Supporting Information

Accelerated Continuous Flow RAFT Polymerization

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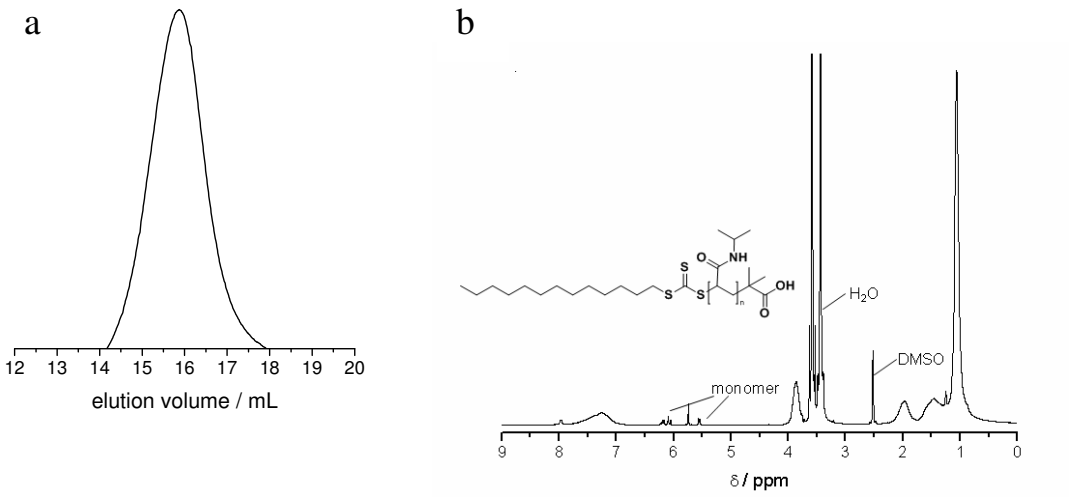
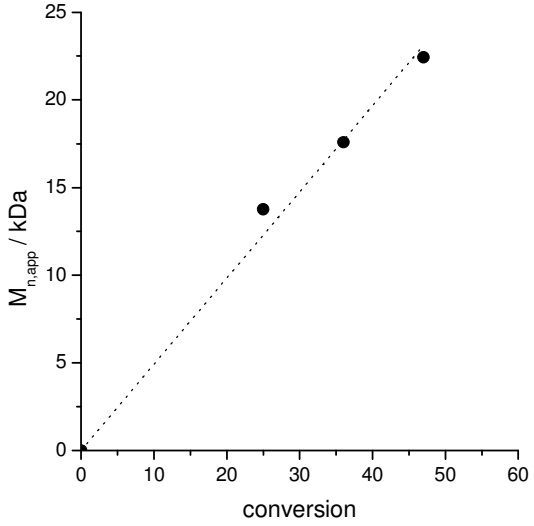
1. NMR and SEC data of PNIPAM

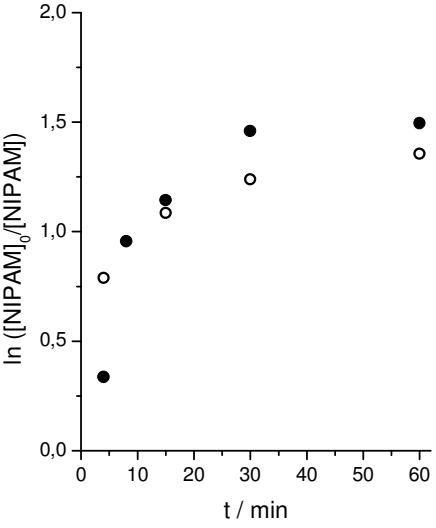


SI 1. Exemplary (a) SEC elugram in NMP and (b) ^{1}H NMR in DMSO d6 of PNIPAM obtained after 1 h at 90 °C in continuous flow (n = 200, yield 88 %).

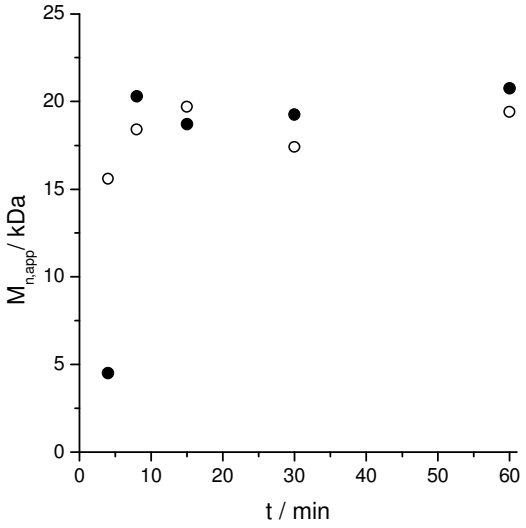
2. Data of kinetics studies



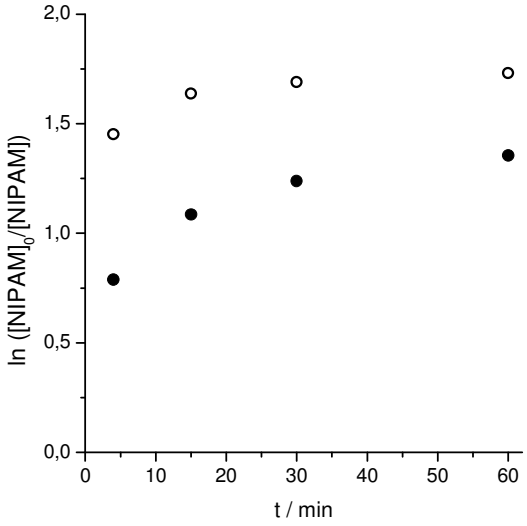
SI 2. Apparent molecular weight $M_{n,app}$ of PNIPAM obtained at 90 °C in continuous flow (n = 1000) plotted against the conversion.



SI 3. Pseudo first-order kinetic plots of the polymerization of NIPAM in continuous flow (n = 200) at 90 °C (●) and 130 °C (○).



SI 4. Evolution of apparent molecular weight of PNIPAM polymerized at 90 °C and n = 200 in continuous flow (●) and under microwave irradiation (○).

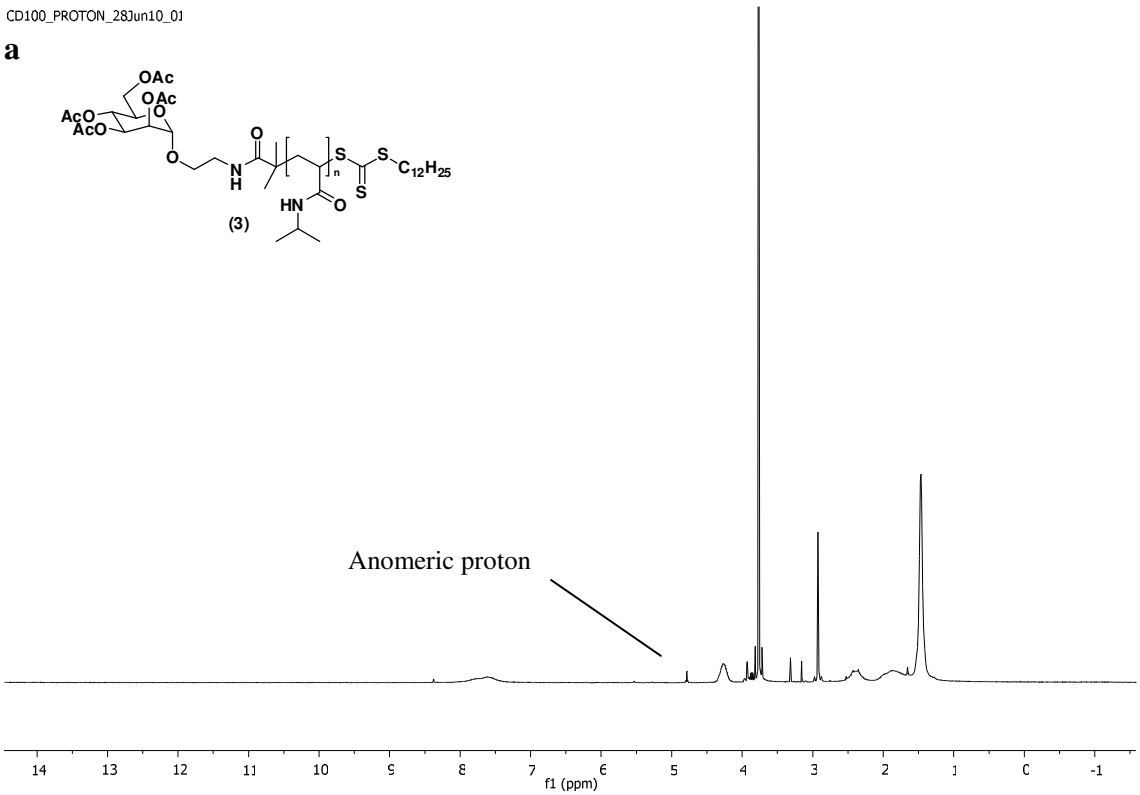


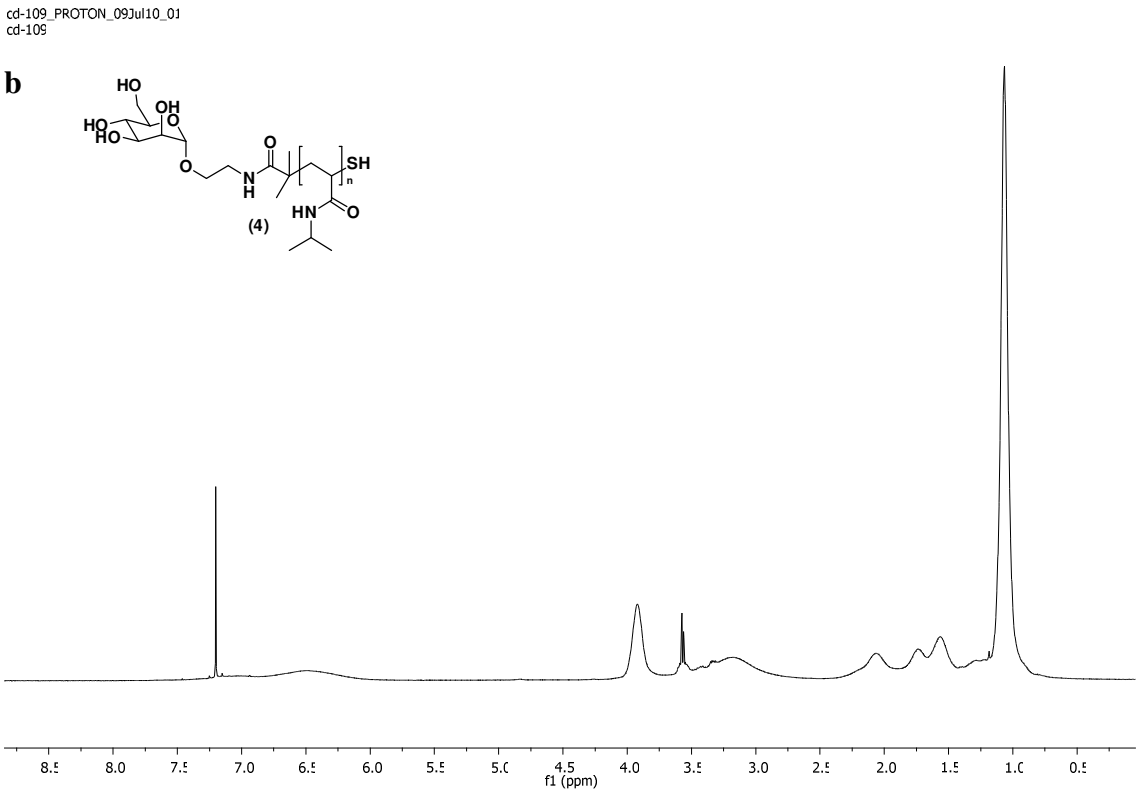
SI 5. Pseudo first-order kinetic plots of the polymerization of NIPAM at 130 °C in continuous flow (●) and under microwave irradiation (○).

3. Mannose functionalized polymer

Functionalization of CTA-PNIPAM-COOH with acetylated mannose. A mixture of CTA-PNIPAM-COOH (40 mg; 2 µmol) and N,N-Diisopropylethylamine (DIPEA, 0.1 mmol, 12.92 mg), benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP, 0.1 mmol, 50.6 mg), 1-Hydroxybenzotriazole (HOBt, 0.1 mmol, 15.30 mg), DMF/DCM (1:1, 5 mL), Mannose-NH_2 (0.1 mmol, 39.1 mg) dissolved in dried DMF was then added dropwise at 0 °C. The reaction mixture was then stirred at room temperature overnight. After dialysis against deionized water for 3 days, the final product (3) was recovered by freeze-drying from water (75%). **^{1}H NMR** (400 MHz, CD_3OD): δ(ppm) = 7.8-7.0 (1H, NH), 4.75 (1H, HC-O, anomeric proton), 4.5-4 (1H, -N-CH<), 2.5-2 (1H, -C-CH-), 2-1.8 (2H, -CH_2-C-), 1.6 (22H, $C_{11}H_{22}$, end group), 1.6-1.4 (6H, CH_3-C-CH_3).

Hydrolysis of 3. The functionalized PNIPAM (**3**, 1.5 µmol, 30 mg) was hydrolyzed and deacetylated by a NaOH solution in methanol (3 mL, 1.0 M, 28%) under nitrogen in the presence of a small amount of EDTA (10 mg). After hydrolysis, the mixture was acidified by 88% formic acid and after dialysis against deionized water for 3 days, the final product (4) was recovered by freeze-drying from water (quant.). **^{1}H NMR** (400 MHz, $CDCl_3$): δ(ppm) = 6.75-6.25 (1H, NH), 4.0-3.7 (1H, -N-CH<), 3.5 (1H, HC-O, anomeric proton), 4.2-3.8 (5H, mannose protons), 3.25-3 (1H, -N-CH<), 1.8-2.2 (1H, -C-CH-), 1.75-1.5 (2H, -CH_2-C-), 1.2-0.8 (6H, CH_3-C-CH_3).

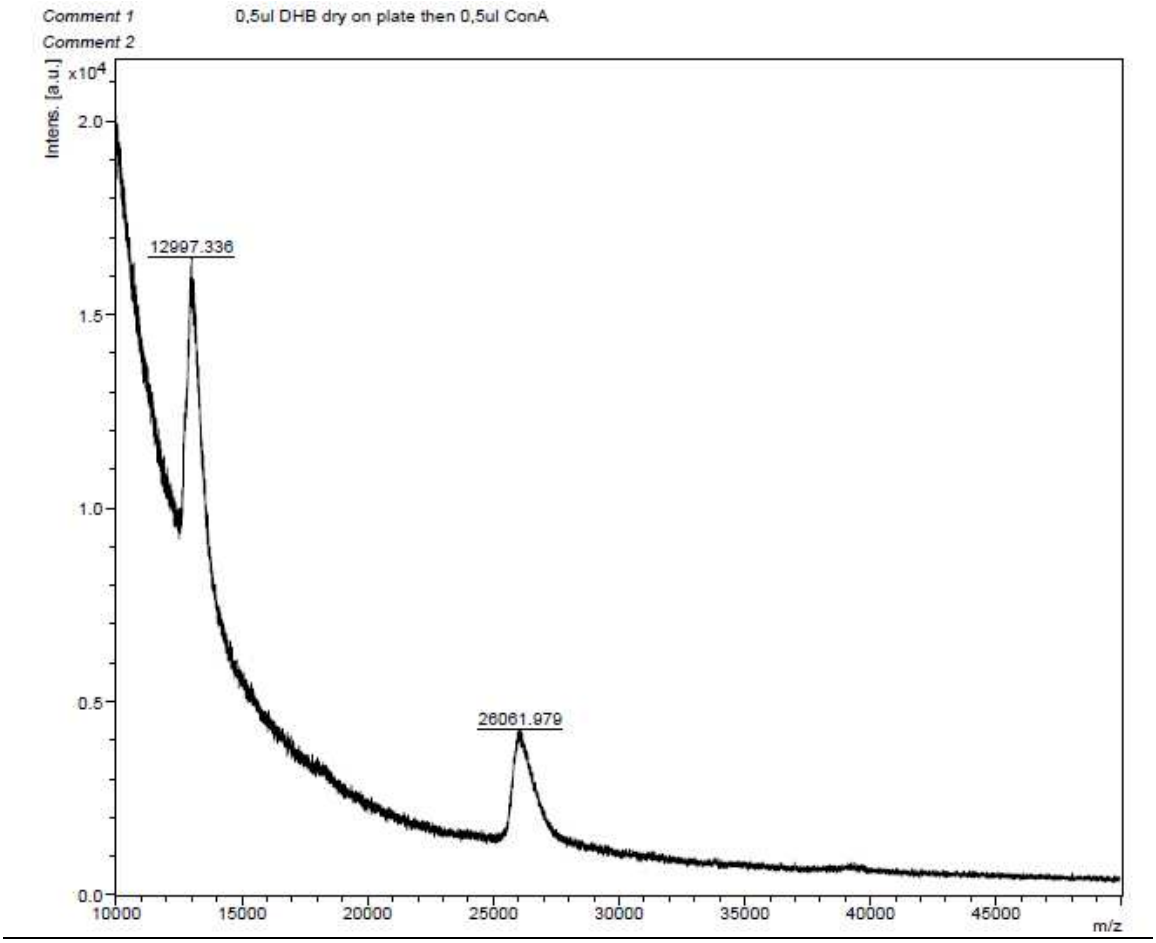




SI6. (a) ^{1}H NMR in DMSO d6 of PNIPAM-acetilated-mannose; (b) ^{1}H NMR in $CDCl_3$ d of PNIPAM-mannose.

4. Microarray experiments

A freshly prepared solution of PNIPAM-mannose 200 μM was printed on a thio-activated microarray glass slide. The polymer has been reacting over night in a humid chamber. After washing out the excess of polymer (3 times with 20 mL water), the slide was incubated for 2 h with ConA or ConA-FITC. The excess of ConA was washed out (3 x 20 mL PBS buffer and 1 x 20 mL water). The slide reacted with ConA- FITC was scanned to detect the binding, then washed at 40 °C to prove the possibility to remove the binding. The slide reacted with ConA was washed intensively over night with water at 40 °C, the washing solution concentrated and MALDI analysis was taken. MALDI sample was dissolved in NH_4HCO_3 (25 mM) and dried on a 2,5- dihydroxybenzoic acid (DHB) matrix previous prepared (Matrix to sample ratio 1:1; matrix preparation: 5 mg DHB dissolved in 100 μl of 1:1 CH_3CN : 0,1% TFA-Water).



SI 7. MALDI analysis of ConA released from the microarray slide

(1) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754-6756.