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SUPPORTING INFORMATION

Synthesis of CO₂-responsive gradient copolymers by switchable RAFT polymerization and its controlled self-assembly

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¹H NMR study of protonation of the switchable RAFT agent with TsOH.

2-Cyanopropan-2-yl *N*-methyl, *N*-(pyridin-4-yl)carbamodithioate was dissolved in chloroform-d₃ and placed in an NMR tube, the ¹H NMR spectrum was recorded. A different amount of 4toluenesulfonic acid (TsOH) was added to the NMR tube, an intense golden solution developed immediately. The ¹H NMR spectra are shown in Figure S1.



Figure S1. ¹H NMR spectra of protonation of the switchable RAFT agent with TsOH.

¹H NMR Study of Reversibility of Protonation by three different acids.

The reversibility of protonation by three different acids was demonstrated by ¹H NMR. For the TfOH, the switchable RAFT agent was dissolved in chloroform-d₃ and placed in an NMR tube (Figure S2a). An equimolar quantity of TfOH with respect to RAFT agent was added to the NMR tube, the ¹H NMR spectrum is shown in Figure S2b (spectrum was recorded ca 2h after addition of acid). An equimolar quantity of 4-(*N*,*N*-dimethylamino)pyridine (D) was then added to the NMR tube. The color intensity reduced immediately. The ¹H NMR spectrum is shown in Figure S2c. The solution from the

NMR tube was transferred to a centrifuge tube and extracted with water (0.5 mL) for three times, the aqueous layer was discarded and the organic layer transferred to an NMR tube. The ¹H NMR spectrum is shown in Figure S2d.



Figure S2. 400 MHz ¹H NMR spectra (CDCl₃) of (a) RAFT agent, (b) with 1 equivalent of TfOH, (c) with 1 equivalent of 4-(*N*,*N*-dimethylamino)pyridine (D) and (d) after aqueous extraction.



Figure S3. 400 MHz ¹H NMR spectra (CDCl₃) of (a) RAFT agent, (b) with 1 equivalent of TsOH, (c) with 1 equivalent of 4-(*N*,*N*-dimethylamino)pyridine (D) and (d) after aqueous extraction.



Figure S4. 400 MHz ¹H NMR spectra (CDCl₃) of (a) RAFT agent, (b) with 1 equivalent of CF₃COOH, (c) with 1 equivalent of 4-(*N*,*N*-dimethylamino)pyridine (D) and (d) after aqueous extraction.

Synthesis of poly(methyl methacrylate) (PMMA) with switchable RAFT agent

For the TfOH, a stock solution (a) of TfOH (0.1082 g) in acetonitrile (1 ml) and a stock solution (b) of AIBN (11.3 mg) in acetonitrile (1 ml) were prepared respectively. The reaction solution was prepared with the dissolution of the RAFT agent (8.4 mg, 0.033 mmol) in a 10 mL volumetric flask followed with

the addition of MMA (1.0 g, 10.0 mmol), different amount of stock solution (a) with respect to the RAFT agent, stock solution(b) (48 μ l, 0.0033 mmol) in acetonitrile (1.0 ml) was prepared. Polymerization of MMA was carried out in ampoule carefully degassed by three freeze-evacuate-thaw cycles under high vacuum and then heated at 70 °C for 16 h.

Table S1. Molar mass and conversion data for PMMA prepared with switchable RAFT agent and TfOH at 70 °C for 16 h.

Entry	Acid / RAFT	Conv. ^a / %	M _n ^b (g/mol)	${\boldsymbol{ D}}^{\mathrm{b}}$
1	0.5	57.8	18 700	1.75
2	0.8	45.9	22 100	1.44
3	1.0	47.8	19 400	1.39
4	1.2	58.8	17 600	1.58
5	1.5	60.8	21 400	1.52
6	2	67.2	24 300	1.85

^a determined by ¹H NMR analysis of the unpurified reaction mixtures. ^b Determined by DMAc SEC.

For the TsOH, a stock solution (a) of TsOH (0.1057 g) in acetonitrile (1 ml) and a stock solution (b) of AIBN (11.3 mg) in acetonitrile (1 ml) were prepared respectively. The reaction solution was prepared with the dissolution of the RAFT agent (8.4 mg, 0.033 mmol) in a 10 mL volumetric flask followed with the addition of MMA (1.0 g, 10.0 mmol), different amount of stock solution (a) with respect to the RAFT agent, stock solution(b) (48 μ l, 0.0033 mmol) in acetonitrile (1.0 ml) was prepared. Polymerization of MMA was carried out in ampoule carefully degassed by three freeze-evacuate-thaw cycles under high vacuum and then heated at 70 °C for 16 h.

Table S2. Molar mass and conversion data for PMMA prepared with switchable RAFT agent andTsOH at 70 ° C for 16 h.

Entry	Acid / RAFT	Conv. ^a / %	M _n ^b (g/mol)	$\boldsymbol{D}^{\mathrm{b}}$
1	0.5	57.1	19 300	2.12
2	0.8	57.6	21 100	1.77
3	1.0	41.7	12 300	1.80
4	1.2	57.0	26 500	1.75
5	1.5	64.0	21 700	1.83
6	2.0	63.7	21 400	1.87

^a determined by ¹H NMR analysis of the unpurified reaction mixtures. ^b Determined by DMAc SEC.

For the CF₃COOH, a stock solution (a) of CF₃COOH (0.0695 g) in acetonitrile (1 ml) and a stock solution (b) of AIBN (11.3 mg) in acetonitrile (1 ml) were prepared respectively. The reaction solution was prepared with the dissolution of the RAFT agent (8.4 mg, 0.033 mmol) in a 10 mL volumetric flask followed with the addition of MMA (1.0 g, 10.0 mmol), different amount of stock solution (a) with respect to the RAFT agent, stock solution(b) (48 μ l, 0.0033 mmol) in acetonitrile (1.0 ml) was prepared. Polymerization of MMA was carried out in ampoule carefully degassed by three freeze-evacuate-thaw cycles under high vacuum and then heated at 70 °C for 16 h.

Table S3. Molar mass and conversion data for PMMA prepared with switchable RAFT agent and CF₃COOH at 70 ° C for 16 h.

Entry	Acid / RAFT	Conv. ^a / %	M _n ^b (g/mol)	${\boldsymbol{ D}}^{\mathrm{b}}$
1	0.5	44.8	53 000	2.07
2	0.8	32.9	43 100	1.98
3	1.0	41.7	42 600	1.75
4	1.2	51.6	44 800	1.62
5	1.5	51.6	27 000	1.70
6	2.0	57.3	28 500	1.66
7	3.0	57.7	24 000	1.63

^a determined by ¹H NMR analysis of the unpurified reaction mixtures. ^b Determined by DMAc SEC.



Figure S5. The degree of polymerization of the monomer DEAEMA and BzMA versus reaction

time.

Self-assembly of PBzMA-b-P(DEAEMA-grad-NVP)-b-PNVP.



Figure S6. The TEM images of aggregates formed in aqueous solution for different reaction time: a) 2h, b) 4h, c) 12h; after CO₂ stimulation: d) 2h, e) 4h, f) 12h; The number average hydrodynamic radius measured by DLS for different reaction time.



Figure S7. The intensity average hydrodynamic radius measured by DLS for different reaction time.