SUPPORTING INFORMATIONS

Mechanism insights in controlling host-guest (de)complexation by thermoresponsive polymer phase transitions

Experimental section

Materials

Acrylamide (Am, ≥ 99%, Aldrich) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako) were used as received. 2,2′-azobis(isobutyronitrile) (AIBN, ≥ 98%, Aldrich) was recrystallized from methanol, *N*-Isopropylacrylamide (NIPAm, ≥ 98%, Aldrich) was recrystallized from *n*-hexane. *N,N*-Diethylacrylamide (DEAm, TCI-Chem) was purified by redistillation prior to synthesis. All organic solvents were analytical grade and water was purified with a Millipore system combining inverse osmosis membrane (Milli RO) and ion exchange resins (Milli Q) for synthesis and purification. RAFT agent Naphtha-CTA and cyclobis(paraquat-*p*-phenylene) (Blue Box, abbreviated as **BBox**) were prepared as previously reported.[1] *N*-Cyanomethylacrylamide (CMAm) monomer was synthesized as previously described.[2]

Nuclear magnetic resonance (NMR)

For chemical analyses, ^{1}H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer at room temperature, in D_2O or DMSO-d_6 and chemical shifts (δ) are given in ppm. For the host-guest complexation studies at different temperatures, ^{1}H NMR spectra were recorded on a Bruker Advance III HD spectrometer operating at 700 MHz, using a standard 5 mm broadband Smart Probe. The temperature control was achieved by a Bruker BCU II unit and a build in temperature control unit. Following experimental conditions were employed for

the variable temperature experiments: 32 scans, 45-degree flip angle, 2.5 sec acquisition time, 2 sec relaxation delay. The analyzes were performed from the soluble state to the precipitated state. The sample was allowed to equilibrate for 10 minutes at each temperature. The chemical shifts were referred to as residual HOD peak at each temperature.

Size exclusion chromatography (SEC)

For Naphtha-PNIPAm and Naphtha-PDEAm, the SEC analyses were carried out at 35°C in THF as mobile phase at a flow rate of 1 mL·min^{-1} using toluene as a flow marker. Polymer solution was prepared at a concentration of 5 mg·mL^{-1} and filtered through a 0.2 µm PTFE membrane. The separation system was composed of three columns from Waters (Styragel HR1, Styragel HR3, Styragel HR4) coupled with Wyatt's modular differential refractive index (RI) detector. The relative number-average molar mass ($\bar{M}_n$), relative weight-average molar mass ($\bar{M}_w$) and the dispersity ($Đ = (\bar{M}_w/\bar{M}_n)$) were calculated from a calibration curve based on narrow polystyrene (PS) standards. For Naphtha-P(CMAm-*co*-Am), the SEC analysis was carried out at 60 °C in DMF (+ LiBr, 1 g·L^{-1}) as mobile phase at a flow rate of 0.8 mL·min^{-1} using toluene as a flow marker. Polymer solution was prepared at a concentration of 5 mg·mL^{-1} and filtered through a 0.2 µm PTFE membrane. The separation system was composed of two PSS GRAM 1000 Å columns and one PSS GRAM 30 Å coupled with a modular differential refractive index (RI) detector Viscotek 3580 from Malvern. The relative number-average molar mass ($\bar{M}_n$), relative weight-average molar mass ($\bar{M}_w$) and the dispersity ($Đ = (\bar{M}_w/\bar{M}_n)$) were calculated from a calibration curve based on narrow poly(methyl methacrylate) (PMMA) standards.

Ultraviolet-Visible Spectrometry

A Cary 3500 Scan UV-Visible spectrometer equipped with a multicell Peltier temperature controller was used. The (co)polymer solution was prepared at 10 mg·mL^{-1} and placed in 10 mm path length quartz cells from Hellma. Absorbance spectra without and with BBox were collected at 20°C for Naphtha-PNIPAm and Naphtha-PDEAm and at 65°C for Naphtha-P(CMAm-*co*-Am). Turbidimetry curves were built by collecting the absorbance at 670 nm (wavelength at which clear solutions do not absorb) with a scanning rate of 1 °C min^{-1}. The LCST-type cloud point temperatures were defined during the heating as the temperature corresponding to a transmittance of 50%. The UCST-type cloud point temperatures were defined during the cooling as the temperature corresponding to a transmittance of 50 %.

Isothermal Titration Calorimetry (ITC)

Isothermal titration calorimetry (ITC) experiments were performed at 15°C for LCST polymers and 60°C for the UCST polymer, using a nano-ITC titration calorimeter from TA Instruments with a standard sample cell volume of 1 mL, following standard procedures. Compounds were dissolved in de-ionized water and the solutions were degassed gently under vacuum before use. A 250 µL injection syringe was used to inject the Blue Box solution and the titrations were performed under stirring at 400 rpm.

Synthesis of Naphtha-PNIPAm

A solution of Naphtha-CTA (97 mg, 1.7×10^{-1} mmol), AIBN (7.0 mg, 4.1×10^{-2} mmol), NIPAm monomer (3.0 g, 26.5 mmol) in DMF (4.8 mL) was deoxygenated by bubbling nitrogen for 30 min at room temperature. The reaction flask was placed in an oil bath at 80 °C. The polymerization was allowed to proceed for 2 h under constant magnetic stirring. The solution was cooled down to room temperature and the polymer isolated by precipitation in diethyl ether.

It was purified further by two consecutive precipitations from acetone into diethyl ether to obtain a pure product after drying overnight under vacuum.

Synthesis of Naphtha-PDEAm

A solution of Naphtha-CTA (89 mg, 1.5×10^{-1} mmol), AIBN (6.0 mg, 3.7×10^{-2} mmol), DEAm monomer (2.70 g, 21.2 mmol) in DMF (20 mL) was deoxygenated by bubbling nitrogen for 30 min at room temperature. The reaction flask was placed in an oil bath at 70 °C. The polymerization was allowed to proceed for 3 h under constant magnetic stirring. Then, the solution was cooled down to room temperature and the polymer isolated by precipitation in *n*-hexane. It was purified further by two successive precipitations from acetone into *n*-hexane to obtain a pure product after drying overnight under vacuum.

Synthesis of Naphtha-P(CMAm-*co*-Am)

A solution of Naphtha-CTA (31.8 mg, 5.4×10^{-2} mmol), V-70 (8.3 mg, 2.7×10^{-2} mmol), CMAm monomer (0.608 g, 5.5 mmol) and Am monomer (0.169 g, 2.4 mmol) in DMF (3 mL) was deoxygenated by bubbling argon for 15 min at 5 °C (cold water bath). The reaction flask was placed in an oil bath at 35 °C. The polymerization was allowed to proceed for 3 h under constant magnetic stirring. The solution was cooled down to room temperature and the polymer isolated by precipitation in chloroform, dried under vacuum, solubilized in water, purified by dialysis against water for 2 days (membrane cut off of 1 kDa) and finally freeze-dried.

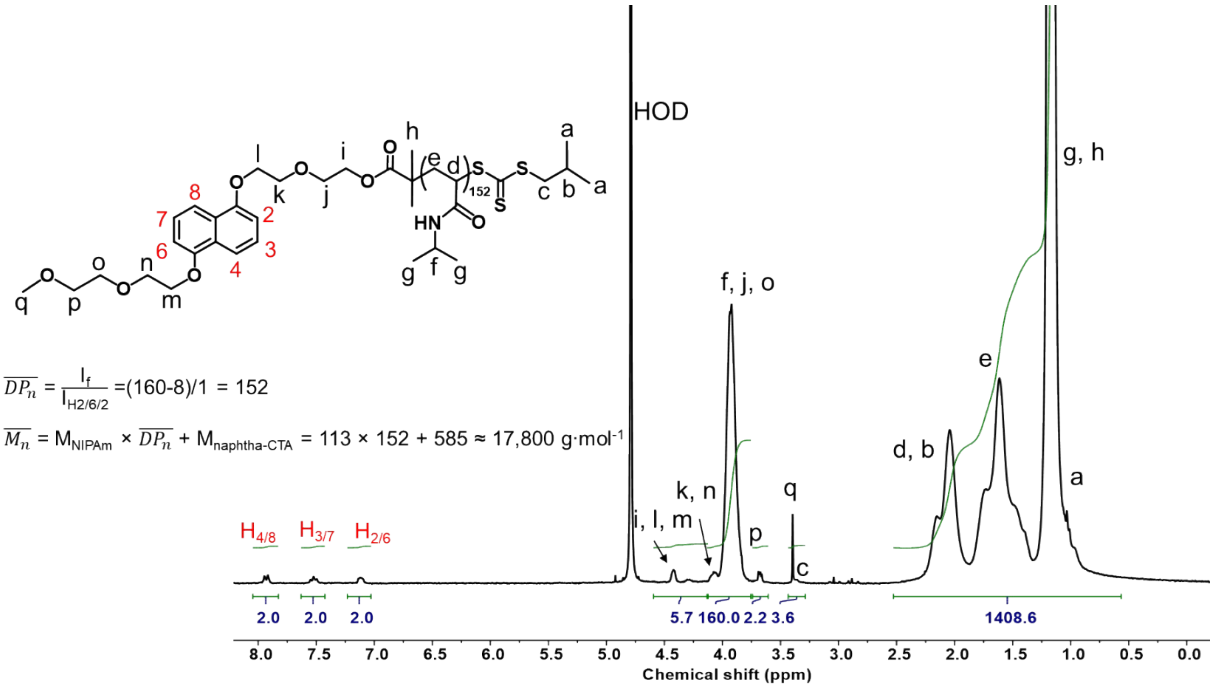

Fig. S1. ^{1}H NMR spectrum of **Naphtha-PNIPAm$_{152}$** in D_2O.

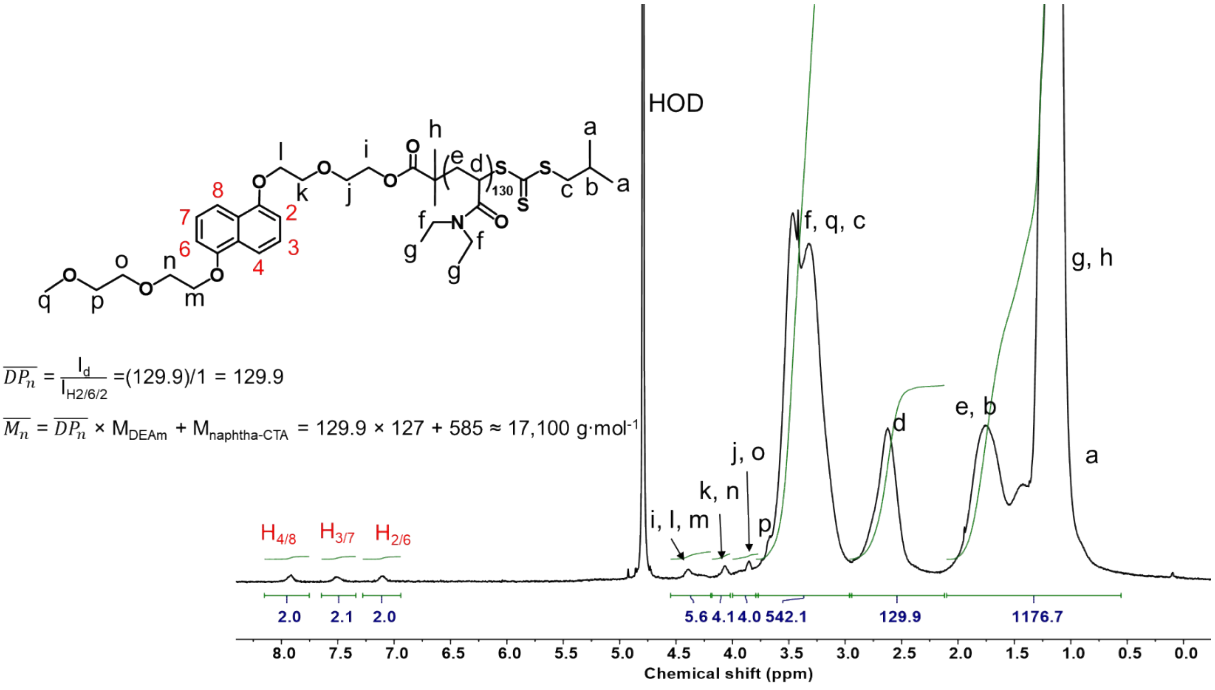

Fig. S2. ^{1}H NMR spectrum of **Naphtha-PDEAm$_{130}$** in D_2O.

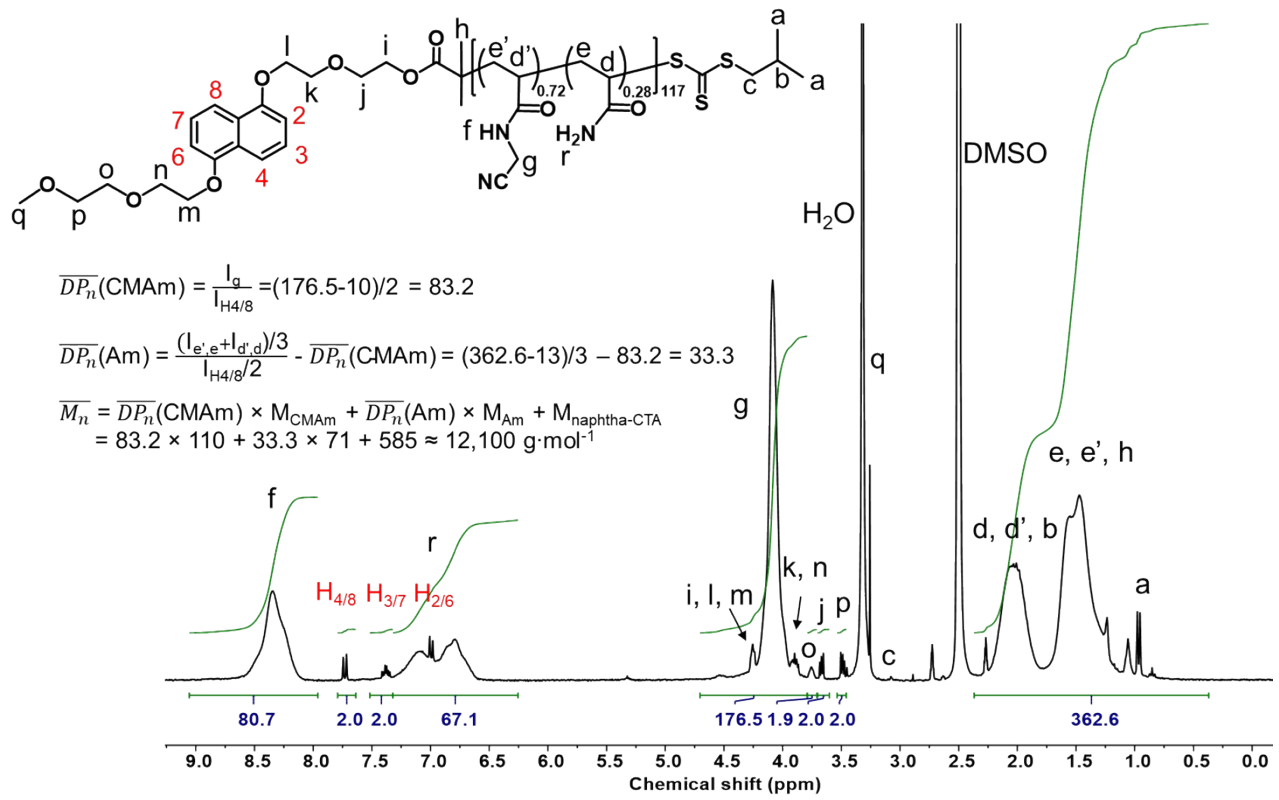

Fig. S3. ^{1}H NMR spectrum of **Naphtha-P(CMAm$_{0.72}$-*co*-Am$_{0.28}$)$_{117}$** in DMSO-d$_6$.

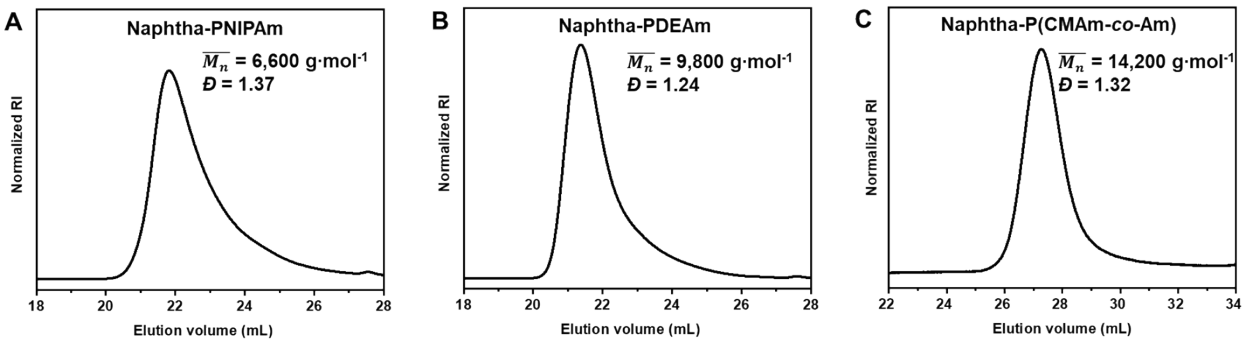

Fig. S4. Size-exclusion chromatography profiles of A) **Naphtha-PNIPAm**, B) **Naphtha-PDEAm** and C) **Naphtha-P(CMAm-*co*-Am).**

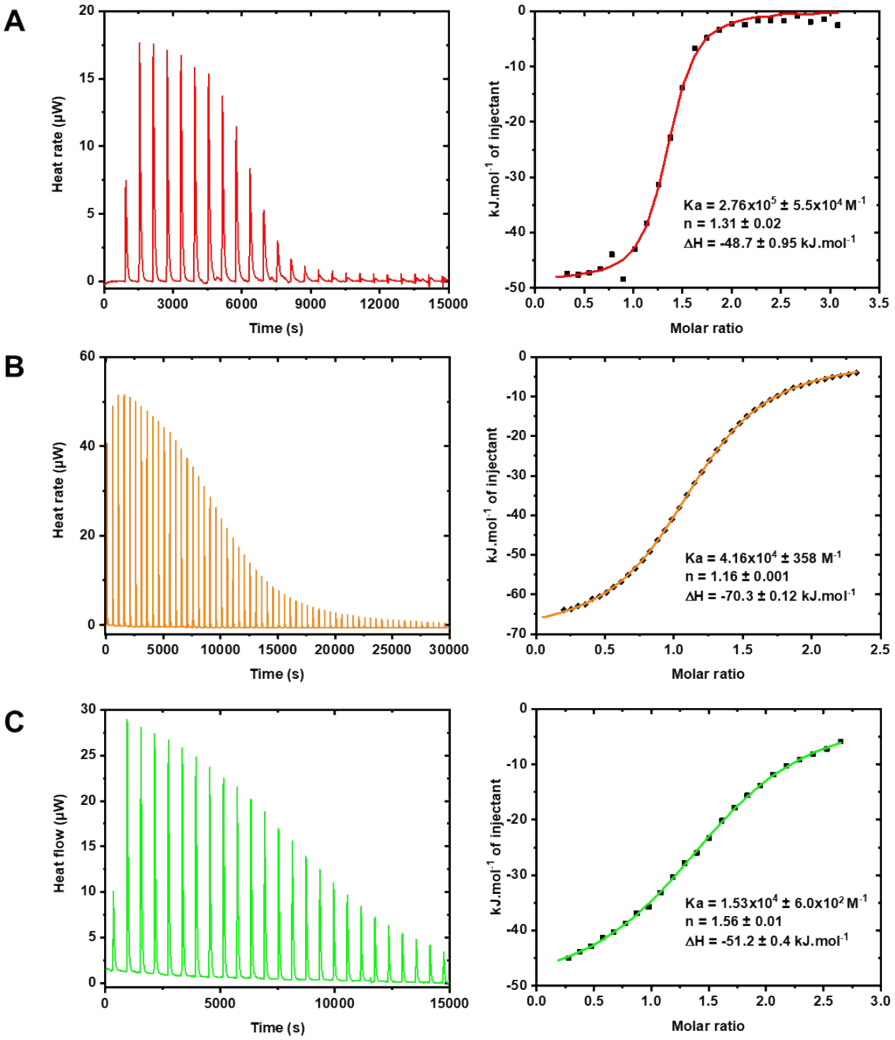

Fig. S5. Isothermal titration calorimetry data for the addition of aliquots of **BBox** to A) **Naphtha-PNIPAm** polymer (recorded in H_2O at 15 °C), B) **Naphtha-PDEAm** polymer (recorded in H_2O at 15 °C), C) **Naphtha-P(CMAm-*co*-Am)** (recorded in H_2O at 60 °C).

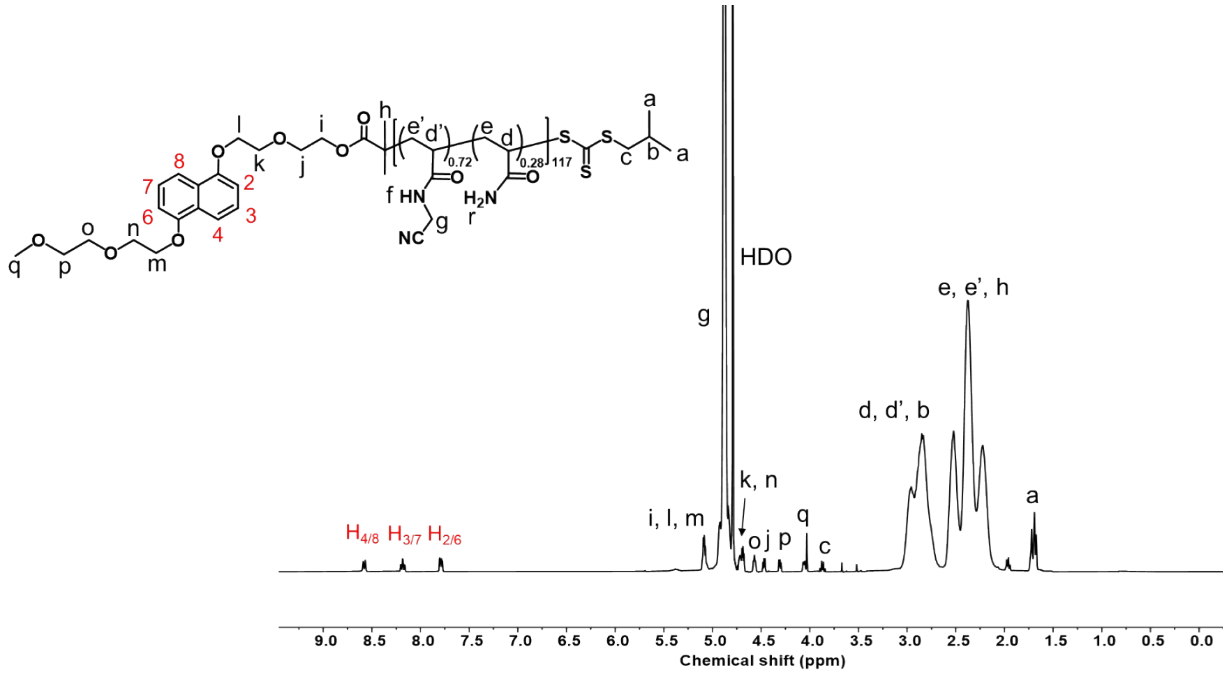

Fig. S6. ^{1}H NMR spectrum **of Naphtha-P(CMAm$_{0.72}$-*co*-Am$_{0.28}$)$_{117}$** in D_2O at 90 °C**.**

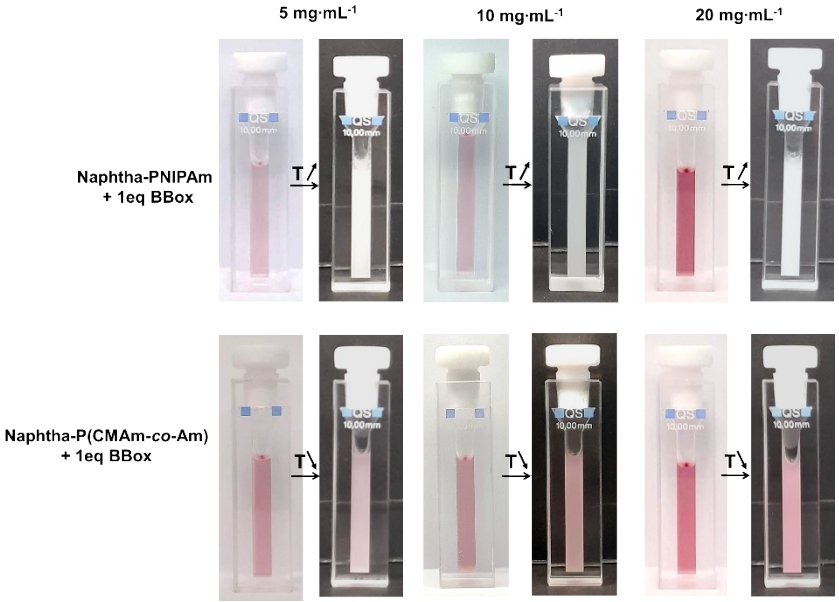

Fig.S7. Photographs of **Naphtha-PNIPAm** (top) and **Naphtha-P(CMAm-*co*-Am)** (bottom) in pure water at 5 mg·mL^{-1}, 10 mg·mL^{-1} and 20 mg·mL^{-1} with 1 equivalent of BBox at different temperatures.

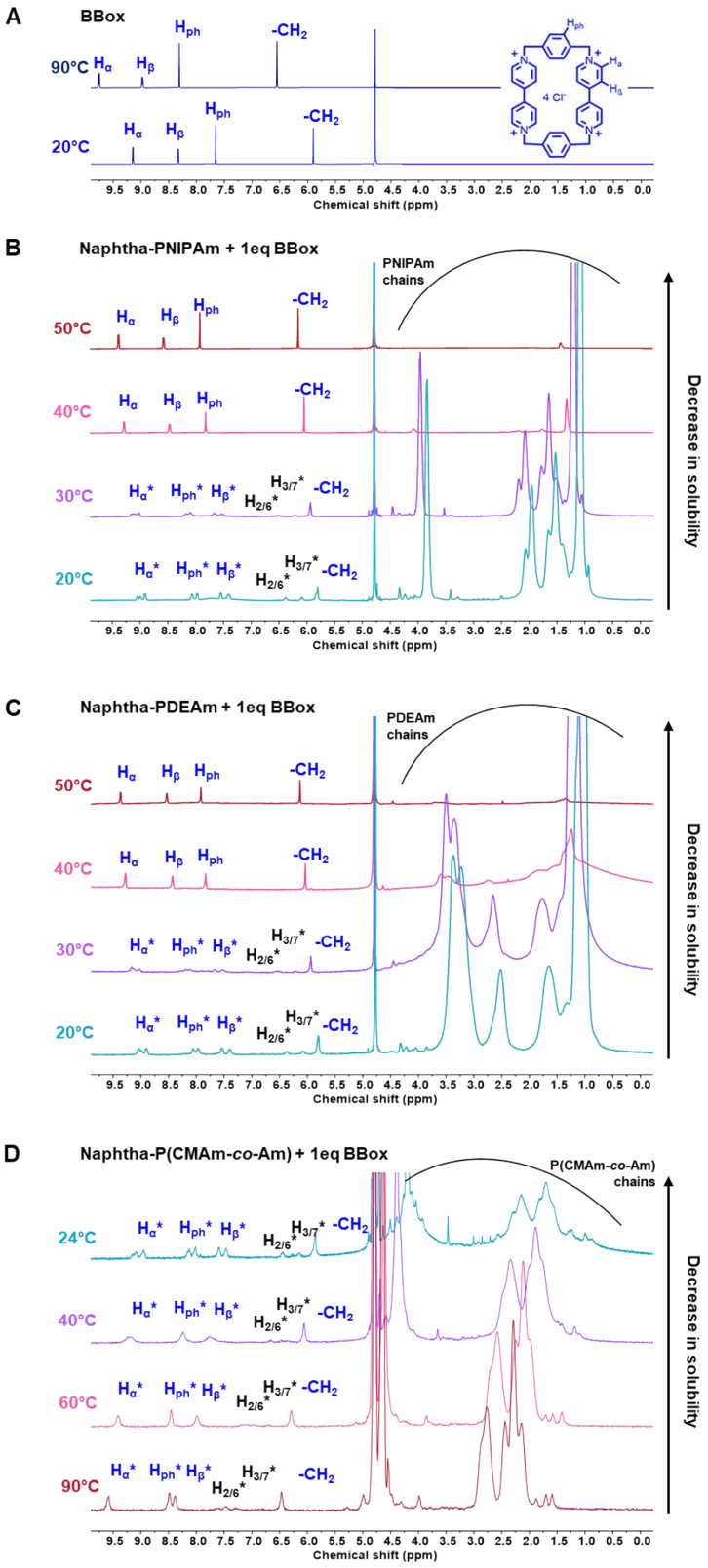

Fig. S8. ^{1}H NMR spectra in D_2O of A) **BBox** alone at 20 and 90 °C (for comparison), B) **Naphtha-PNIPAm** polymer with 1 eq of **BBox** at 20, 30, 40 and 50 °C, C) **Naphtha-PDEAm** polymer with 1 eq of **BBox** at 20, 30, 40 and 50 °C, D) **Naphtha-P(CMAm-*co*-Am)** with 1 eq of **BBox** at 90, 60, 40 and 24 °C. The protons H* denote complexed protons from naphthalene moieties and **BBox.**

References

1. J. Bigot, M. Bria, S. T. Caldwell, F. Cazaux, A. Cooper, B. Charleux, G. Cooke, B. Fitzpatrick, D. Fournier, J. Lyskawa, M. Nutley, F. Stoffelbach and P. Woisel, *Chemical Communications*, 2009, **35**, 5266-5268.

2. N. Audureau, C. Veith, F. Coumes, T. P. T. Nguyen, J. Rieger and F. Stoffelbach, *Macromolecular Rapid Communications*, 2021, **42**, 2100556.