Supporting Information for

CO_2-triggered UCST transition of amphiphilic triblock copolymer and their self-assemblies

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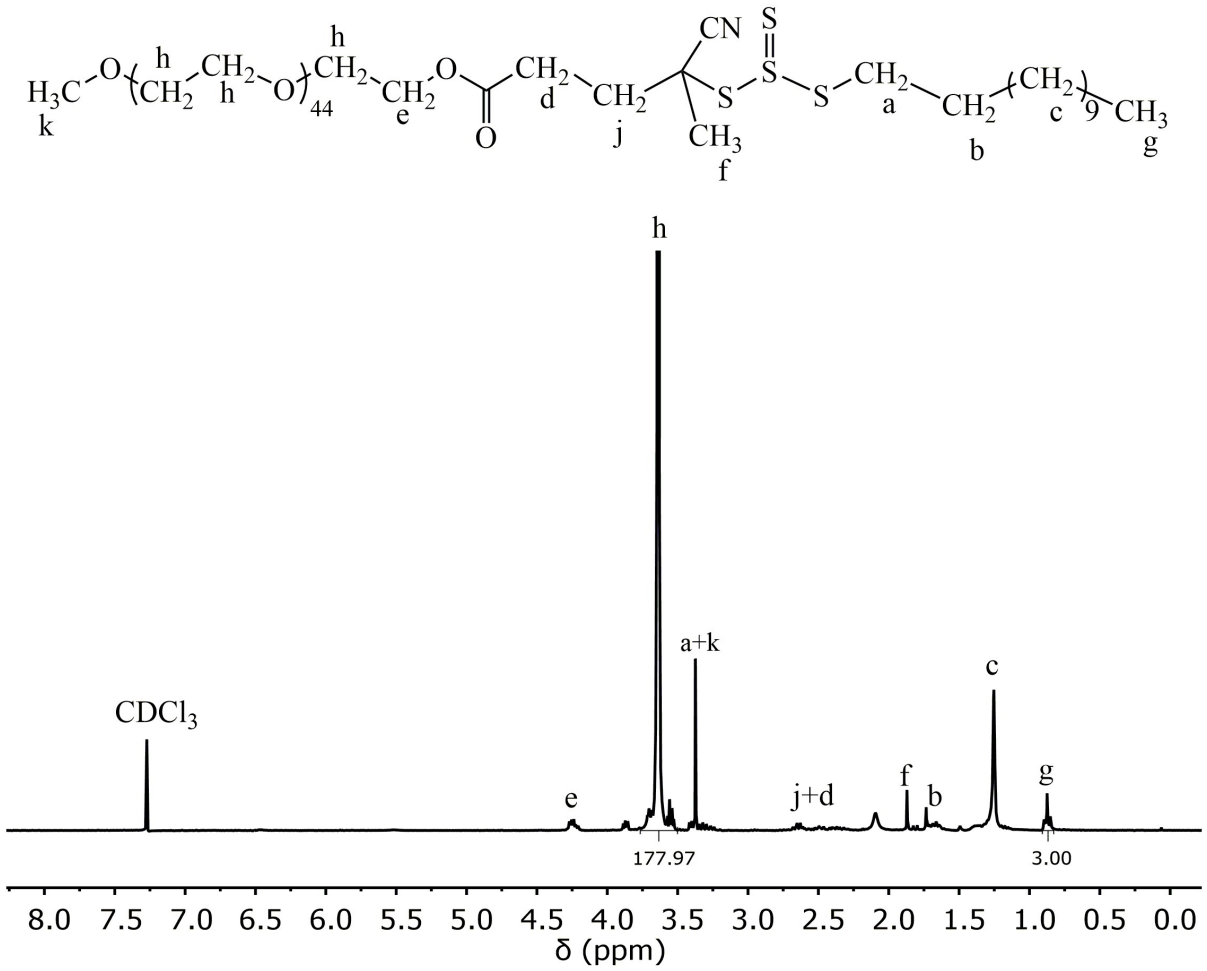

Fig. S1 ^{1}HNMR of macromolecular chain transfer agent-mPEG$_{45}$-CDTPA (macro-CTA)

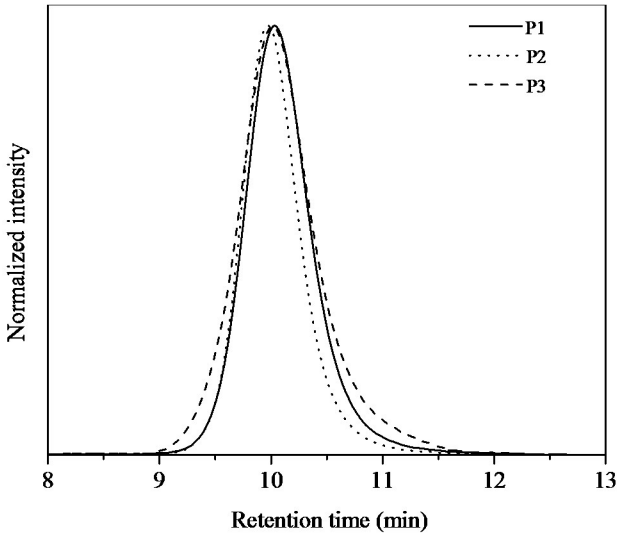

Fig. S2 The GPC curves of PEG-*b*-P(AAm-*co*-AN)s P1 (solid line), P2 (dotted line) and P3 (dashed line) in DMF.

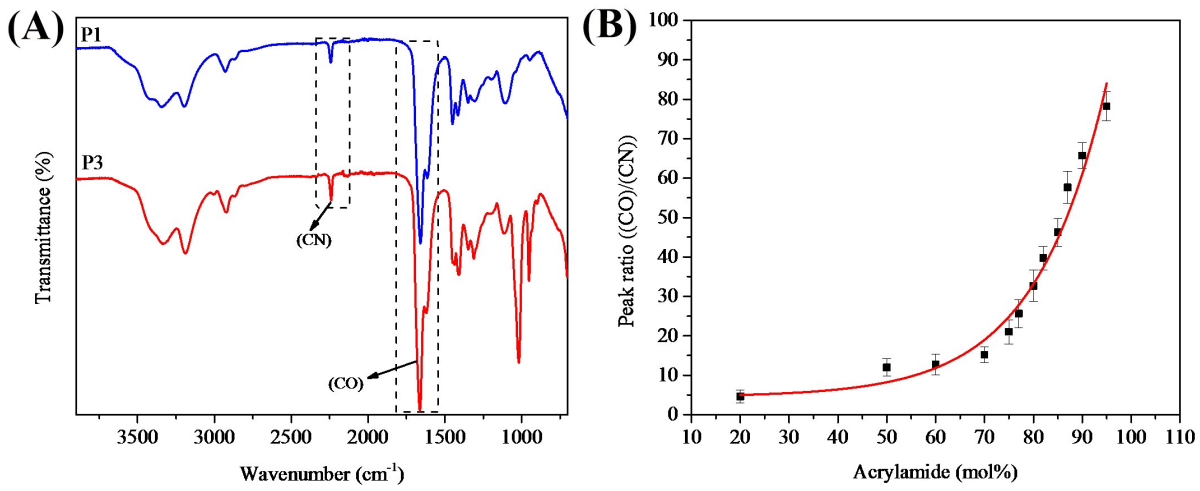

Fig. S3 FT-IR spectra of PEG-*b*-P(AAm-*co*-AN)s showing the characteristic bands at 2243 cm^{-1} from CN in acrylonitrile and at 1655 cm^{-1} from CO in acrylamide (A); Calibration curve derived from plotting the integral ratio of the CO band to the CN band *vs* known molar content of AAm in mixtures of PAAm and PAN homopolymers to determine the composition of PEG-*b*-P(AAm-*co*-AN)s (B).[1]

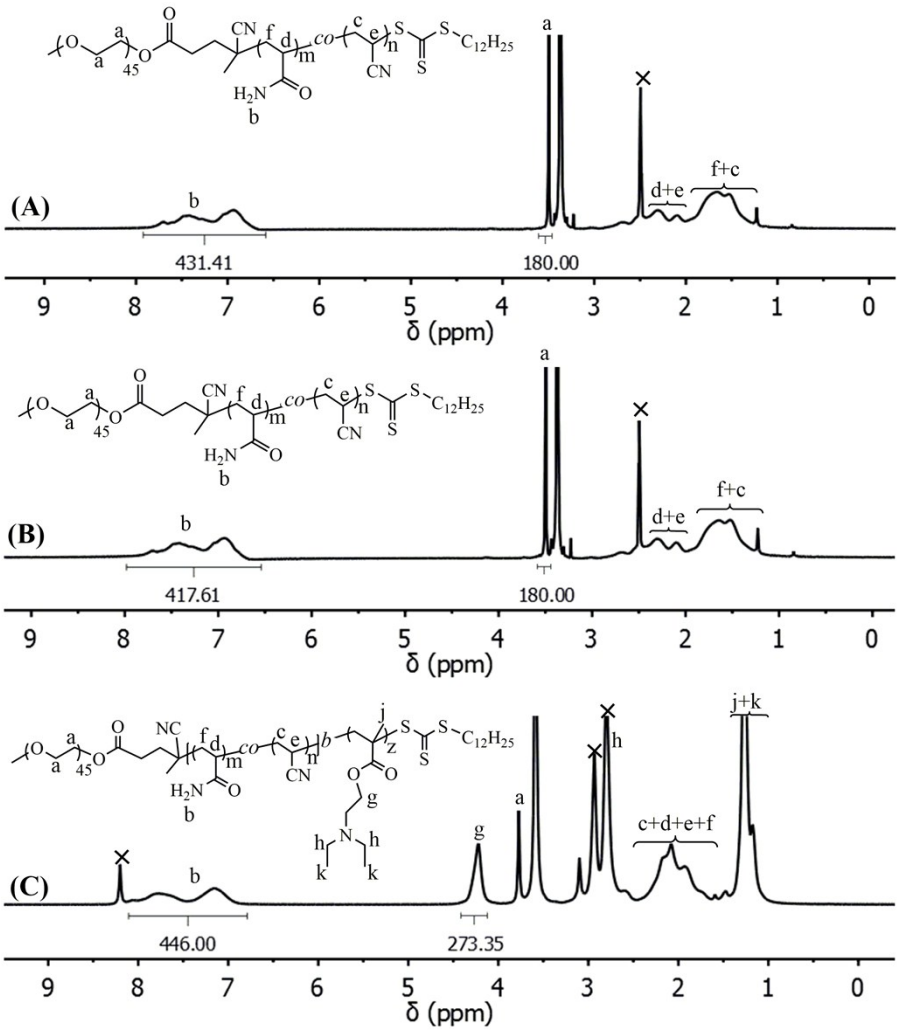

Fig. S4 ^{1}H NMR spectra of diblock copolymers: P1(A) and P3 (B) in DMSO-d_6, triblock copolymer P5 (C) in DMF-d_7. "×" denotes solvent peaks.

Confirmation of composition and molecular weight of prepared block copolymers

In this work, a series of block copolymers were successfully prepared by RAFT polymerization. Their chemical structures were checked by FT-IR (Fig. 1 and Fig. S3) and ^{1}H NMR (Fig. 2 and Fig. S4). Based on these measurements, their compositions were further confirmed according to below equations as follows:

The composition of prepared block copolymers is confirmed based on below equations (1), (2) and (3):

$$\frac{\delta_a}{4}:\frac{\delta_b}{2}:\frac{\delta_g}{2} = DP_{PEG}:DP_{AAm}:DP_{DEAEMA} \qquad (1)$$

$$\frac{\delta_a}{4} = DP_{PEG} = 45 \qquad (2)$$

$$H = \frac{DP_{AAm}}{DP_{AN}} \qquad (3)$$

Where δ_y stands for integral area from ^{1}H NMR spectrum and subscripted y is label for peaks in ^{1}H NMR spectrum. DP_x represents degree of polymerization, herein, x refers to monomers using for polymerization. H represents molar ratio of AAm to AN, which is confirmed from the known AAm molar content versus integral ratio from the bands (CO : CN) (see Fig. S3B) after calculating integral area ratio of bands from CN in acrylonitrile at 2243 cm^{-1} and CO in acrylamide at 1655 cm^{-1}, respectively. (Fig. 1 and Fig. S3A). Then, the molar ratios of AAm : AN (H) in P1, P2 and P3 are confirmed to be 74.0 : 26.0, 68.4: 31.6 and 63.7 : 36.3, respectively.

After successfully confirming the composition of prepared block copolymers, their molecular weights can be determined according to equation (4) as follows:

$$M_n = M_{n,\,macro-CTA} + M_{n,AAm} \times DP_{AAm} + M_{n,AN} \times DP_{AN} + M_{n,\,DEAEMA} \times DP_{DEAEMA} = 2400 + 71.0 + 53.06 \times DP_{AN} + 185.26 \times DP_{DEAEMA} \quad (4)$$

The above mentioned results are all summarized in Table 1.

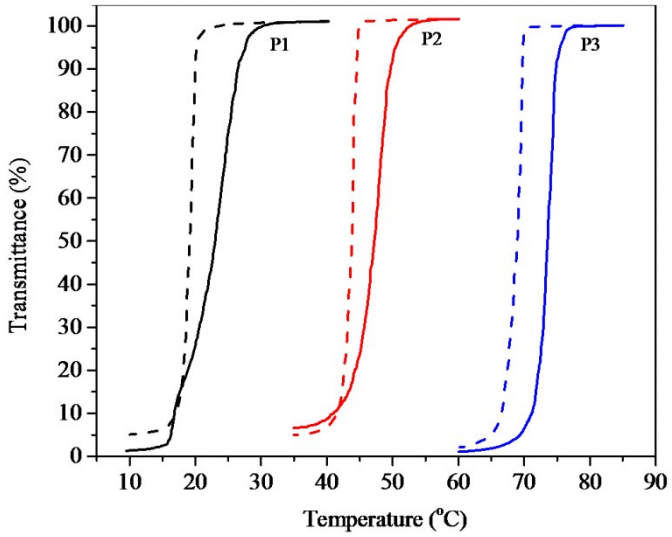

Fig. S5 Curves of transmittance *vs* temperature of PEG-*b*-P(AAm-*co*-AN)s solutions (concentration of solutions: 10 mg/mL, heating curve: solid line and cooling curve: dash line)

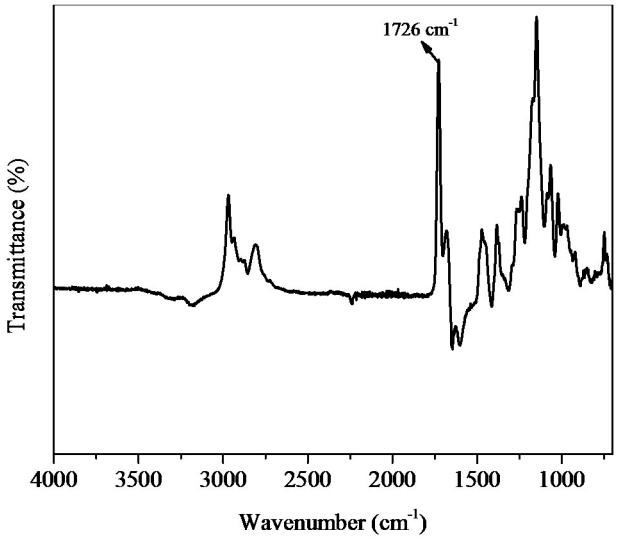

Fig. S6 The differential spectrum based on the FT-IR spectra of P2 and P4.

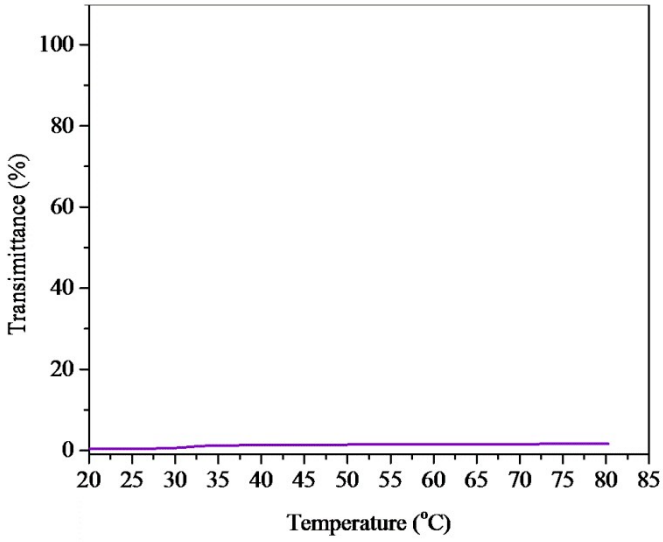

Fig. S7 The curve of transmittance vs temperature of P4 in absence of CO_2.

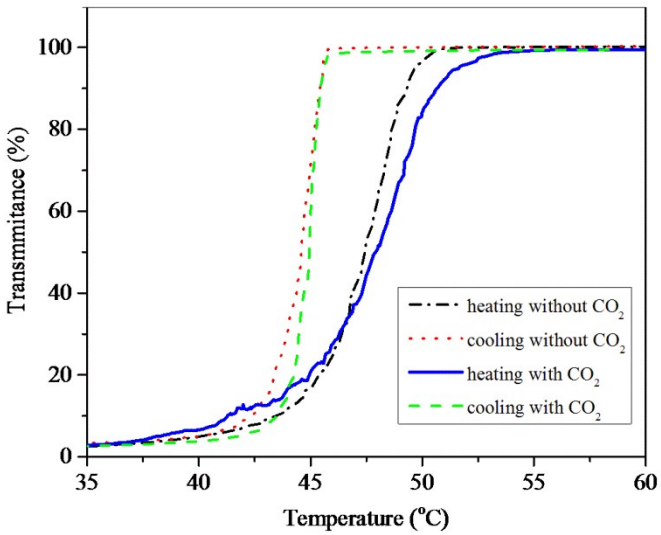

Fig. S8 The curves of transmittance *vs* temperature of P2 solution under with or without CO_2. (concentration of P4 solution: 10 mg/mL)

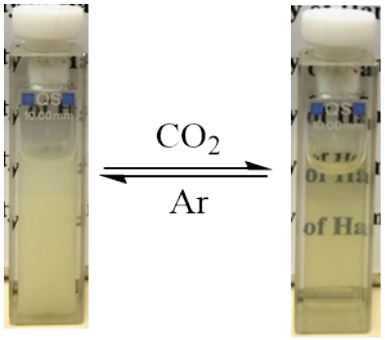

Fig. S9 The optical images of turbidity transition of P5 solution before and after purging CO_2. (concentration of P5 solution: 10 mg/mL.

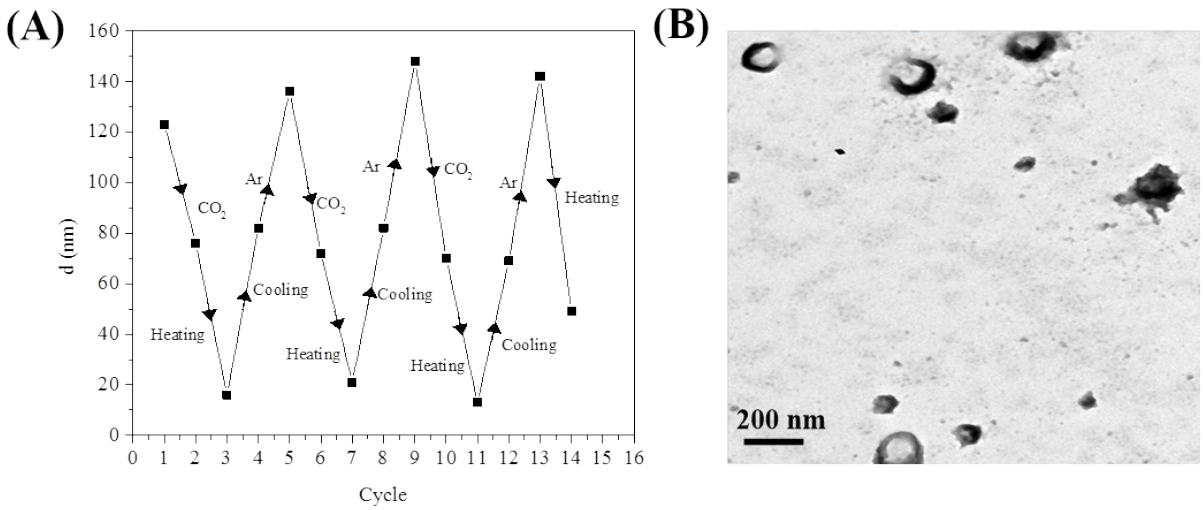

Fig. S10 Plotting of size transition of P4 nanoaggregates upon three cycles of CO_2-Heating-Cooling-Ar successive stimulation (A); the TEM image of P4 nanoaggregates after two cycles of CO_2-Heating-Cooling-Ar successive stimulation.

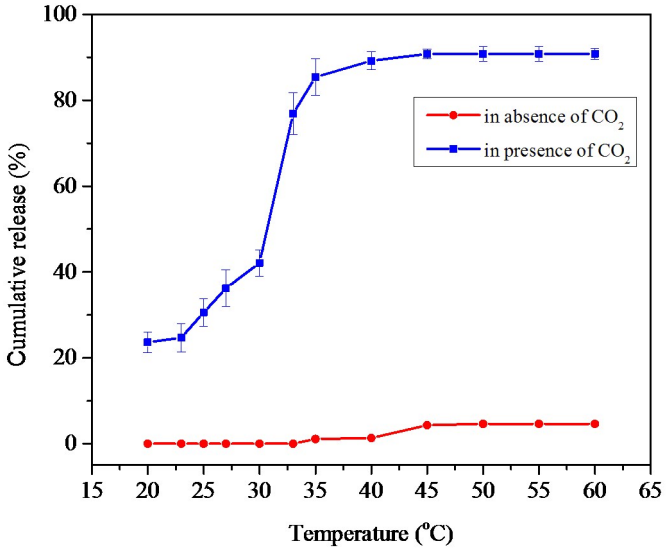

Fig. S11 Plotting of released percentage of Nile red from P4 nanoaggregate at different temperature in the absence or presence of CO_2 based on UV-vis absorption measurement. (Concentration of P4 nanoaggregate solution: 1 mg/mL)

References

1. J. Seuring and S. Agarwal, Macromolecules, 2012, 45, 3910–3918.