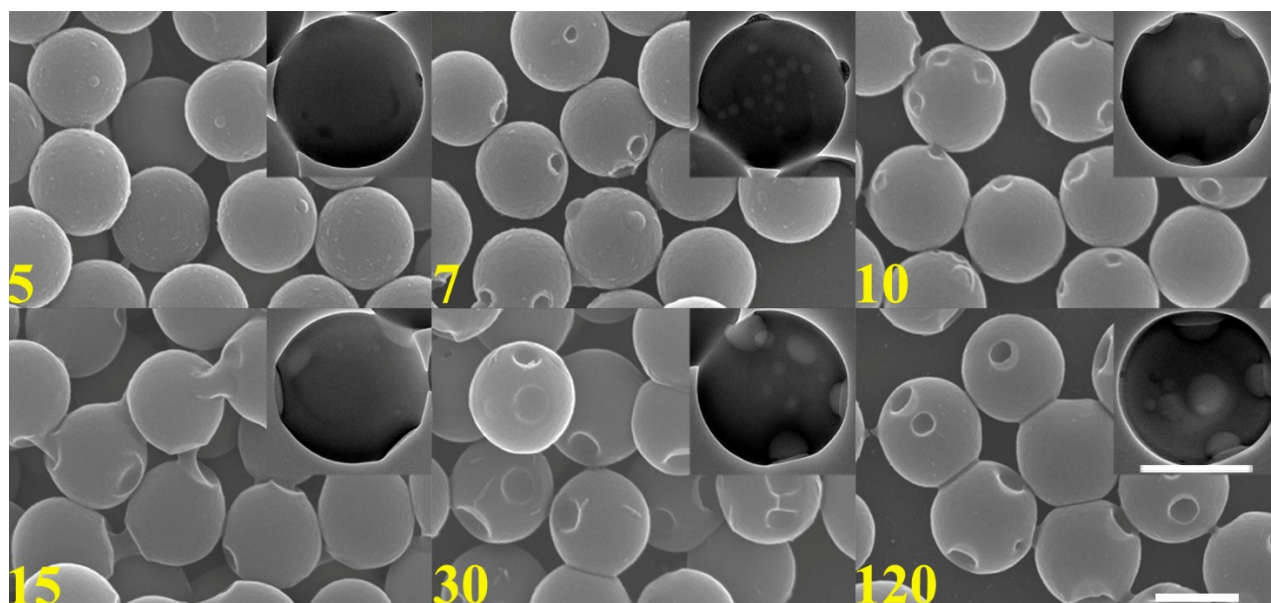


Fig. S6 SEM and TEM images (the upper right inserted) of particles formed after TMPMP (10%) and TTT (10%) were added at 240 min during polymerization of St. Mole ratio of $-C=C-/-SH=1/1$. 5 ~ 120 represents that the time after addition was 5, 7, 10, 15, 30, 120 min, respectively. Scale bars are 500 nm.

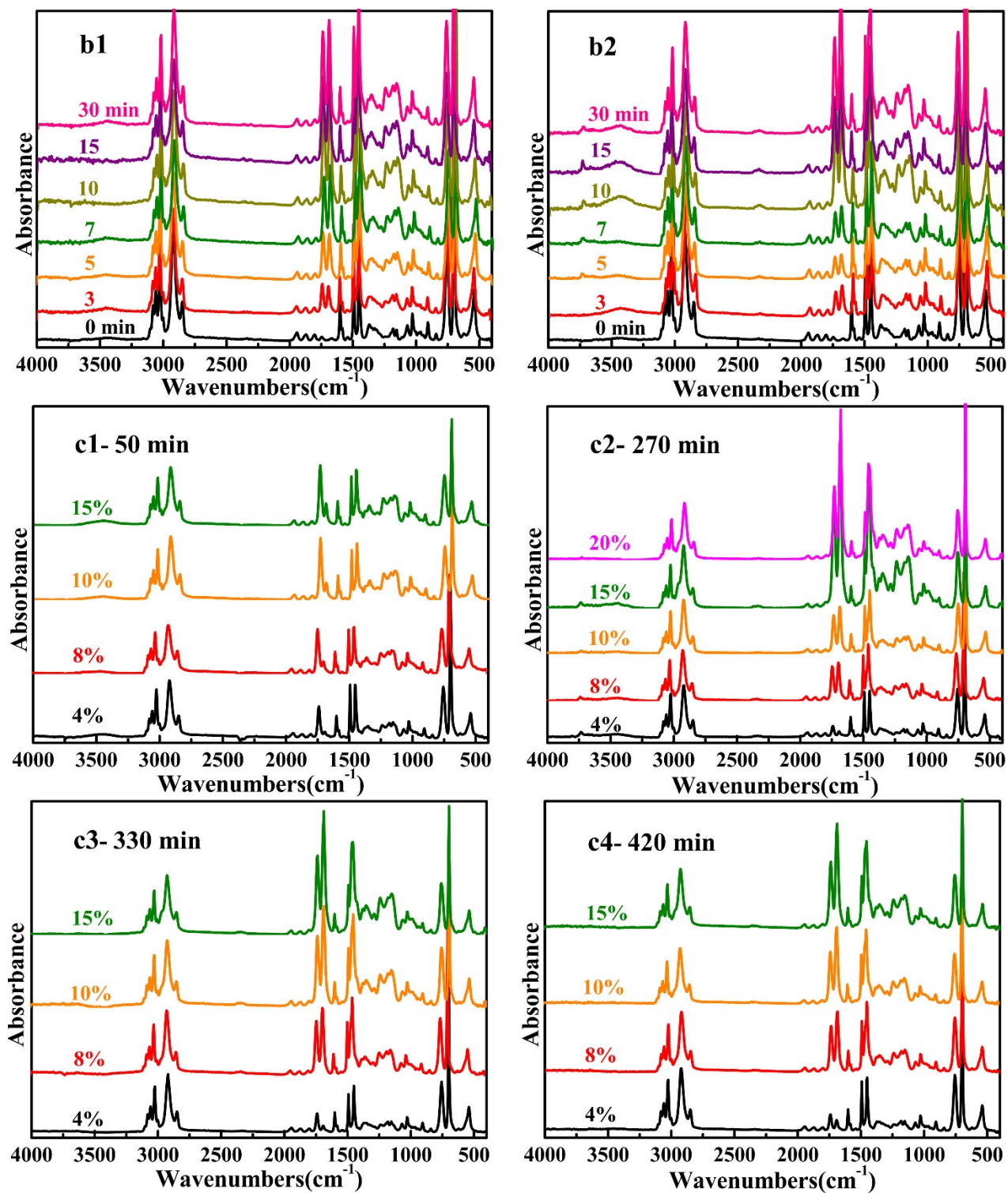


Fig. S7 FTIR spectra of particles produced after (b1) TMPMP (8%) and TTT (8%), or (b2) TMPMP (10%) and TTT (10%) were added at 330 min, or prepared by adding various amounts of TMPMP (4-20%) and TTT (4-20%) at (c1) 50, (c2) 270, (c3) 330, (c4) 420 min, respectively, during polymerization of St. Mole ratio of -C=C-/-SH =1/1.

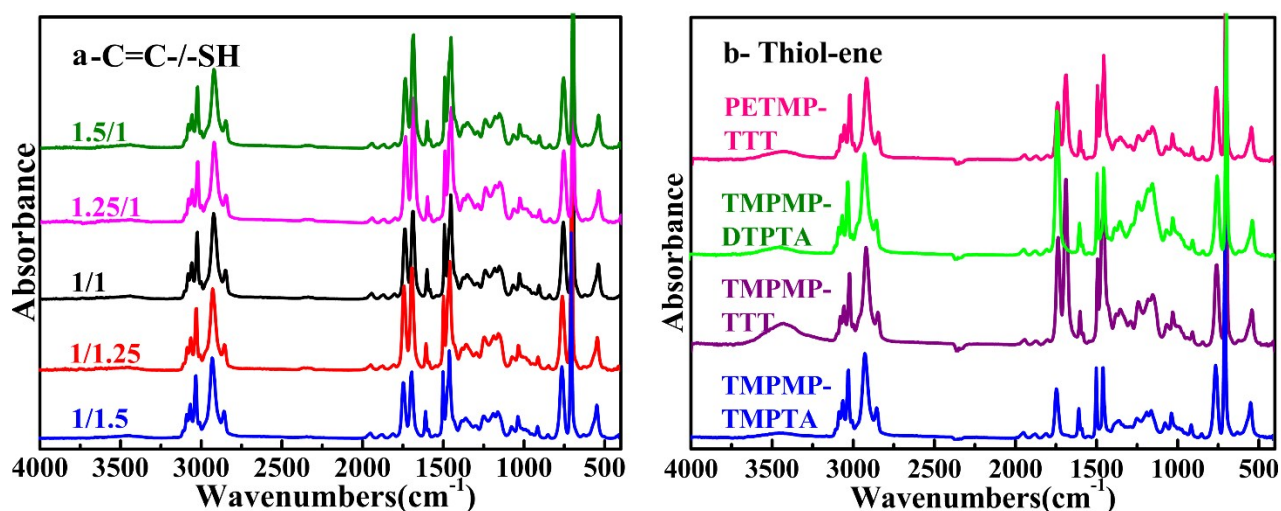


Fig. S8 FTIR spectra of particles fabricated by adding (a) TMPMP (8%) and TTT (8%) with different mole ratio of -C=C-/SH (1/1.5, 1/1.25, 1/1, 1.25/1, 1.5/1), or (b) different thiol-ene pairs (mole ratio of $\text{-C=C-/SH}=1/1$) at 330 min during polymerization of St.

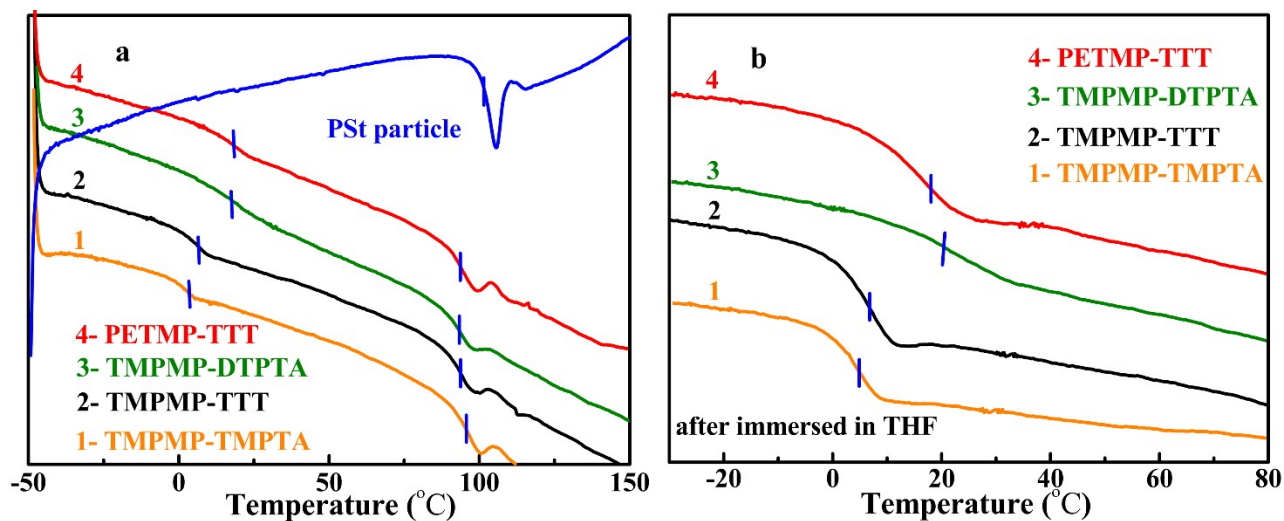
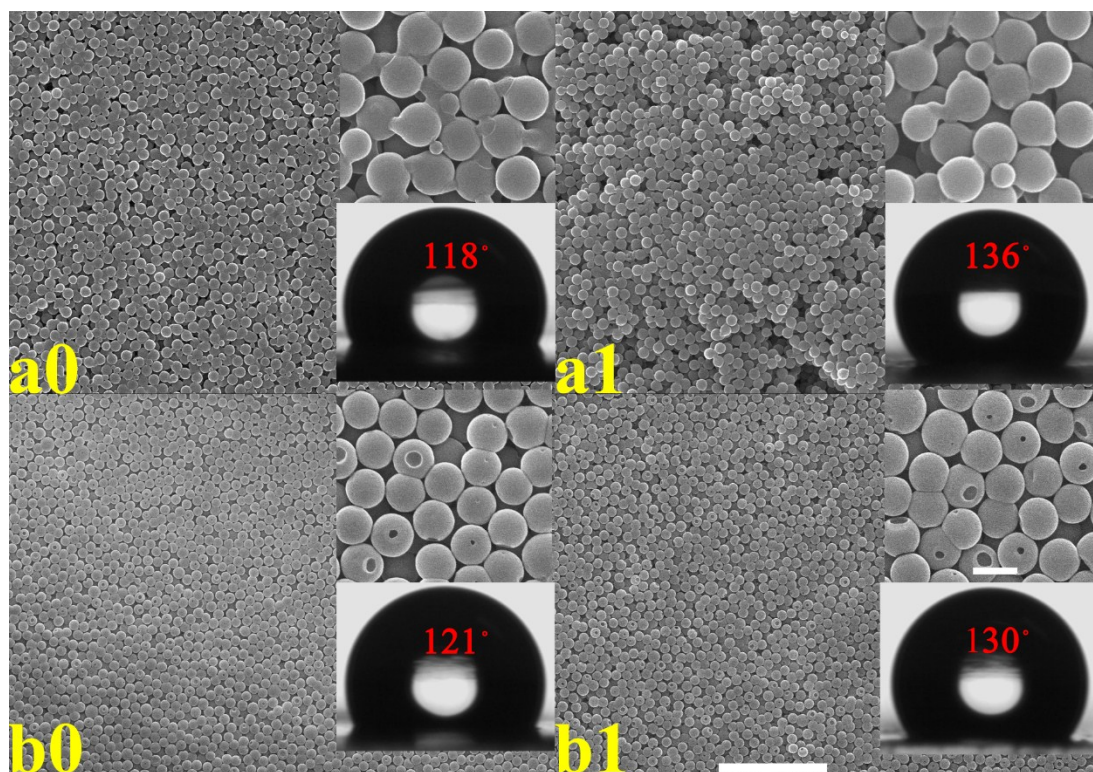
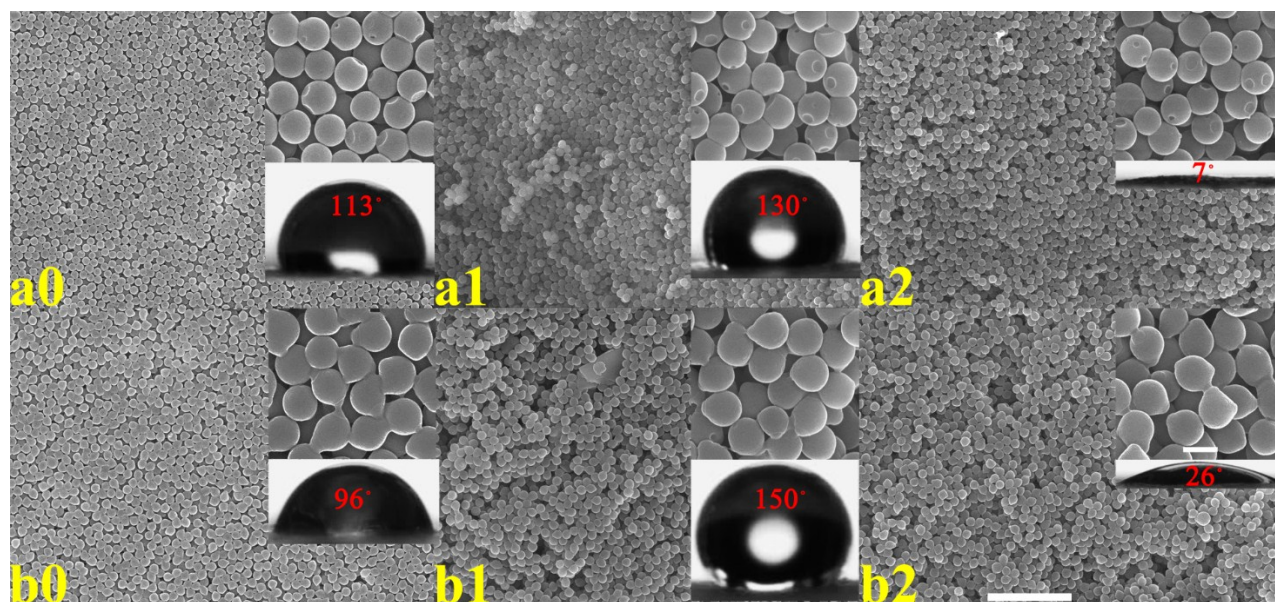


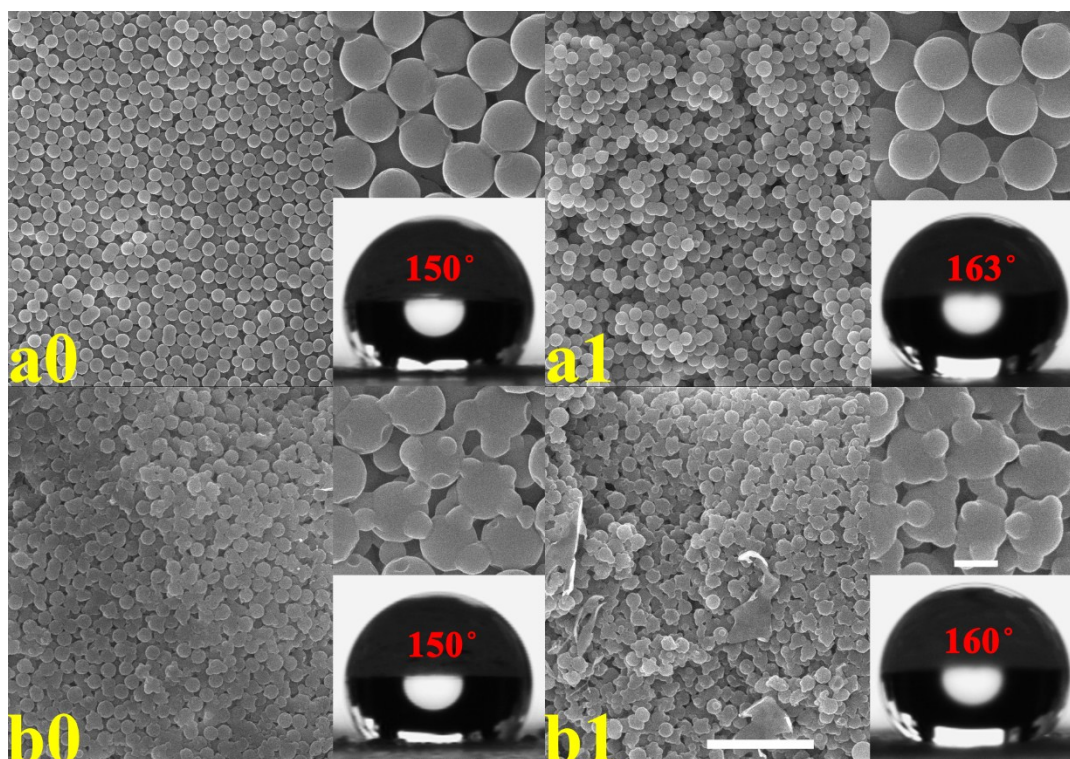
Fig. S9 DSC curves of (a) plain PSt particles prepared without using thiol, ene monomers, particles synthesized by adding different thiol-ene pairs (mole ratio of $\text{-C=C-/SH}=1/1$) at 330 min during polymerization of St, and (b) click polymer gels obtained by immersing the particles in THF to remove PSt.



1- Films were formed from PPs in Fig. 4 c20 (a0), c21 (b0) and corresponding PPs post-modified with PFOA (a1, b1)



2- Films were prepared from PPs in Fig. 4 c22 (a0), c23 (b0) and corresponding PPs post-modified with OT (a1, b1), or GSH (a2, b2).



3- Films were generated from PPs in Fig. 1 b4 (a0), c4 (b0) and corresponding PPs post-modified with OT (a1, b1).

Fig. S10 SEM images of particulate films and CA measured on them

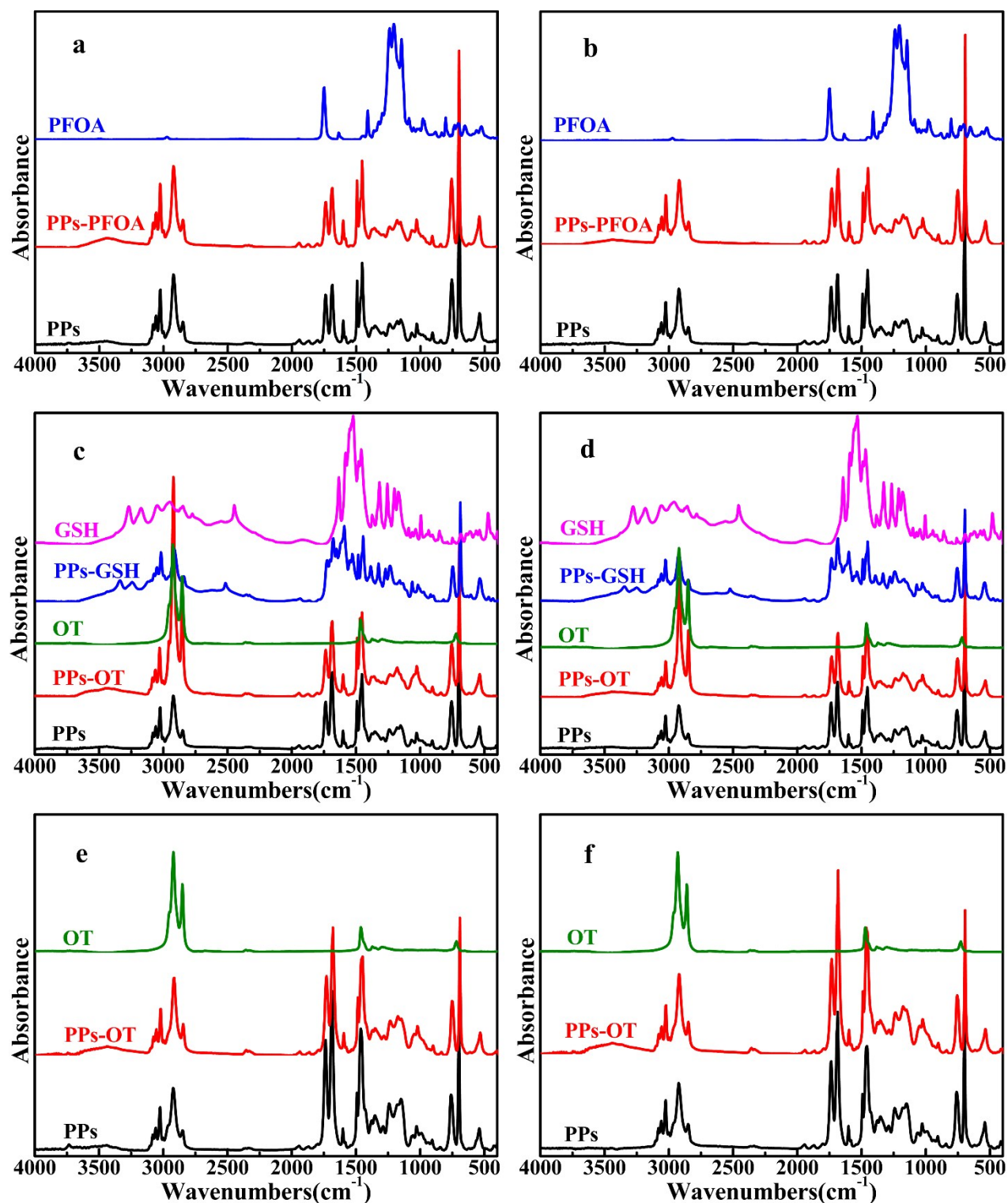


Fig. S11 FTIR spectra of particles displayed in (a) Fig. 4 c20 ($-\text{C}=\text{C}-/\text{SH}=1/1.5$), (b) Fig. 4 c21 ($-\text{C}=\text{C}-/\text{SH}=1/1.25$), (c) Fig. 4 c22 ($-\text{C}=\text{C}-/\text{SH}=1.25/1$), (d) Fig. 4 c23 ($-\text{C}=\text{C}-/\text{SH}=1.5/1$), (e) Fig. 1 b4 ($-\text{C}=\text{C}-/\text{SH}=1/1$), (f) Fig. 1 c4 ($-\text{C}=\text{C}-/\text{SH}=1/1$) and post-modified with PFOA, GSH, or OT.