Supporting information for

First Polyallene-Based Well-Defined Amphiphilic Diblock Copolymer via RAFT Polymerization

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Experimental Section

Materials

N-Isopropylacrylamide (NIPAM, Aldrich, 97%) was recrystallized from a mixture of benzene and *n*-hexane (v:v = 1:3). 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from anhydrous ethanol. *N*-phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol three times. Phenol (97%, Aladdin), 3-bromopropyne (Aladdin, 97%), potassium *tert*-butylate (*t*-BuOK, Aladdin, 97%) and potassium carbonate (K_2CO_3, Aladdin, 98%) were used as received. Toluene (99.5%, J&K), tetrahydrofuran (THF, 99.5%, J&K) and *N*,*N*-dimethylformamide (DMF, 99.5%, J&K) were distilled from sodium and benzophenone under Ar prior to use. 2-(Dodecylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid was synthesized according to a previous report.[1]

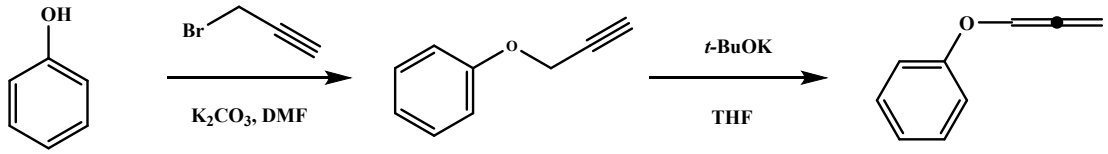
Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FTIR spectrophotometer with a 4 cm^{-1} resolution. ^1H and ^{13}C NMR analyses were performed on a JEOL resonance ECZ 400S spectrometer (400 MHz) in $CDCl_3$. Tetramethylsilane (TMS) and $CDCl_3$ were used as internal standards for ^1H and ^{13}C NMR, respectively. Sulfur content was determined by the titration with $Ba(ClO_4)_2$. Relative molecular weights and molecular weight distributions were measured by 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 (HR3

(500-30,000), HR4 (5,000-600,000), and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μm). GPC measurements were carried out at 35°C using THF as eluent with a flow rate of 1.0 mL·min^{-1}. The system was calibrated with linear polystyrene standards. Steady-state fluorescent spectra of PNA were measured on a Hitachi F-4500 spectrophotometer with the band width of 5 nm for excitation and emission, the emission intensity at 418 nm was recorded to determine the critical micelle concentration (*cmc*) where λ_{ex} was 340 nm. Transmission electron microscopy (TEM) images were obtained by a JEOL JEM-2100 instrument operated at 80 kV.

Synthesis of phenoxyallene

Phenoxyallene (POA) was synthesized from phenol as shown in Scheme S1.



Scheme S1. Synthesis of phenoxyallene.

Phenol (20.2 g, 214 mmol), 3-bromopropyne (30.6 g, 257 mmol), K_2CO_3 (77.0 g, 557 mmol) and DMF (250 mL) were firstly added to a 500 mL flask under Ar followed by stirring at room temperature for 24 h. Subsequently, water (50 mL) was added and the resulting mixture was extracted with diethyl ether (150 mL×4) followed by drying over anhydrous Na_2SO_4. After concentration, the residue was purified by flash chromatography (silica gel column, eluent: ethyl acetate/*n*-hexane (v:v = 1:100)) to give phenyl propargyl ether (22.4 g, 79.2%) as a colorless liquid. ^{1}H NMR: δ (ppm): 7.34 (d, 3H, J = 13.0 Hz), 6.99 (t, 2H, J = 8.6 Hz), 4.69 (s, 2H), 2.51 (s, 1H).

^{13}C NMR: δ (ppm): 157.6, 129.3, 121.3, 115.1, 78.5, 75.5, 55.8.

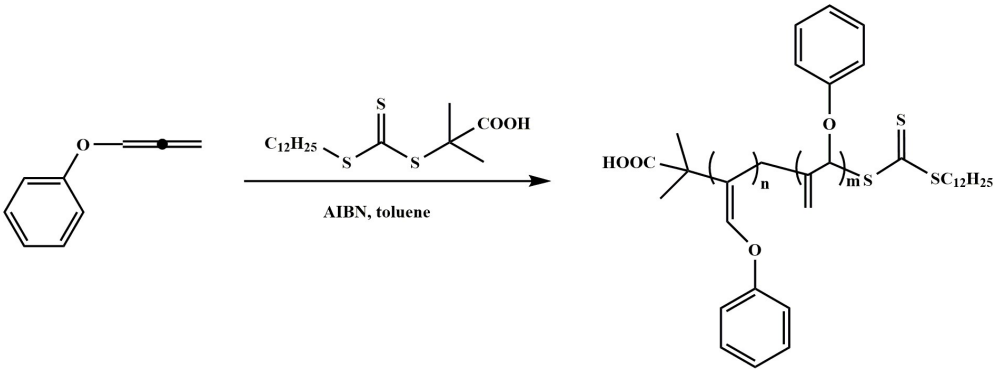
The as-prepared phenyl propargyl ether (22.4 g, 170 mmol) *t*-BuOK (9.5 g, 85 mmol) and THF (300 mL) were firstly added to a 500 mL flask under Ar at 0ºC. The mixture was stirred at room temperature for 36 h followed by filtration over a pad of celite. The celite was washed with dry THF several times. After concentration, the crude product was purified by flash chromatography (silica gel column, eluent: *n*-hexane) to afford phenoxyallene (9.5 g, 42.3%) as a colorless liquid. ^{1}H NMR: δ (ppm): 7.32 (d, 3H, J = 13.0 Hz), 7.07 (d, 2H, J = 10.5 Hz), 6.85 (dd, 1H, J = 21.2 Hz), 5.45 (s, 2H). ^{13}C NMR: δ (ppm): 202.6, 157.1, 129.7, 122.8, 118.1, 116.7, 89.9.

AIBN-initiated free radical homopolymerization of POA

AIBN (7.3 mg, 0.044 mmol) and POA (1.03 g, 7.8 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, dry toluene (2.0 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. The polymerization lasted 16 h and it was terminated by putting the flask into liquid N_2. The reaction mixture was precipitated into *n*-hexane. The crude product was purified by repeated dissolution in THF and precipitation in *n*-hexane followed by drying *in vacuo* overnight to give 0.31 g of polyphenoxyallene (PPOA) as a white solid. GPC: $M_{n,GPC}$ = 5,600 g/mol, M_w/M_n = 1.71.

RAFT homopolymerization of POA

RAFT homopolymerization of POA was performed in toluene at 60°C as shown in Scheme S2.



Scheme S2. RAFT homopolymerization of phenoxyallene.

In a typical procedure (Scheme S2), AIBN (7.3 mg, 0.044 mmol), POA (1.03 g, 7.8 mmol) and 2-(dodecylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (47.3 mg, 0.13 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, dry toluene (2.0 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. The polymerization lasted 16 h and it was terminated by putting the flask into liquid N_2. The reaction mixture was precipitated into *n*-hexane. The crude product was purified by repeated dissolution in THF and precipitation in *n*-hexane followed by drying *in vacuo* overnight to give 0.29 g of PPOA as a yellow solid. GPC: $M_{n,GPC}$ = 4,200 g/mol, M_w/M_n = 1.26. FT-IR: ν (cm^{-1}): 3060, 3038, 2920, 1702, 1596, 1492, 1227, 1168, 882, 750, 689. ^{1}H NMR: δ (ppm): 7.38-6.44 (5H, C_6H_5 and 1H×n, C=C*H*OC_6H_5), 5.30-4.48 (2H×m, CH_2=CCHO and 1H×m, CH_2=CC*H*O), 3.32 (2H, S$CH_2(CH_2)_{10}CH_3$), 3.00-1.99 (2H×n, =C-CH_2), 1.86 (2H,

$SCH_2CH_2(CH_2)_9CH_3$ and 6H, $C(CH_3)_2CO_2H$), 1.26 (18H, $SCH_2CH_2(CH_2)_9CH_3$), 0.88 (3H, $SCH_2CH_2(CH_2)_9CH_3$). ^{13}C NMR: δ (ppm): 158.1, 155.8, 129.6, 122.8, 120.9, 115.4, 73.9, 34.8, 32.0, 29.6, 22.7, 13.9. Element analysis: S% = 2.45%.

The "absolute" molecular weight and composition of 1,2- and 2,3-polymerized repeat unit were determined by ^1H NMR: $M_{n,NMR}$ = 4,600 g/mol, DP_{POA} = 35, m = 30, n = 5. RAFT homopolymerization with different feeding ratios are listed in Table S1.

Table S1. RAFT Homopolymerization of Phenoxyallene[a]

entry	[M]:[CTA]:[AIBN]	$M_{n,GPC}$[b] (g/mol)	M_w/M_n[b]	$M_{n,NMR}$[c] (g/mol)	DP[d]
1	60:3:1	2,100	1.28	2,100	13
2	120:3:1	3,200	1.25	3,700	25
3	180:3:1	4,200	1.26	4,600	35
4	240:3:1	4,500	1.32	5,800	41

[a] Polymerization temperature: 60°C, polymerization time: 16 h, solvent: toluene (2 mL). [b] Measured by GPC in THF at 35°C. [c] Determined by ^1H NMR. [d] Degree of polymerization determined by ^1H NMR.

RAFT block copolymerization of POA

PNIPAM-based macro-CTA was first prepared by RAFT homopolymerization of NIPAM at 60°C in DMF (Scheme 1).[2] AIBN (22.0 mg, 0.13 mmol), NIPAM (2.26 g, 20.0 mmol) and 2-(dodecylsulfanylthiocarbonylsulfanyl)-2-methylpropionic acid (145.8 mg, 0.40 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2.

Next, dry DMF (10.0 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. The polymerization lasted 16 h and it was terminated by putting the flask into liquid N_2. The reaction mixture was precipitated into cold diethyl ether. The crude product was purified by repeated dissolution in THF and precipitation in *n*-hexane followed by drying *in vacuo* overnight to give 2.2 g of poly(*N*-isopropyl acrylamide) (PNIPAM-CTA) as a white solid. GPC: $M_{n,GPC}$ = 5,100 g/mol, M_w/M_n = 1.12. FT-IR: ν (cm^{-1}): 3445, 3292, 2971, 2930, 1653, 1558, 1457, 1171, 517. ^1H NMR: δ (ppm): 6.53 (1H, -N*H*CH$(CH_3)_2$), 3.98 (1H, -NHC*H*$(CH_3)_2$), 3.33 (4H, -SC*H*$_2$), 1.11 (6H, -NHCH(C*H*$_3)_2$), 0.88 (3H, -S$(CH_2)_{11}$C*H*$_3$). The "absolute" molecular weight was determined by ^1H NMR. $M_{n,NMR}$ = 5,800 g/mol, DP_{NIPAM} = 48.

PNIPAM-*b*-PPOA diblock copolymers were synthesized by RAFT block copolymerization of POA mediated by PNIPAM-CTA at 60°C in DMF (Scheme 1). In a typical procedure, $PNIPAM_{48}$-CTA (174.0 mg, 0.03 mmol), POA (1.98 g, 15.0 mmol), AIBN (1.7 mg, 0.01 mmol) and DMF (2.0 mL) were first added to a 5 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. The flask was degassed by three cycles of freezing- pumping-thawing followed by immersing the flask into an oil bath set at 60°C. After 24 h, the polymerization was terminated by immersing the flask into liquid N_2. DMF was then evaporated under reduced pressure and the crude product was purified by dissolving in THF and precipitating in methanol three times followed by drying *in vacuo* overnight to give 230 mg of PNIPAM-*b*-PPOA as a white solid.

GPC: M_n = 53,800 g/mol, M_w/M_n =1.31. FT-IR: ν (cm^{-1}): 3340, 3060, 3035, 2960, 2927, 1597, 1487, 1344, 1290, 1241, 1035, 757, 690. ^{1}H NMR: δ (ppm): 7.30-6.27 (5H, C_6H_5; 1H×n, C=C*H*OC_6H_5; 1H, -N*H*CH$(CH_3)_2$), 5.42-4.42 (2H×m, CH_2=CCHO and 1H×m, CH_2=CC*H*O), 3.99 (1H, -NHC*H*$(CH_3)_2$), 3.48 (2H, S$CH_2(CH_2)_{10}CH_3$), 3.07-1.85 (2H×n, =C-CH_2; 3H, CH_2CHCONH; 6H, C$(CH_3)_2CO_2$H), 1.26 (18H, $SCH_2CH_2(CH_2)_9CH_3$), 1.13 (6H, -NHCH$(CH_3)_2$), 0.87 (3H, $SCH_2CH_2(CH_2)_9CH_3$).

Table S2. RAFT Block Copolymerization of POA[a]

entry	[POA]:[PNIPAM-CTA]:[AIBN]	M_n[b] (g/mol)	M_w/M_n[b]
1	150:3:1	5,500	1.05
2	300:3:1	6,600	1.12
3	600:3:1	18,700	1.33
4	1500:3:1	53,800	1.31

[a] Polymerization temperature: 60°C, polymerization time: 24 h. [b] Measured by GPC in THF at 35°C.

Determination of critical micelle concentration

PNA was used as fluorescence probe to measure the *cmc* of PNIPAM-*b*-PPOA diblock copolymer (M_n = 53,800 g/mol, M_w/M_n =1.31) in aqueous solution. Acetone solution of PNA ([PNA] = 2 mM) was added to a large amount of water until [PNA] reached 0.002 mM. The solutions for fluorescence measurement were obtained by adding different amounts of THF solution of homopolymer (1, 0.1, 0.01, 0.001 or 0.0001 mg/mL) to water containing PNA ([PNA] = 0.002 mM).

PISA micellar morphology

$PNIPAM_{48}$-CTA (174.0 mg, 0.03 mmol), POA (1.98 g, 15.0 mmol), AIBN (1.7 mg, 0.01 mmol) and methanol (2.0 mL) were first added to a 5 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 60°C. At appropriate intervals, an aliquot (0.10 mL) was removed from the reaction mixture. A half of the aliquot was diluted 100-fold with methanol for TEM measurement to determine the morphology. Another half of the aliquot was used for GPC measurement to determine the molecular weight and molecular weight distribution.

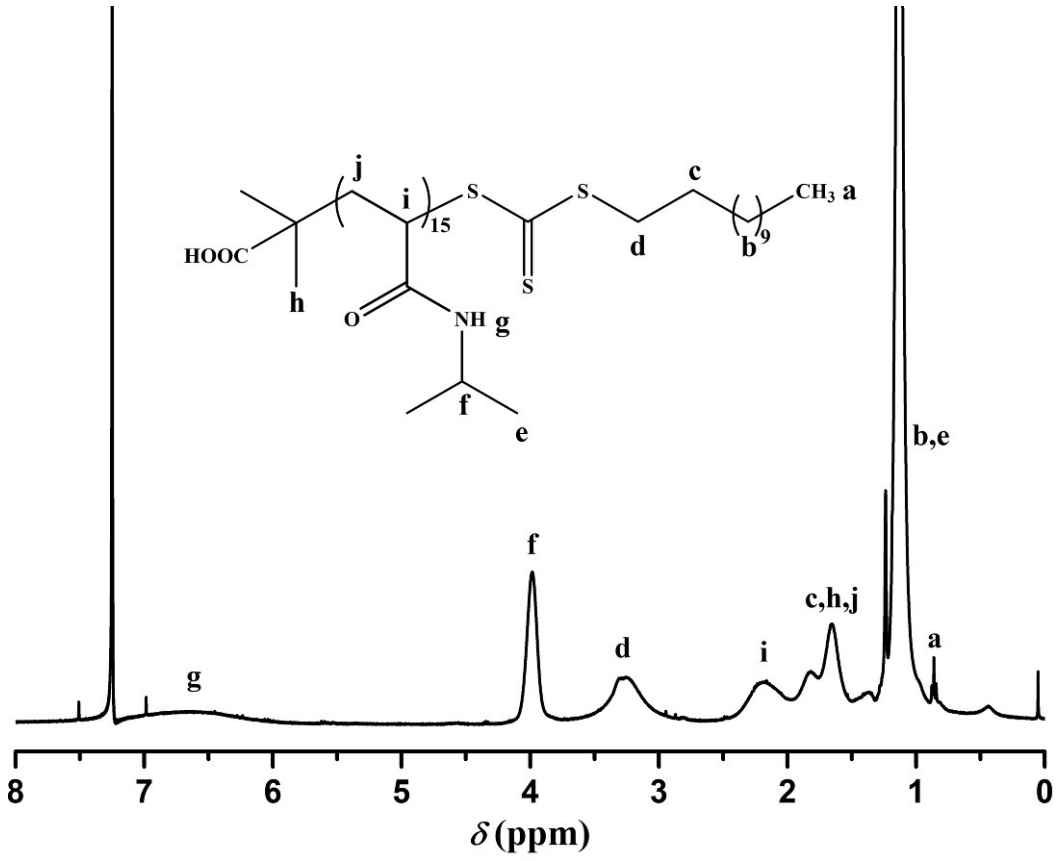


Figure S1. ^1H NMR spectrum of PNIPAM-CTA in $CDCl_3$.

References

1. Lai, J. T.; Filla, D.; Shea, R. Functional polymers from novel carboxyl-terminated trithiocarbonates as highly efficient RAFT agents. *Macromolecules* **2002**, *35*, 6754-6756.
2. Wu, Z.; Liang, H.; Lu, J. Synthesis of poly(*N*-isopropylacrylamide)-poly(ethylene glycol) miktoarm star copolymers via RAFT polymerization and aldehyde-aminooxy click reaction and their thermoinduced micellization. *Macromolecules* **2010**, *43*, 5699-5705.