Supporting information for

Facile synthesis of asymmetric molecular brushes with triple side chains using a multivalent monomer strategy

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1. Materials

2,2,3,3,3-Pentafluoropropyl acrylate (FA, Aladdin, 98%) was passed through a basic alumina column to remove the stabilizer and distilled under reduced pressure from CaH_2 prior to use. Lactide (Aldrich, 99%) was distilled under reduced pressure from CaH_2 prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from anhydrous ethanol twice. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3COOH at room temperature, followed by washing with ethanol, diethyl ether and acetone prior to drying at 40 °C *in vacuo* for one day. Tetrahydrofuran (THF, Aldrich, 99.9%), toluene (Aldrich, 99.8%), and dichloromethane (DCM) were dried over CaH_2 and distilled from sodium and benzophenone under N_2 prior to use. Cumyl dithiobenzoate (CDB)[1] and 6-(4-butyl-4′-oxyazobenzene) hexyl acrylate (Azo)[2] were synthesized according to previous reports. Glycidol, poly(ethylene glycol) methyl ether thiol (PEG-SH, $M_n \approx 2000$ g mol^{-1}, Aldrich, 99%), 2,2'-bipyridyl (Macklin, 99%), and 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA, Aldrich, 97%) were used as received. Other reagents that were not specially mentioned were analytically pure and used without further purification.

2. Instrumentations

^{1}H and ^{19}F Nuclear Magnetic Resonance (NMR)

All NMR analyses were performed on a MERCURY plus 400 spectrometer (Varian, Inc., USA) in $CDCl_3$ and $(CD_3)_2SO$; tetramethylsilane was used as internal standards.

Gel Permeation Chromatography (GPC)

Relative molecular weights and molecular weight distributions were measured by a conventional gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector and a set of Waters Styragel columns. GPC measurements were carried out using THF as eluents with a flow rate of 1.0 mL/min. The system was calibrated with linear poly(methyl methacrylate) standards.

Transmission Electron Microscopy (TEM)

The morphologies of assemblies were measured by Transmission Electron Microscopy on JEM-1400 JEOL at an accelerating voltage of 100 kV. 6 μL of the aggregate solution was dropped onto a grid coated with pure carbon film and then dried under ambient conditions.

Optical Microscopy (OM)

The microscope was Cryo-CSS450 (Nikon) equipped with a CCD camera. The emulsion samples were observed directly.

3. Synthesis of *t*BA-Br Monomer

*t*BA-Br was prepared according to our previous work[3] and briefly described here (Scheme 2a). *t*BA (20.5 g, 0.16 mol), DABCO (1.8 g, 0.016 mol), and TEA (1.7 g, 0.016 mol) were dissolved in 25 mL of THF followed by adding formalin (20.8 g, 0.25 mol) and water (15 mL). The solution was stirred at room temperature for 3 h followed by stirring at 55 ^{o}C for 24 h. The aqueous phase was extracted by diethyl

ether, and all organic layers were merged and washed by brine followed by drying over anhydrous Na_2SO_4. The filtrate was concentrated and distilled under reduced pressure to give 18.1 g of colorless liquid, *tert*-butyl (2-hydroxymethyl) acrylate. ^{1}H NMR ($CDCl_3$): δ (ppm): 1.49 (s, 9H), 2.18 (s, 1H), 4.28 (s, 2H), 5.74 (d, 1H), 6.15 (d, 1H).

tert-Butyl (2-hydroxymethyl)acrylate (15.8 g, 0.1 mol), 2-bromopropionic acid (15.3 g, 0.1 mol), and DMAP (122.2 mg, 1 mmol) were dissolved in 200 mL of dry CH_2Cl_2. The mixture was cooled to 0 ^{o}C before DCC (20.6 g, 0.1 mol) was added. The system was stirred at 0 ^{o}C for 1 h, and was then warmed to room temperature with stirring overnight followed by filtration. A colorless liquid, *tert*-butyl 2-((2-bromopropanoyloxy)methyl)acrylate (*t*BA-Br) (25.1 g), was obtained by silica column chromatography (eluent: ethyl acetate/hexane, v:v = 1:50). ^{1}H NMR ($CDCl_3$): δ (ppm): 1.49 (s, 9H), 1.85 (d, 3H), 4.42 (q, 1H), 4.82 (d, 1H), 4.90 (d, 1H), 5.82 (d, 1H), 6.30 (d, 1H).

4. Synthesis of Br-acrylate-epoxide Functional Monomer

*t*BA-Br (3 g, 10.23 mmol) and dry CH_2Cl_2 (100 mL) were added to a 250 mL round bottom flask. The solution was stirred at 0 ^{o}C for 30 min followed by adding TFA (35 g, 307 mmol) and the reaction mixture was warmed to 25 ^{o}C. After stirring at room temperature for 4 h, the solution was concentrated and viscous solid was obtained after drying *in vacuo*. The crude product of 2-((2-bromopropanoyloxy)-methyl)acrylic acid was used without further purification.

2-((2-Bromopropanoyloxy)methyl)acrylic acid (2.97 g, 12.5 mmol), glycidol (1.86 g, 25.08 mmol), DMAP (0.15 g, 1.25 mmol), and 20 mL of DCM were first added to a 100 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum and kept under N_2. The reaction mixture was stirred at 0 ^oC for 20 min. A solution of DCC (5.17 g, 25.08 mmol) in 20 mL of DCM were added. The reaction mixture was warmed to 25 ^oC with stirring for 14 h. The reaction was quenched by adding NaCl aqueous solution. The aqueous phase was extracted by CH_2Cl_2, and all organic layers were merged. The combined organic extracts were washed with brine three times, dried over $MgSO_4$, and concentrated. The residue was purified by silica column chromatography (eluent: ethyl acetate/hexane, v:v = 1:10) to afford Br-acrylate-epoxide. ^1H NMR, ^{13}C NMR, and HRMS spectra of Br-acrylate-epoxide monomer are shown in Fig. 1a, Fig. S1, and Fig. S2, respectively. ^1H NMR ($CDCl_3$): δ (ppm): 1.87 (d, 3H, CH_3CH), 2.66, 2.85 (dd, 2H, O-CH_2-CH), 3.25 (m, 1H, -OCH-), 4.03, 4.51 (dd, 2H, -OCH_2-), 4.41 (q, 1H, CHBr), 4.92 (ABq, 2H, CH_2OCO), 5.97, 6.45 (dd, 2H, CH_2=C). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 22.3 (CH$_3$CHBr), 39.8 (CH$_3$$C$HBr), 44.7 (CH$_2CHOCH_2$), 49.3 (CH$_2$$C$HOCH$_2$), 63.6 (CH$_2$=C$CH_2O_2$C), 65.6 (CH$_2$=CCO$_2$$CH_2$), 129.7 ($CH_2$=C), 134.3 (CH$_2$=$C$), 164.7 (CH$_2$=C$CO_2CH_2$), 169.7 (CH$_2$=CCH$_2O_2$$C$). HRMS (m/z): calcd for $C_{10}H_{14}BrO_5$ $[M+H]^+$: 293.0025, found: 293.0027.

5. RAFT homopolymerization of Br-acrylate-epoxide Monomer

CDB (14.0 mg, 0.051 mmol) and AIBN (3.0 mg, 0.017 mmol) were first added to a

10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, Br-acrylate-epoxide (0.88 g, 3.0 mmol) and dry toluene (1.0 mL) were added via a gastight syringe. The flask was degassed by three cycles of freeze-pump-thaw followed by immersing the flask into an oil bath set at 65 ^oC. The polymerization was terminated by immersing the flask into liquid N_2 after 16 h. The solution was precipitated into cold *n*-hexane. The crude product was purified by repeated dissolution and precipitation followed by drying *in vacuo* overnight to give 0.47 g of poly(Br-acrylate-epoxide) functional macro-agent. GPC: M_n = 9,000 g mol^{-1}, M_w/M_n =1.19. ^1H NMR spectrum of poly(Br-acrylate-epoxide) is shown in Fig. 1b. According to the integration area of the peaks between 7.00 ppm and 8.00 ppm (CTA end group) and the peak at 3.20 ppm (-CO_2CH in Br-acrylate-epoxide repeat unit) in ^1H NMR spectrum, the average degree of polymerization of poly(Br-acrylate-epoxide) backbone (n) was calculated to be 35. ^1H NMR (CD_2Cl_2): δ (ppm): 1.84 (3H, CH_3CHBr), 2.03 (2H, CH_2C), 2.59, 2.81 (2H, OCH_2CH), 3.20 (1H, OCH_2CH), 3.61~4.45 (2H, $COOCH_2CH$; 2H, $CH_2CCH_2O_2C$), 4.49 (1H, CH_3CHBr).

6. Synthesis of PA-*g*-PAzo/PEG/PLA Heterografted Molecular Brushes

CuBr (14 mg, 0.10 mmol), Azo monomer (2.16 g, 5.11 mmol), and poly(Br-acrylate-epoxide) (14 mg, 0.05 mmol ATRP initiating group) were first added to a 50 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, HMTETA (36 μL, 0.10 mmol) and 1,4-dioxane (15 mL) were charged via a gastight syringe. The flask was degassed by

three cycles of freeze-pump-thaw followed by immersing the flask into an oil bath set at 80 °C. The polymerization and coupling reaction lasted 7 h and were terminated by immersing the flask into liquid N_2. The mixture was diluted by THF and passed through an alumina column to remove the residual copper catalyst. The solution was concentrated and precipitated into a mixture of hexane/diethyl ether (v:v = 1:1). After repeated purification by dissolving in THF and precipitating in hexane/diethyl ether three times to completely remove the unreacted Azo monomer, 0.32 g of PA-*g*-PAzo was obtained after drying *in vacuo* overnight. GPC: M_n = 66,400 g mol^{-1}, M_w/M_n = 1.26. ^{1}H NMR (CD_2Cl_2): δ (ppm): 0.88 ($CH_2CH_2CH_2CH_3$, CH_3CHCO_2, CH_3CCO_2), 1.35, 1.61, 1.73 ($CH_2CH_2CH_2CH_3$, CH_2CCO_2, $OCH_2CH_2CH_2CH_2CH_2CH_2O$), 2.61 ($CH_2CH_2CH_2CH_3$), 3.57-4.02 ($OCH_2CH_2CH_2CH_2CH_2CH_2O$, $CH_2CCO_2CH_2$, CH_2CCH_2OCO), 6.85, 7.20, 7.75 ($C_6H_4N_2C_6H_4$).

To a stirred and ice-cold solution of PA-*g*-PAzo (0.11 g, 0.03 mmol of epoxide group) and PEG-SH (0.18 g, 0.09 mmol) in THF (9 mL), LiOH (1.0 mg, 0.04 mmol) in water (0.5 mL) was added slowly under argon atmosphere. The reaction mixture was stirred for 30 h at ambient temperature. THF was evaporated, the resulting solid was dried, and the crude polymer was dissolved in DCM and washed with water. The organic layer was dried, concentrated, and precipitated three times in methanol. In addition, the reaction mixture could also be dialyzed against methanol using dialysis membrane (MW cut-off = 2.0 kDa) to remove excess PEG-SH until the dialysate did not show any detectable PEG-SH. The precipitate was collected and dried under vacuum to give 0.11 g of PA-*g*-PAzo/PEG. According to the integration area of 2

protons of azobenzene at 7.20 ppm and 3 protons of methoxyl at 3.30 ppm in ^{1}H NMR spectrum, the graft efficiency of PEG side chains was calculated to be 91.6%. GPC: M_n = 109,700 g mol^{-1}, M_w/M_n = 1.27. ^{1}H NMR (CD_2Cl_2): δ (ppm): 0.88 ($CH_2CH_2CH_2CH_3$, CH_3CHCO_2, CH_3CCO_2), 1.35, 1.61, 1.73 ($CH_2CH_2CH_2CH_3$, CH_2CCO_2, $OCH_2CH_2CH_2CH_2$ CH_2CH_2O), 2.61 ($CH_2CH_2CH_2CH_3$), 3.30 (OCH_3), 3.57 (OCH_2CH_2), 3.63-4.02 ($OCH_2CH_2CH_2CH_2CH_2CH_2O$, $CH_2CCO_2CH_2$, CH_2CCH_2OCO), 6.85, 7.20, 7.75 ($C_6H_4N_2C_6H_4$).

PA-*g*-PAzo/PEG (20 mg, 0.003 mmol) and lactide (40 mg, 0.28 mmol) were loaded into a round bottom flask, and placed under high vacuum at 35 °C for ~5 h. After backfilling with argon, anhydrous DCM (1 mL) was added to dissolve the reagents. DBU (0.5 mg, 0.003 mmol) was then injected and the reaction was allowed to proceed for 1 h under argon at room temperature. Polymerization was quenched. DCM was removed under vacuum and the polymer was re-dissolved in THF, followed by precipitation into methanol. The precipitate was collected and dried under vacuum to give 0.05 g of PA-*g*-PAzo/PEG/PLA. GPC: M_n = 147,600 g mol^{-1}, M_w/M_n = 1.30. ^{1}H NMR (CD_2Cl_2): δ (ppm): 0.88 ($CH_2CH_2CH_2CH_3$, CH_3CHCO_2, CH_3CCO_2), 1.35, 1.61, 1.73 ($CH_2CH_2CH_2CH_3$, CH_2CCO_2, $OCH_2CH_2CH_2CH_2$ CH_2CH_2O, $OCHCH_3$), 2.61 ($CH_2CH_2CH_2CH_3$), 3.30 (OCH_3), 3.57 (OCH_2CH_2), 3.63-4.02 ($OCH_2CH_2CH_2CH_2$ CH_2CH_2O, CH_2CCO_2 CH_2, CH_2CCH_2OCO), 5.15 ($OCHCH_3$), 6.85, 7.20, 7.75 ($C_6H_4N_2C_6H_4$).

7. Synthesis of PA-*g*-PFA/PEG/PLA Heterografted Molecular Brushes

CuBr (16 mg, 0.12 mmol), FA monomer (4.58 g, 22.40 mmol), and poly(Br-acrylate-epoxide) (16 mg, 0.06 mmol ATRP initiating group) were first added to a 50 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, 2,2'-bipyridyl (18 mg, 0.12 mmol) and THF (7 mL) were charged via a gastight syringe. The flask was degassed by three cycles of freeze-pump-thaw followed by immersing the flask into an oil bath set at 65 ^{o}C. The polymerization and coupling reaction lasted 16 h and were terminated by immersing the flask into liquid N_2. The mixture was diluted by THF and passed through an alumina column to remove the residual copper catalyst. The solution was concentrated and precipitated into a mixture of hexane. After repeated purification by dissolving in THF and precipitating in hexane three times to completely remove the unreacted FA monomer, 0.16 g of PA-*g*-PFA was obtained after drying *in vacuo* overnight. GPC: M_n = 46,100 g mol^{-1}, M_w/M_n = 1.29. ^{1}H NMR ($(CD_3)_2SO$): δ (ppm): 1.15-1.63 (CH_2CHCO_2, CH_2CCO_2), 1.85-2.21 (CH_2CHCO_2), 4.56 ($CO_2CH_2C_2F_5$).

To a stirred and ice-cold solution of PA-*g*-PFA (0.16 g, 0.08 mmol of epoxide group) and PEG-SH (0.16 g, 0.08 mmol) in THF (8 mL), LiOH (1.0 mg, 0.04 mmol) in water (0.4 mL) was added slowly under argon atmosphere. The reaction mixture was stirred for 2.5 d at ambient temperature. THF was evaporated, the resulting solid was dried, and the crude polymer was dissolved in DCM and washed with water. The organic layer was dried, concentrated, and precipitated into a mixture of diethyl ether/methanol (v:v = 5:1). The precipitate was collected and dried under vacuum to give 150 mg of PA-*g*-PFA/PEG. GPC: M_n = 79,300 g mol^{-1}, M_w/M_n = 1.31. ^{1}H NMR

($(CD_3)_2SO$): δ (ppm): 1.15-1.63 (CH_2CHCO_2, CH_2CCO_2), 1.85-2.21 (CH_2CHCO_2), 3.30 (OCH_3), 3.57 (OCH_2CH_2), 4.56 ($CO_2CH_2C_2F_5$).

PA-*g*-PFA/PEG (20 mg, 0.003 mmol) and lactide (40 mg, 0.28 mmol) were loaded into a round bottom flask, and placed under high vacuum at 35 °C for ~5 h. After backfilling with argon, anhydrous DCM (1 mL) was added to dissolve the reagents. DBU (0.5 mg, 0.003 mmol) was then injected and the reaction was allowed to proceed for 1 h under argon at room temperature. Polymerization was quenched. DCM was removed under vacuum and the polymer was re-dissolved in THF, followed by precipitation into methanol. The precipitate was collected and dried under vacuum to give 45 mg of PA-*g*-PFA/PEG/PLA. GPC: M_n = 108,300 g mol^{-1}, M_w/M_n = 1.35. ^{1}H NMR ($(CD_3)_2SO$): δ (ppm): 1.15-1.63 (CH_2CHCO_2, CH_2CCO_2), 1.85-2.21 (CH_2CHCO_2), 3.30 (OCH_3), 3.57 (OCH_2CH_2), 4.56 ($CO_2CH_2C_2F_5$), 5.17 ($OCHCH_3$).

8. Preparation of Self-Assembled Aggregates of PA-*g*-PAzo/PEG/PLA

PA-*g*-PAzo/PEG/PLA was first dispersed in a mixture of methanol and THF ($V_{methanol}$: V_{THF} = 92 : 8 or 95 : 5) by ultrasonication for 5 min. Then the solution was heated to 68 °C and kept for 3 h to ensure the polymer completely dissolve in solvent. The solution was slowly cooled to room temperature, followed by aging at 10 °C. The formed aggregates were observed by TEM analysis. For the study of effect of concentration, solution with various concentration were prepared.

9. Preparation of Emulsion using PA-*g*-PFA/PEG/PLA as Surfactant

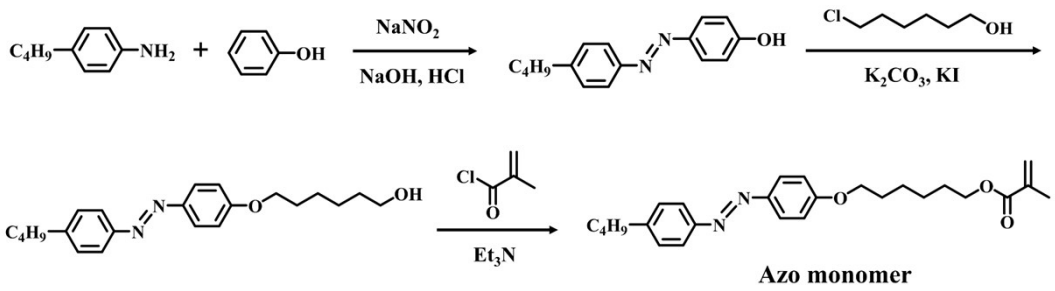
Surfactant (PEG-*b*-PLA or PA-*g*-PFA/PEG/PLA), toluene (or hexafluorobenzene), and water were added to a vial ($W_{toluene}$: $W_{polymer}$ = 50 : 1, V_{water} : $V_{toluene}$ = 7 : 1). After setting the vial in a water bath at room temperature, 20 min of ultrasonication was conducted for the mixture. The sizes of the nanodroplets in the resulting emulsions were monitored by DLS.

10. Supplementary Tables and Figures

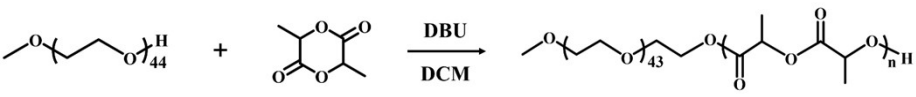
Table S1. Synthesis of macro-agent and heterografted molecular brushes

Polymers	$M_{n,GPC}$[a] (g mol^{-1})	$Đ$[a]	Repeat Units[b]
Poly(Br-acrylate-epoxide)	9,000	1.19	35
PA-*g*-PAzo	66,400	1.26	10
PA-*g*-PAzo/PEG	109,700	1.27	44
PA-*g*-PAzo/PEG/PLA	147,600	1.30	18

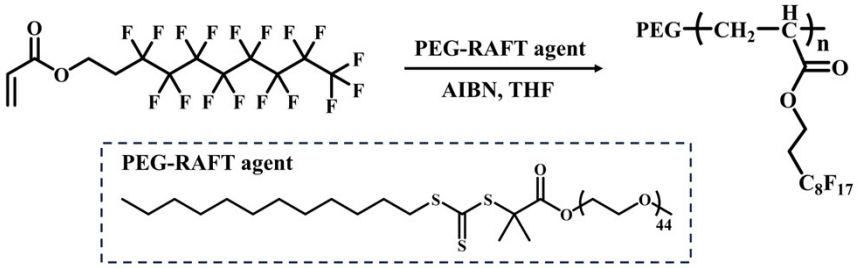
[a] Measured by GPC at 35 °C in THF. [b] The number of repeat units of Br-acrylate-epoxide, Azo, EG, and LA obtained from ^{1}H NMR.



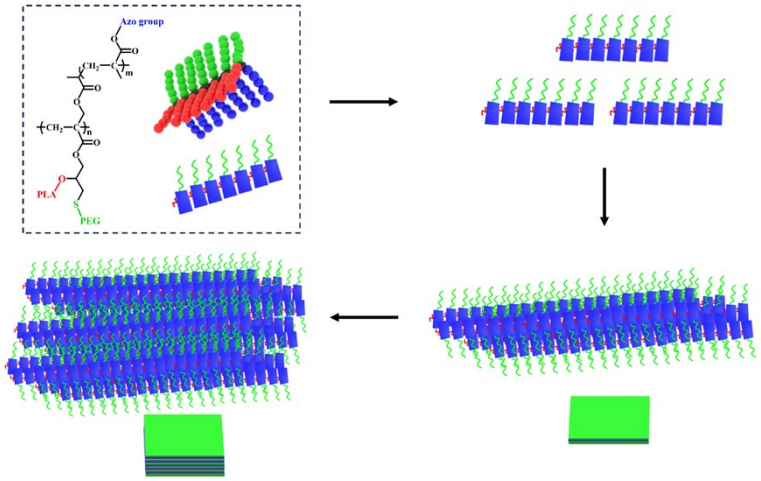
Scheme S1. Synthesis of azobenzene monomer.



Scheme S2. Synthesis of PEG-*b*-PLA copolymer.



Scheme S3. Synthesis of PEG-*b*-PFA copolymer.



Scheme S4. Schematic representation of possible packing mode of PA-*g*-PAzo/PEG/PLA in 2D platelets.[4]

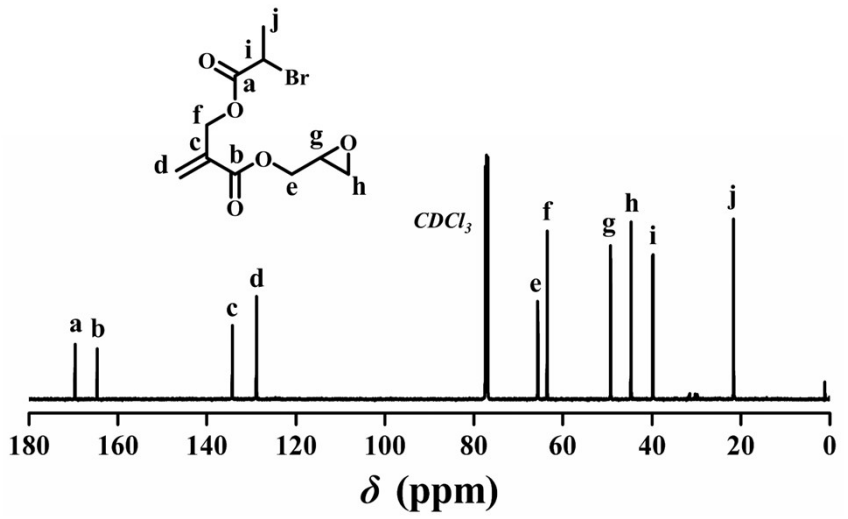


Fig. S1 ^{13}C NMR spectrum of Br-acrylate-epoxide functional monomer in $CDCl_3$.

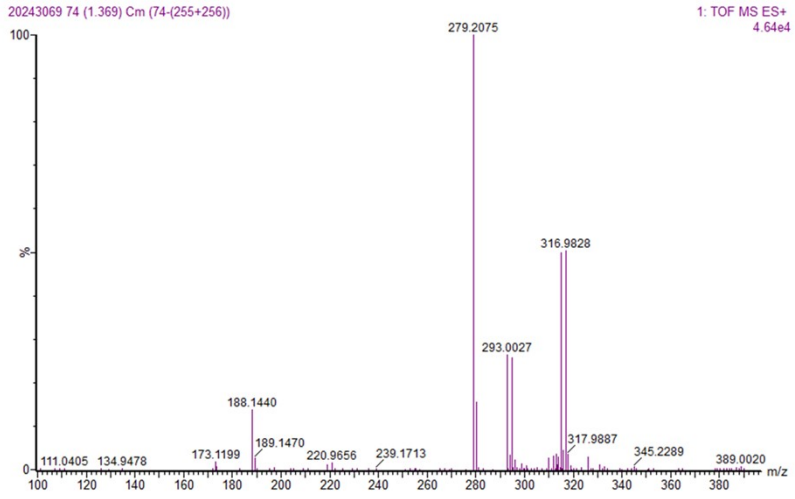


Fig. S2 HRMS spectrum of Br-acrylate-epoxide functional monomer.

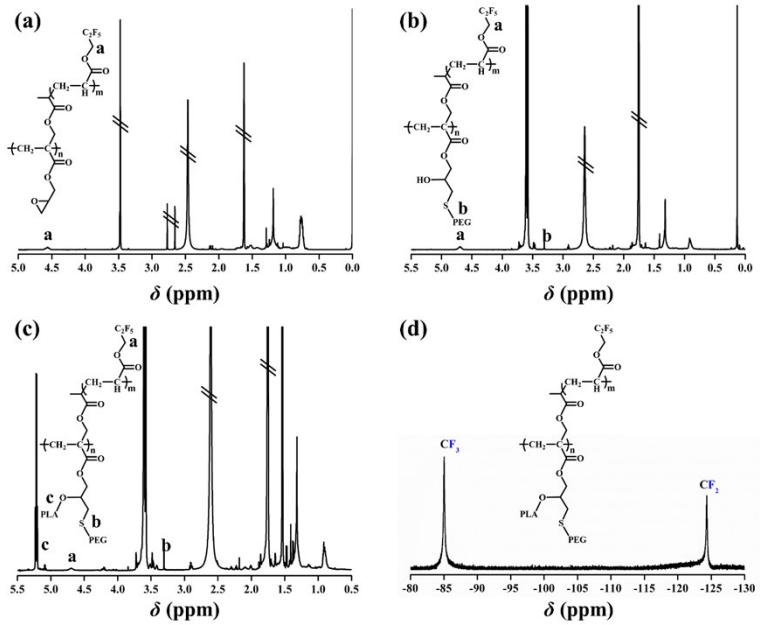


Fig. S3 ^{1}H NMR spectra of (a) PA-*g*-PFA, (b) PA-*g*-PFA/PEG, and (c) PA-*g*-PFA/PEG/PLA in $(CD_3)_2SO$. (d) ^{19}F NMR spectrum of PA-*g*-PFA/PEG/PLA in $(CD_3)_2SO$.

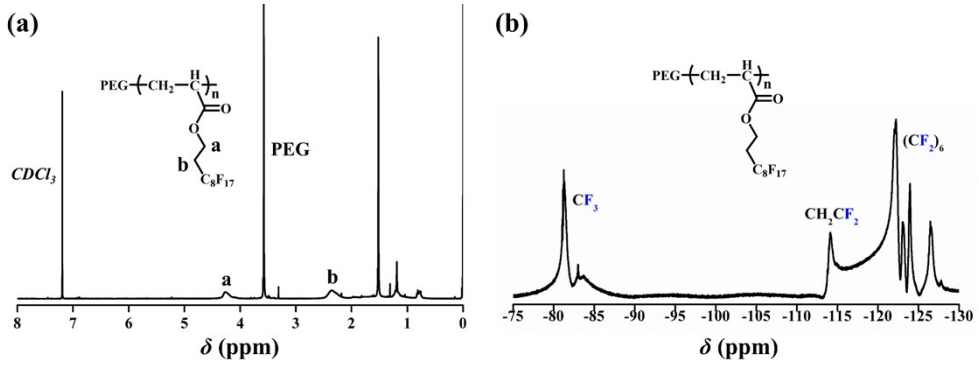


Fig. S4 (a) ^{1}H NMR spectrum of PEG-*b*-PFA copolymer in $CDCl_3$. (b) ^{19}F NMR spectrum of PEG-*b*-PFA copolymer in $CDCl_3$.

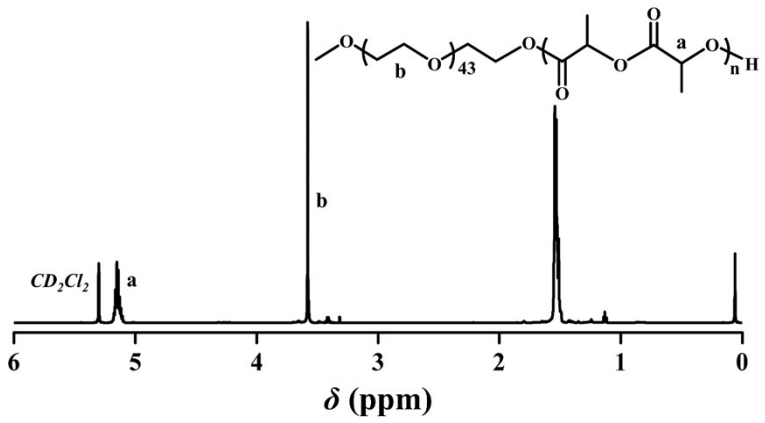


Fig. S5 ^{1}H NMR spectrum of PEG-*b*-PLA copolymer in CD_2Cl_2.

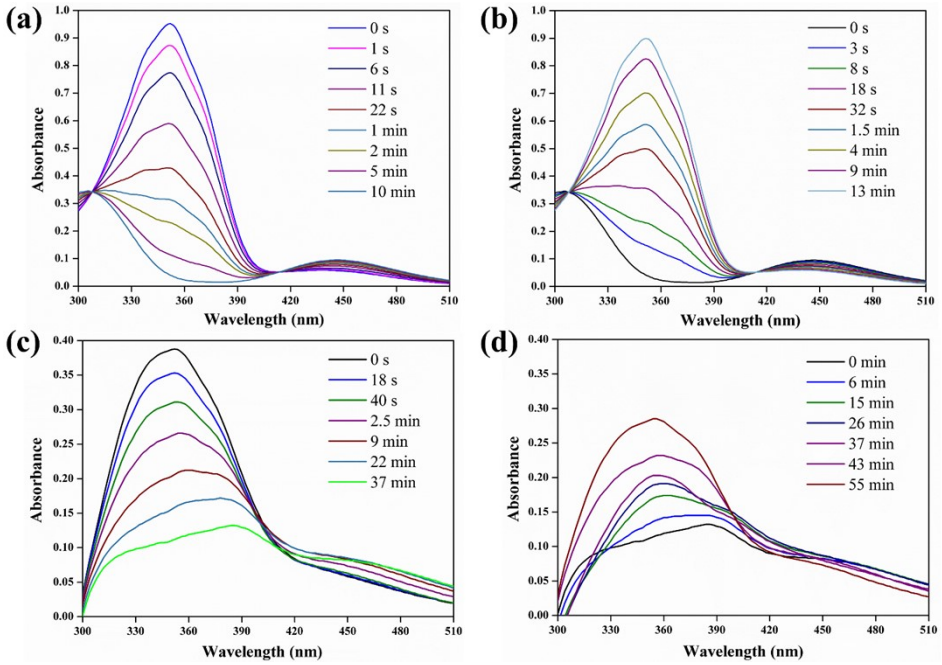


Fig. S6 UV-vis absorption spectra (a) PA-*g*-PAzo/PEG/PLA in THF and micellar solution: (a) in THF upon irradiation of 365 nm light; (b) in THF upon irradiation of 450 nm light; (c) in mixture of methanol and THF upon irradiation of 365 nm light; (d) in mixture of methanol and THF upon irradiation of 450 nm light.

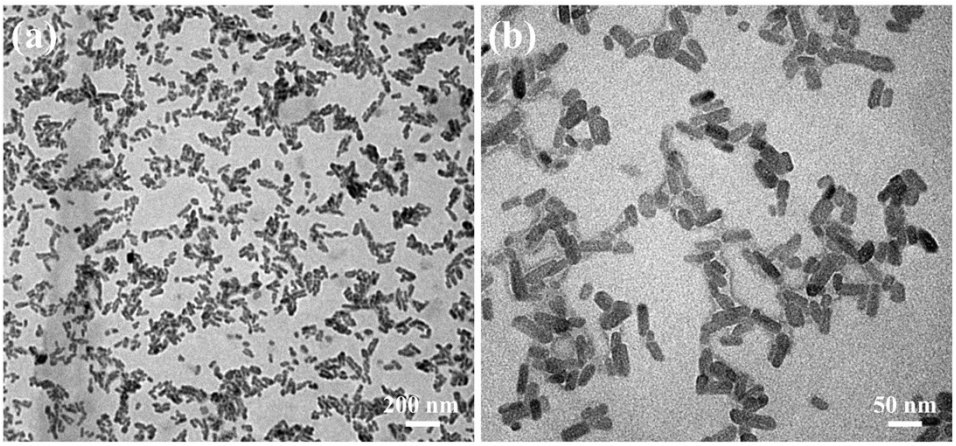


Fig. S7 (a) TEM image of platelet-1 formed by PA-*g*-PAzo/PEG/PLA in a mixture of methanol and THF ($V_{methanol}$: V_{THF} = 92 : 8) with concentration of 0.015 mg mL^{-1}. (b) Magnified TEM image of platelet-1.

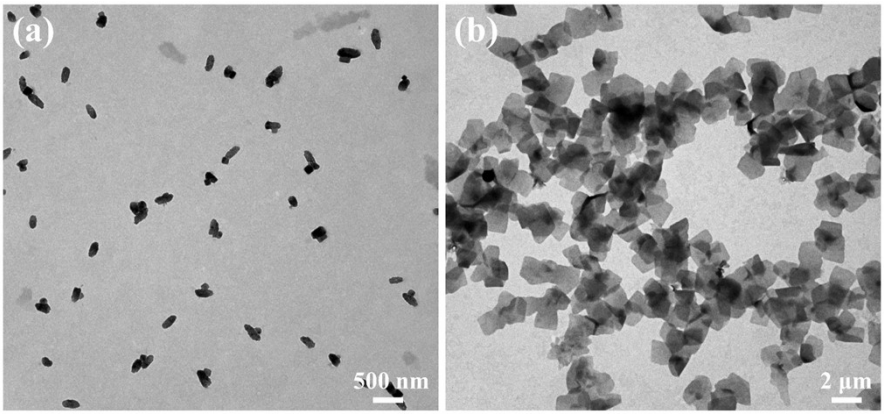


Fig. S8 TEM images of platelets formed by PA-*g*-PAzo/PEG/PLA at different concentrations in a mixture of methanol and THF ($V_{methanol}$: V_{THF} = 92 : 8): (a) platelet-2, 0.02 mg mL^{-1} and (b) platelet-3, 0.04 mg mL^{-1}.

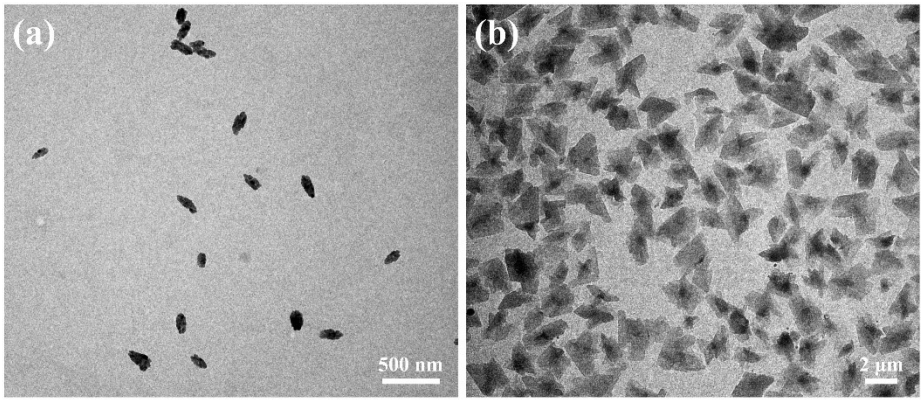


Fig. S9 TEM images of typical intermediate morphology during the formation of (a) platelet-2 and (b) platelet-3.

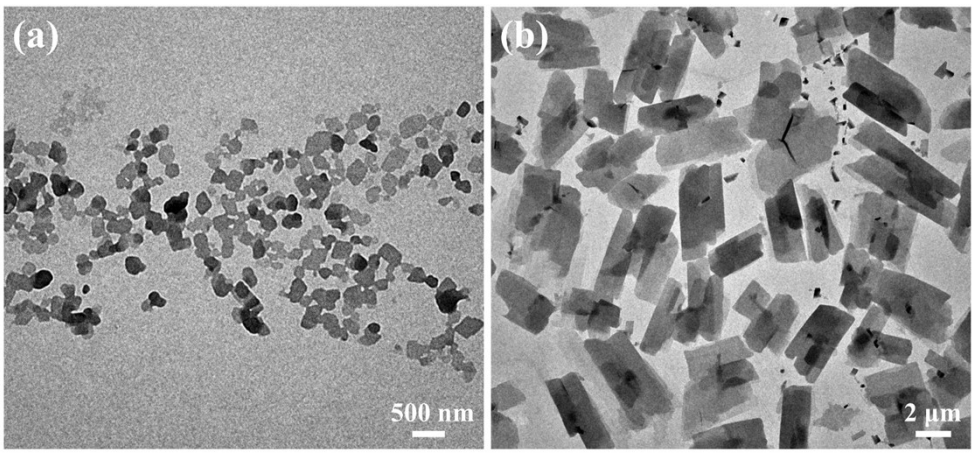


Fig. S10 TEM images of platelets formed by PA-*g*-PAzo/PEG/PLA at different concentrations in a mixture of methanol and THF ($V_{methanol}$: V_{THF} = 95 : 5): (a) 0.01 mg mL^{-1} and (b) 0.05 mg mL^{-1}.

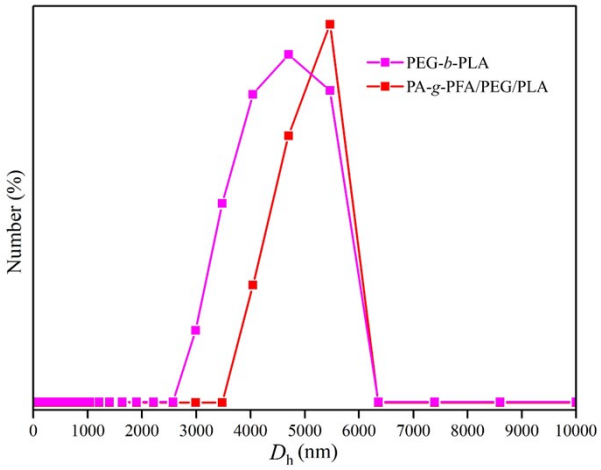


Fig. S11 DLS results of the emulsions prepared using toluene as oil phase and PEG-*b*-PLA (or PA-*g*-PFA/PEG/PLA) as surfactant. The samples were taken after 24 h of standing at the room temperature.

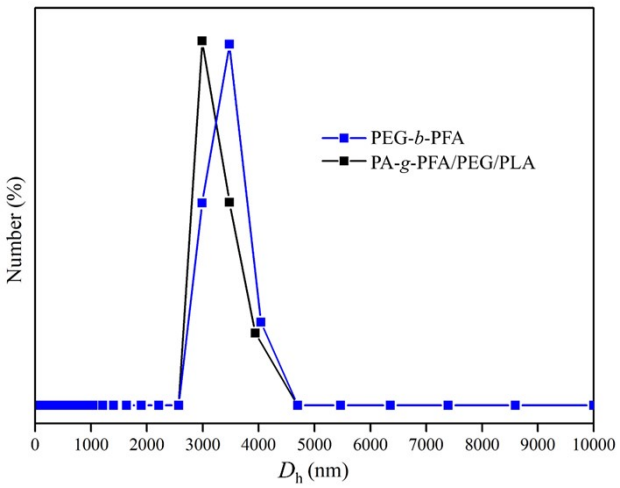


Fig. S12 DLS results of the emulsions prepared using hexafluorobenzene as fluoro phase and PEG-*b*-PFA (or PA-*g*-PFA/PEG/PLA) as surfactant. The samples were taken after 24 h of standing at the room temperature.

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