Supporting Information

for

Preparation of Mechanoresponsive Hairy Particles Using Polymeric Surfactant in Emulsion Polymerization

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1. Materials and methods

1.1. Instrumentation

^{1}H-NMR spectra were obtained using a 400 MHz Varian Mercury VX spectrometer at room temperature using residual protonated solvent signals[1] as internal standards. Gel permeation chromatography (GPC) was performed with a DAWN HELEOS-Ⅱ GPC system employing THF as solvent at a flow rate of 0.5 mL/min. An Agilent PLgel MIXED-C column was utilized and run at: 45 °C. Molecular weights were determined with respect to narrow polystyrene standards and not corrected. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry was carried out using a Bruker SolariX FTMS (9.4 T) equipped with a 337 nm nitrogen laser. The sample was dissolved in CDCl3, 2,5-dihydroxybenzoic acid was used as the matrix. TLC was carried on Merck Silica Gel 60 F254 TLC plates with a fluorescent indicator employing a 254 nm UV-lamp for visualization. The particle size distributions of micelles were characterized by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS instrument at 25 °C. Data acquisition and analysis were carried out on Malvern Dispersion Software，using the

general purpose algorithm for calculating size distributions. The particle size distribution of latex was determined using a laser particle analyzer (LS13320, Beckman Coulter Instruments). Fluorescence spectroscopy was performed on a F-4600 FL spectrometer (Hitachi, Japan) at room temperature. Scanning electron microscopy (SEM, JSM 6700F, JEOL, Japan) and transmission electron microscope (TEM, JEOL, Japan) were used to observe the morphology of latices particles before and after sonication. Sonochemical irradiation experiments were carried out with a Sonics VCX 500 W ultrasonic processor purchased from Sonics & Materials Inc.

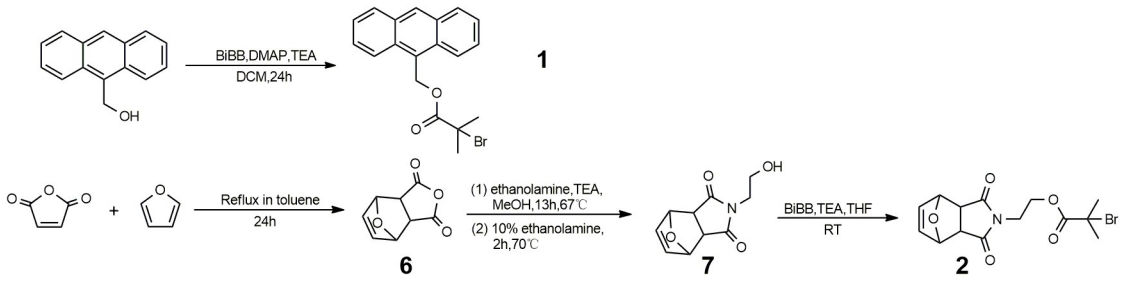
1.2. Materials

All starting materials and solvents were obtained from commercial suppliers. Monomers were filtered through a short column of inhibitor remover before use. All solvents were dried before use, if necessary, employing an MBraun MB-SPS-800 solvent purification system. Silica gel for chromatography (0.040-0.063 mm, 60 Å) was used for column chromatography.

2. Experimental details

2.1 Synthesis of Anthracene and Maleimide-derived initiators

The synthesis of target initiators **1** and **2** was carried out according to Scheme S1.



Scheme S1. Synthesis procedures of anthracene and maleimide-derived initiators **1** and **2**.

2.1.1. Synthesis of 9-anthyryl-methyl 2-bromo-2-methyl propanoate (1)

The compound was prepared according to a literature procedure by Moore and coworkers.[2] A solution of 9-anthracene methanol (10 g, 48 mmol) and 4-dimethyl-aminopyridine (586 mg, 4.8 mmol) in dichloromethane (240 mL) was prepared. Triethylamine (8.4 ml, 60 mmol) was added and the reaction mixture was cooled to 0 °C, 2-bromo *iso*butyryl bromide (6 mL, 60 mmol) was added dropwise over the course of 5 min. The reaction mixture was stirred for 1 h at 0 °C and

then for 24 h at room temperature. The resultant solution was washed with water, a sat. aq. soln. of $NaHCO_3$, and then again with water. Traces of water were removed by drying over $MgSO_4$. Solvent removal under reduced pressure yielded a yellow oil. Purification by column chromatography (silica, cyclohexane/ethyl acetate = 9/1 (v/v)) provided a light yellow solid (14.0 g, 39 mmol, 82%). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ(ppm) = 8.54 (s, 1H, CH_{ar}), 8.36 (d, 2H, 2xCH_{ar}), 8.04 (d, 2H, 2xCH_{ar}), 7.51-7.61 (m, 4H, 2x2xCH_{ar}), 6.24 (s, 2H, CH_2O), 1.89 (s, 6H, C(CH_3)$_2$Br) (Figure S1).

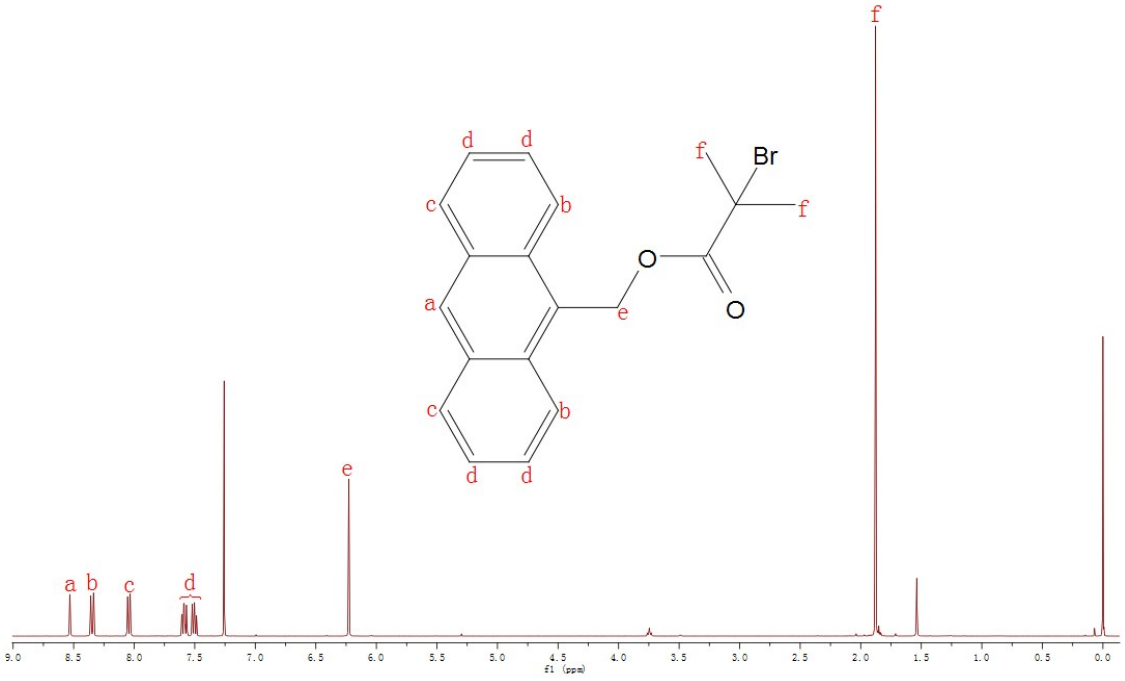


Figure S1. ^{1}H NMR spectrum of anthracene-derived initiator **1**

2.1.2. Synthesis of 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-en-4-yl) ethyl ether (2)

This compound was synthesized according to a literature procedure by Haddleton and coworkers.[3] Maleic anhydride (30.0 g, 306 mmol) was dissolved in toluene (150 mL) by heating the solution to 80 °C. Furan (33.4 mL, 459 mmol) was added *via* a syringe and the reaction mixture was refluxed at 120 °C for 24 h and then cooled down to room temperature. White crystals were obtained after lowering the temperature to 0 °C for 1 h. They were washed with petroleum ether (3×30 mL). After drying, the Diels-Alder adduct **6** was obtained as white crystals (27.7 g, 167 mmol) with a

yield of 55%. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ(ppm) = 6.59 (t, ^3J = 0.9 Hz, 2H, C*H*=C*H*), 5.47 (t, ^3J = 0.9 Hz, 2H, C*H*-O-C*H*), 3.19 (s, 2H, C*H*-C*H*).

The Diels-Alder adduct **6** (15.0 g, 90 mmol) was dissolved in methanol (375 mL). The solution was purged with N_2 for 10 min while immersed in an ice bath. Ethanolamine (6 mL, 99 mmol, 1.1 eq) was added as well as triethylamine (12.5 mL, 90 mmol). The temperature was increased to 67 °C and the reaction mixture was stirred. After 13 h, 10% additional ethanolamine (0.6 mL, 1 mmol) was added and the temperature was increased to 70 °C over 2 h. The reaction mixture was cooled to room temperature and white crystals precipitated. They were washed with isopropyl alcohol to obtain compound **7** (13.1 g, 63 mmol) with a yield of 70%. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ(ppm) = 6.53 (t,$^3J_{H,H}$ = 0.9 Hz, 2H, C*H*=C*H*), 5.29 (t, $^3J_{H,H}$ = 0.9 Hz, 2H, C*H*-O-C*H*), 3.80-3.69 (m, 4H, NCH_2CH_2OH), 2.90 (s, 2H, C*H*-C*H*), 2.25 (s, 1H, CH_2OH).

Compound **7** (6.0 g, 29 mmol) was dissolved in triethylamine (4.33 mL, 31.6 mmol) and THF (325 mL). The solution was cooled to 0 °C. A solution of 2-bromo *iso*butyryl bromide (3.78 mL, 31 mmol) in THF (110 mL) was added dropwise during 30 min. The reaction mixture was stirred at 0 °C for 3 h and then let to react overnight at room temperature. The ammonium salt was filtered off and a pale yellow residue was obtained after solvent removal under reduced pressure. The product was purified by column chromatography (silica, cyclohexane/ethyl acetate = 9/1 (v/v)) to yield compound **2** (3.2 g, 9 mmol) as a light brown solid with a yield of 31%. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ(ppm) = 6.52 (t, $^3J_{H,H}$ = 0.9 Hz, 2H, C*H*=C*H*), 5.27 (t, $^3J_{H,H}$ = 0.9 Hz, 2H, C*H*-O-C*H*), 4.34 (t, $^3J_{H,H}$ = 5.28 Hz, 2H, CH_2O), 3.82 (t, $^3J_{H,H}$ = 5.28 Hz, 2H, NCH_2), 2.88 (s, 2H, C*H*-C*H*), 1.90 (s, 6H, C(CH_3)$_2$Br) (Figure S2).

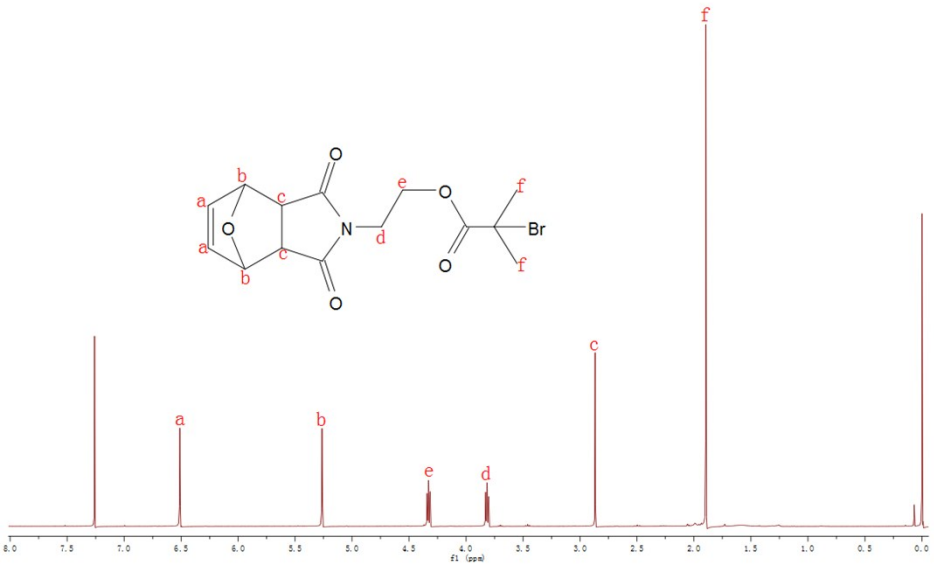


Figure S2. ^{1}H NMR spectrum of maleimide-derived initiator

2.2. Synthesis of anthracene functionalized P*t*BA by ATRP (3)

tert-butyl acrylate (5.0 mL, 34.44 mmol), Me_6TREN (32.22 µL, 120.57 µmol), CuBr (17.29 mg, 120.57 µmol), the anthracene initiator **1** (41.02 mg, 120.57 µmol), DMSO (1.0 mL) were added in a Schlenk flask. Three freeze-pump-thaw cycles were carried out to remove oxygen. Then, the Schlenk flask was allowed to stir under argon at room temperature. After 8 h, the isolated solution was diluted with THF and then filtered through a plug of basic Al_2O_3 to remove the copper catalyst. The polymer solution was added dropwise to stirred, ice-cold methanol/water (1:1, v/v) mixture. Methanol/water mixture was decanted and the polymer solid redissolved in THF. After repeating the precipitation process 3 times, the obtained polymer solid was dried under vacuum. **GPC:** M_n = 18.52 kg/mol, $Đ$ = 1.29.

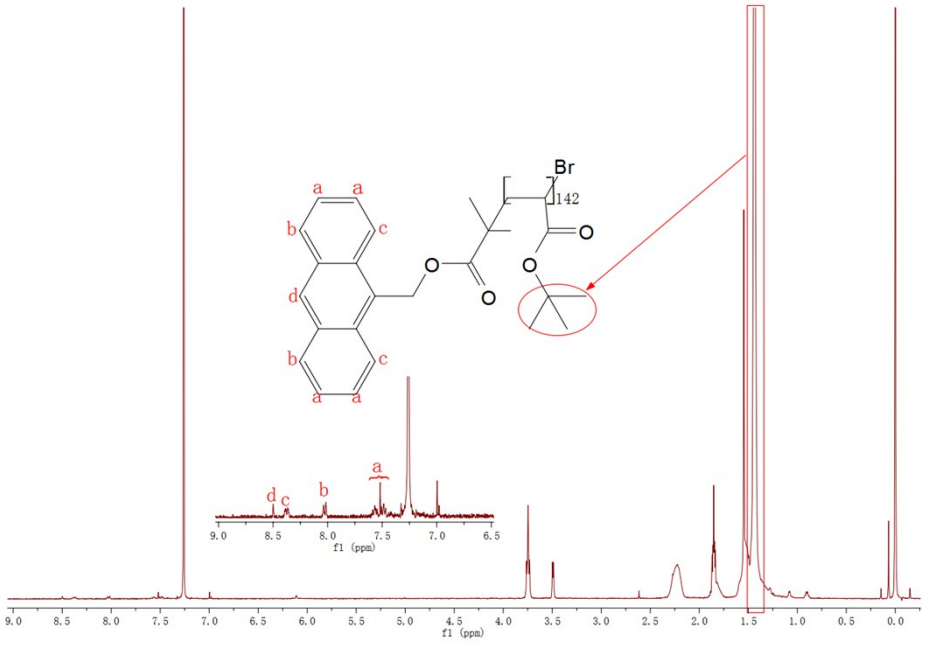


Figure S3. ^{1}H MNR spectrum of anthracene functionalized P*t*BA **3**.

2.3. Synthesis of maleimide functionalized PS by SET-LRP (4)

In a Schlenk flask, styrene (1.0 mL, 8.73 mmol), PMDETA (9.08 µL, 43.6 µmol), the maleimide initiator **2** (15.6 mg, 43.6 µmol), $CuBr_2$ (1 mg, 4.6 µmol), and DMF (0.5 mL) were added. Three freeze-pump-thaw cycles were carried out to remove oxygen. At the same time, copper wire (0.5 cm) was activated with conc. HCl, subsequently rinsed with water and acetone and then dried.

The polymerization was started by adding the activated copper wire under argon. After 20 h, the reaction mixture was diluted with THF and then filtered through a plug of basic Al_2O_3 to remove the copper catalyst. The polymer solution was added dropwise to stirred, ice-cold methanol. Methanol was decanted and the white solid product redissolved in THF. After repeating the precipitation process 3 times, the final white solid product was dried under vacuum. **GPC:** M_n = 5.1 kg/mol, $Đ$ = 1.14.

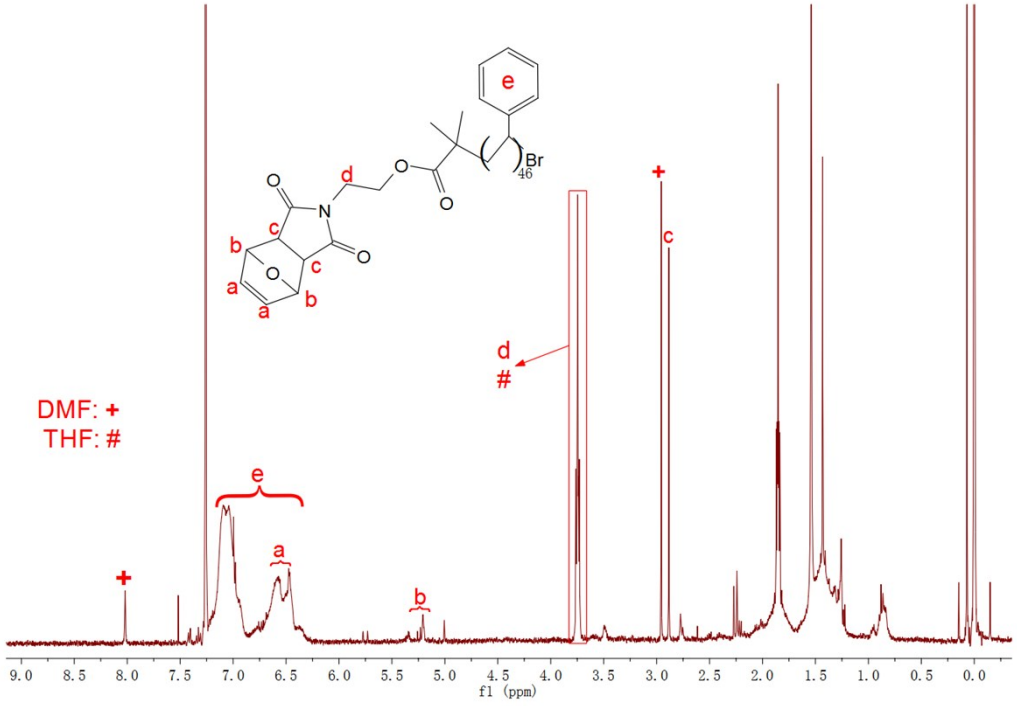
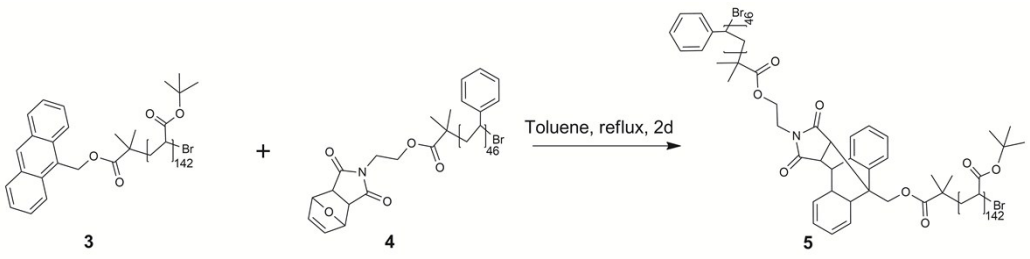


Figure S4. ^{1}H MNR spectrum of maleimide functionalized PS **4**.

2.4. Synthesis of block copolymer PS_{46}-*b*-P*t*BA_{142} by Diels Alder reaction



Scheme S2. Synthesis procedures of block copolymer PS_{46}-*b*-P*t*BA_{142}.

As shown in Scheme S2, a solution of anthracene functionalized P*t*BA (0.378 g, 20 µmol) in 5 mL of toluene was added to 0.116 g of maleimide functionalized PS (23 µmol) in 5 mL of toluene.

The mixture was degassed by bubbling argon for 1 h and then refluxed for 48 h under argon. The solvent was removed under vacuum. The obtained polymer was added dropwise to stirred, ice-cold methanol. Methanol was decanted and the polymer solid redissolved in THF. After repeating the precipitation process 3 times, the obtained polymer solid was dried under vacuum. **GPC:** M_n = 17.51 kg/mol, $Đ$ = 2.03.

2.5. Acidolysis procedure of PS-*b*-P*t*BA to PS-*b*-PAA (5)

PS-*b*-P*t*BA block copolymer was dissolved in dichloromethane to obtain a concentration of 150 g/mol and 5 eq. of trifluoroacetic acid relative to the *t*BA units was added.[4] The solution was stirred at room temperature for 48 h. After removing the solvent and trifluoroacetic acid *in vacuo*, further elimination of the residual acid and solvent traces was carried out by 2 cycles of redissolution in dichloromethane/methanol (10/1, v/v) and drying under vacuum.

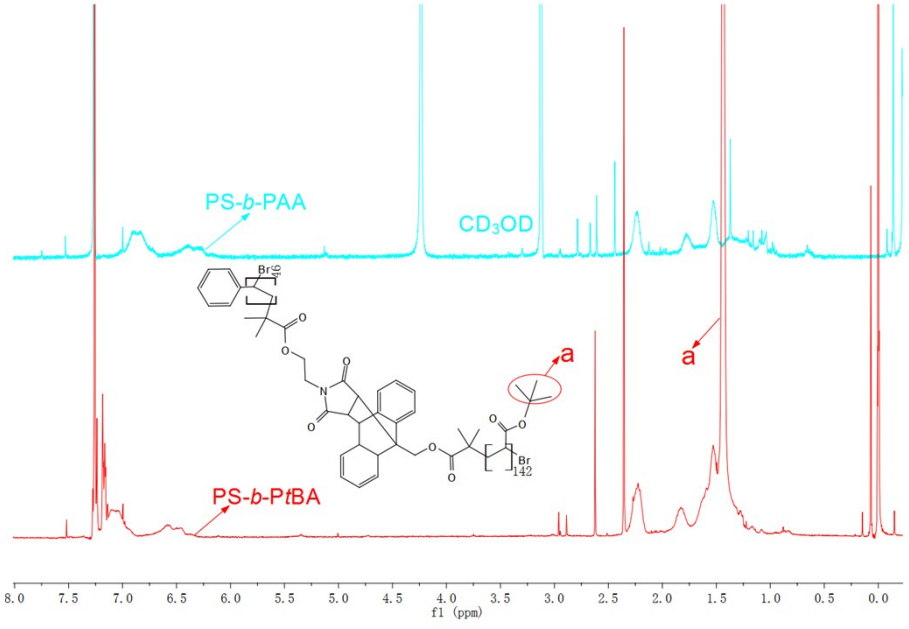


Figure S5. ^{1}H MNR spectra of PS-*b*-P*t*BA and PS-*b*-PAA **5**.

2.6. Emulsion polymerization of butyl acrylate with PS_{46}-*b*-PAA_{142} amphiphilic block copolymers as surfactant

All the emulsion polymerizations of butyl acrylate were carried out in a three-neck flask with a reflux condenser, an argon inlet, and magnetic stirrer. The recipes used for preparation of mechanically responsive latex particles are summarized in Table 1. In a typical reaction process,

the micellar solution self-assembled by PS_{46}-*b*-PAA_{142} (2.16 mL, 0.054 g) was transferred to a 25 mL flask, and then 3 mL water was added. The monomer butyl acrylate (1.8 g) was added to above mixture solution under stirring. After the mixture solution was purged with argon 30 min, the redox initiator $Na_2S_2O_3$/($(NH_4)_2S_2O_8$) (9.1×10^{-5} mol /6.3×10^{-5} mol) was injected into reaction solution by syringe, respectively. At different reaction times, a latex sample was extracted using syringe for determination of monomer conversion.

Table 1. Recipes for emulsion polymerization of butyl acrylate with PS_{46}-*b*-PAA_{142} block copolymer as stabilizers

sample	BA[a] (wt %)	EGDMA[b] (wt %)	Surfactant[c] (wt %)	initiator[d] (wt %)	*T* (℃)	D_{DLS}[e] (nm)	*PDI* by DLS	D_{TEM}[f] (nm)	M_n (kDa)	*PDI* by GPC
1	15	0	3.0	0.8	35	366	0.265	92±10	916	1.61
2	15	1	3.0	0.8	35	278	0.124	105±10	550	1.67
3	15	3	3.0	0.8	35	295	0.197	110±10	-	-

[a]*BA* content was based on overall composition. [b]The dosage of EGDMA was based on butyl acrylate. [c]The amount of PS_{46}-*b*-PAA_{142} was based on total monomer. [d]Redox initiator system ($Na_2S_2O_3$/$(NH_4)_2S_2O_8$) based on total monomer was used in all the polymerizations at 35 ℃. [e]Particle size was measured by DLS. [f]Number-average particle diameter was calculated from TEM using software ImageJ.

3. Sonication experiments

Sonication experiments were carried out using a Sonics VCX 500 W ultrasonic processor with a 13 mm probe, a frequency of 20 kHz and 30% of the maximum amplitude of 125 μm. Pulsed sonication (1s on, 2s off) was used. Block copolymer PS_{46}-*b*-PAA_{142} (ρ = 3 mg·mL^{-1}, 0.5 mL of micellar solutions and 9.5 mL water) was dissolved in water and injected into a cooled Suslick cell (2 °C) with a constant flow of CH_4. Samples were withdrawn at different intervals with a syringe for analyzing by DLS (Figure S7) and fluorescence spectroscopy. Fluorescence spectroscopy, samples of 0.5 mL were withdrawn from the sonicated solution and diluted with 2 mL of water (c = 3.98×10^{-6} mol/L). To roughly quantify the amount of Diels-Alder adducts cleaved by ultrasonication of a micellar aqueous solution of PS_{46}-*b*-PAA_{142}, the emission of anthracene was calibrated with solutions of known concentrations. As anthracene is not soluble in water, sodium dodecyl sulfate was employed as surfactant (Figure S6). However, this slightly changes absorption and emission spectra so the calibration curve can only be regarded as a rough

estimate. A concentration of 1.86×10^{-6} mol/L of free anthracene end groups was calculated for a solution of PS_{46}-b-PAA_{142} that had been sonicated for 120 min. This corresponds to approximately 45% scission of block copolymer.

Emulsion samples (ρ = 20 mg·mL^{-1}) were injected into a cooled Suslick cell (2 °C) with a constant flow of CH_4. Samples were withdrawn with a syringe at regular intervals for analysis by DLS and fluorescence spectroscopy. For fluorescence spectroscopy, samples of 0.5 mL were withdrawn from the sonicated solution and water was removed water by rotary evaporation. Then the sample was dissolved in 2 mL MeOH/$CHCl_3$ mixture ($c = 1.25 \times 10^{-5}$ mol/L). A concentration of 1.75×10^{-6} mol/L of free anthracene end groups was calculated for the sample containing 3% crosslinker after sonication for 150 min, corresponding to approximately 15% scission of the block copolymer.

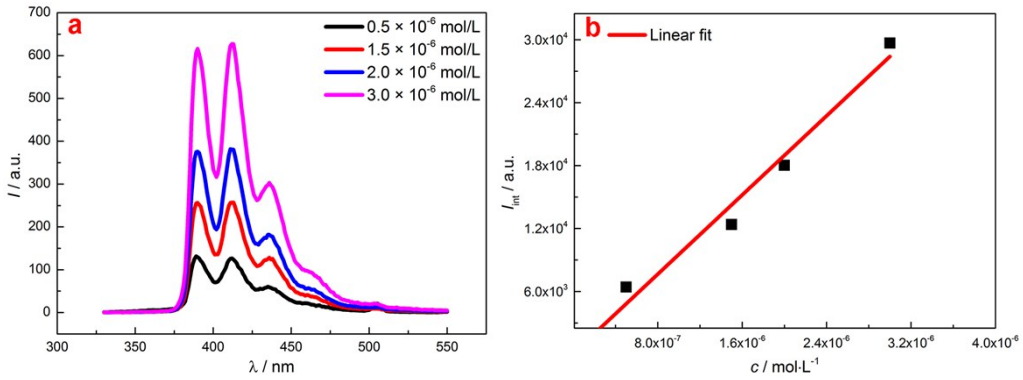


Figure S6. Concentration calibration for fluorescence of anthracene in aqueous 0.1 M sodium dodecyl benzene sulfonate solution (λ_{exc} = 252 nm). a) Emission spectra at different anthracene concentrations. b) Integrated fluorescence intensity as a function of concentration including linear fit.

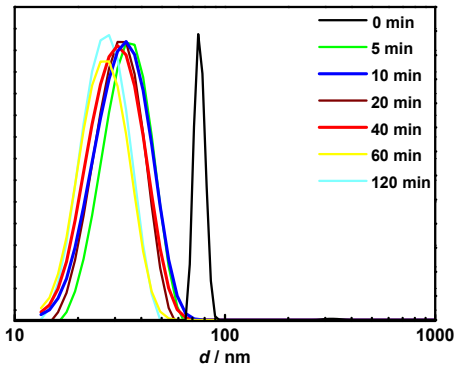


Figure S7. Size distribution of micellar solutions of PS_{46}-*b*-PAA_{142} in water before and during sonication

4. References

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(3) Syrett, J. A.; Mantovani, G.; Barton, W. R.; Price, D.; Haddleton, D. M. *Polymer Chemistry* **2010**, *1*, 102-106.

(4) Colombani, O.; Ruppel, M.; Schubert, F.; Zettl, H.; Pergushov, D. V.; Müller, A. H. *Macromolecules* **2007**, *40*, 4338-4350.