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Access to Poly{N-[3-(dimethylamino)propyl](meth)acrylamide} via Microwave Assisted Synthesis and Control of LCST-Behavior in Water

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Materials and Methods

Syntheses were carried out in a CEM monomode microwave apparatus, type Discover. 8 ml microwave vials were used as reaction vessels. The reactions took place in a closed system using an infrared sensor for the temperature control. In each case the chosen preheating time was 1 min.

The structures of the synthesized monomers and polymers were proven by ¹H- and ¹³C-NMR spectroscopy using a Bruker Avance DRX 500 spectrometer at 500.13 MHz for proton and 125.77 MHz for carbon, using [1D]CHCl₃ and [4D]MeOH as solvents. Infrared spectra were recorded on a Nicolet 5SXB FT-IR spectrometer. MALDI-TOF analyses were performed

using a Bruker Ultraflex TOF mass spectrometer. Turbidity measurements were carried out by using a TP1 turbidity photometer from TEPPER-Analytic. The measurements took place in the temperature range from 10 to 85 °C with a heating/cooling rate of 1 °C / min. The relative transmittance of the sample was determined by use of a power regulated semiconductor laser (wavelength of 670 nm) and a silicon photodiode.

Glass transition temperatures (T_g) were determined using a Mettler DSC-30 instrument in a temperature range of 0 to 200 °C at a heating rate of 10 °C / min. The T_g values are reported as the average of three to five measurements using the midpoint method. For calibration, standard tin, indium and zinc samples were used. GPC analyses were performed with a Viscotek GPCmax VE2001, using DMF as eluent at 60 °C (flow 1 ml / min) (relative method). 100 μ l were injected on the column arrangement of one Viscotek TSK guard column H_{HR}-H 6.0 mm (ID)*4 cm(L) and two 2 Viscotek TSK GMH_{HR}-M 7.8 mm (ID)*30 cm (L) columns. A Viscotek Viscometer model 250 and a Viscotek VE 3500 RI detector were used for detection. Evaluation was performed using OmniSEC 4.0 software. Polystyrene standards were used for universal calibration. This method is a relative method.

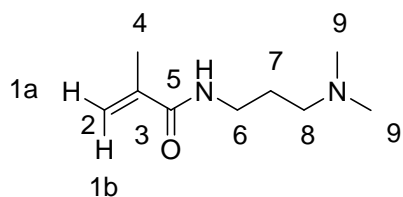
Experimental

NMR of N-[3-(Dimethylamino)propyl]methacrylamide (4)

Yield (2.5 mbar, 104 °C) = 1.03 g

¹H-NMR (500 MHz, [4D]CH₃OH, 25°C): δ [ppm] = 1.73 (quint., 2H; 7-H), 1.93 (s, 3H; 4-H), 2.24 (s, 6H; 9-H), 2.36 (t, 2H; 8-H), 3.27 (t, 2H; 6-H), 5.36 (s, 1H; 1a-H), 5.69 (s, 1H; 1b-H)

¹³C-NMR (500 MHz, [4D]CH₃OH, 25°C): δ [ppm] = 19.22 (1C; 4-C), 28.44 (1C; 7-C), 39.46 (1C; 6-C), 45.85 (2C; 9-C), 58.75 (1C; 8-C), 120.75 (1C; 2-C), 141.77 (1C; 3-C), 171.53 (1C; 4-C)

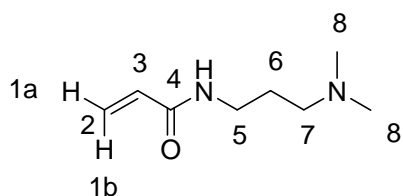


NMR of N-[3-(Dimethylamino)propyl]acrylamide (5)

Yield (2.5 mbar, 98 °C): 0.97 g

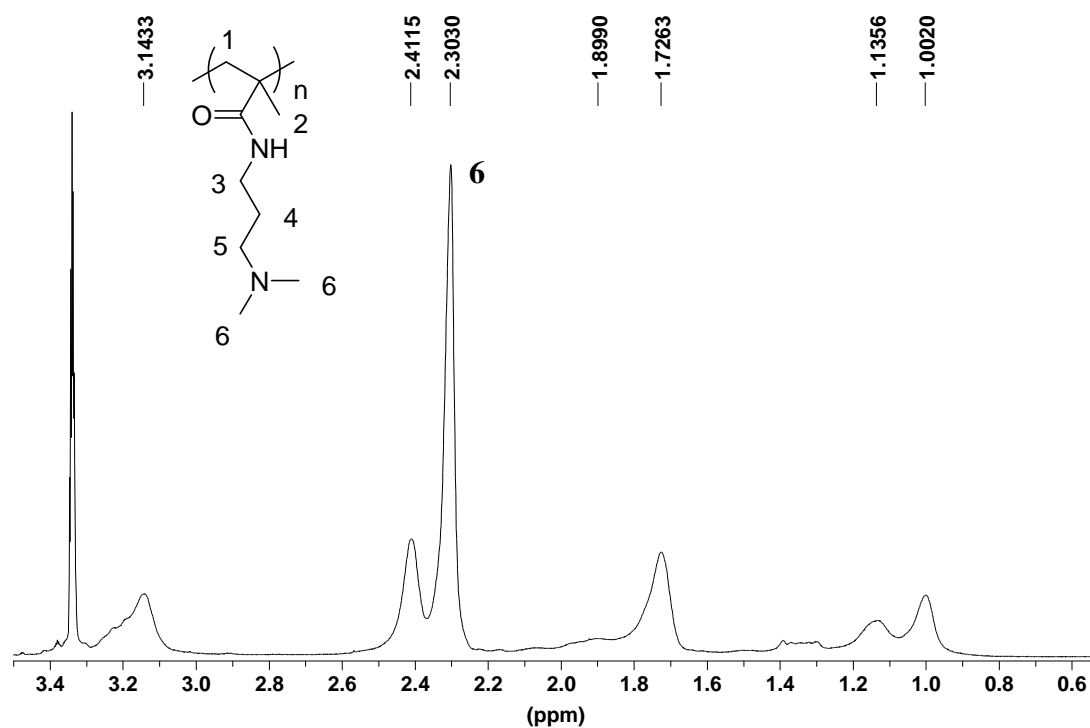
¹H-NMR (500 MHz, [D₄]CH₃OH, 25°C): δ [ppm] = 1.66 (m, 2H; 6-H), 2.18 (s, 6H; 8-H), 2.30 (m, 2H; 7-H), 3.22 (m, 2H; 5-H), 5.59 (q, 1H; 3-H), 6.12 (m, 2H; 1a+1b-H)

¹³C-NMR (500 MHz, [D₄]CH₃OH, 25°C): δ [ppm] = 28.54 (1C; 6-C), 39.06 (1C; 5-C), 45.82 (2C, 8-C), 58.53 (1C; 7-C), 127.10 (1C; 2-C), 132.44 (1C; 3-C)



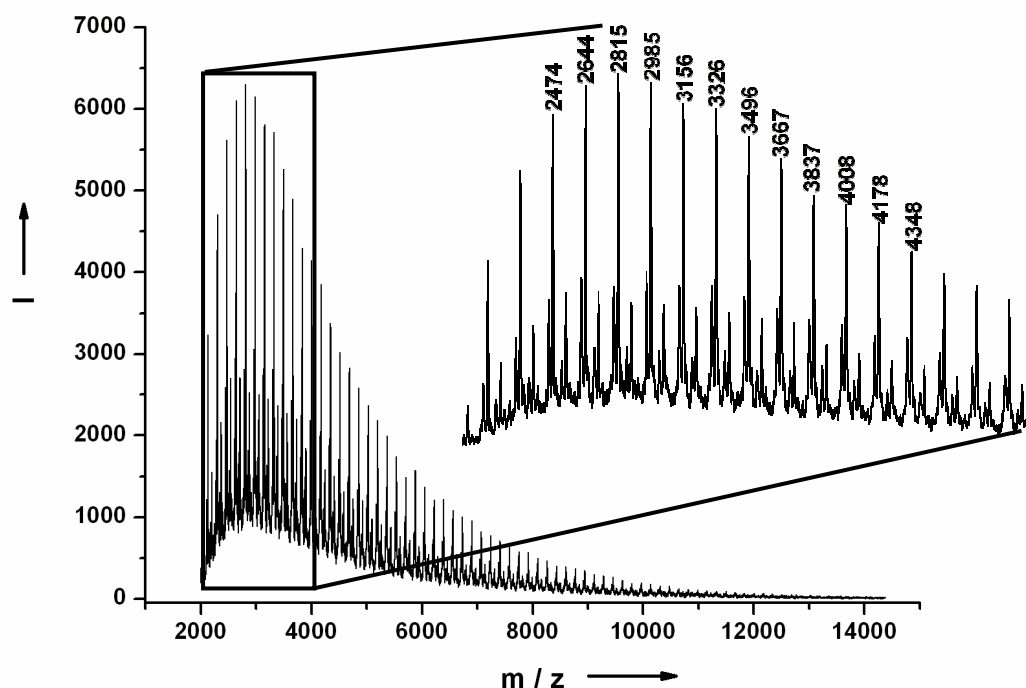
Poly{N-[3-(dimethylamino)propyl]methacrylamide} (6) and Poly{N-[3-(dimethylamino)propyl]acrylamide} (7)

1.5 g of **4** / **5** were dissolved in 5 ml of toluene. The solution was flushed with argon for 20 minutes before addition of 2.5 mol -% AIBN. After polymerization for 24 hours at 70°C the solvent was removed under reduced pressure. The yellowish residue was dissolved in 5 ml of methylene chloride and poured into 500 ml hexane. This precipitation procedure was repeated three times before drying the polymer under reduced pressure.

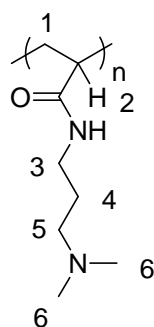


^1H -NMR (500 MHz, $[\text{4D}]\text{MeOH}$, 25°C): δ [ppm] = 1.0-1.14 (bd, 3H; 2-H), 1.73 (bs, 2H; 4-H), 1.90 (bs, 2H; 1-H), 2.30 (bs, 6H; 6-H), 2.41 (bs, 2H; 5-H), 3.14 (bs, 2H; 3-H)

FT-IR (diamond): $\tilde{\nu}$ [cm^{-1}] = 3316 [$\nu(\text{N-H})$], 2941 [$\nu(\text{C-H})$], 2861 [$\nu(\text{C-H})$], 2816 [$-\text{N}(\text{CH}_3)_2$], 2773 [$-\text{N}(\text{CH}_3)_2$], 1639 [$\nu(\text{C=O})$, amide I], 1521 [$\delta(\text{N-H})$, amide II], 1464 [$\delta(\text{C-H})$], 1373 [$\delta_s(-\text{CH}_3)$], 1262, 1201, 1039



MALDI-TOF spectrum of Poly{*N*-[3-(dimethylamino)propyl]methacrylamide} (**6**). The difference between the signals can be determined to 170 g/mol. This corresponds to the molecular mass of one monomer unit. The spectrum shows a molecular weight distribution from ~ 2000 g/mol to ~ 10000 g/mol.

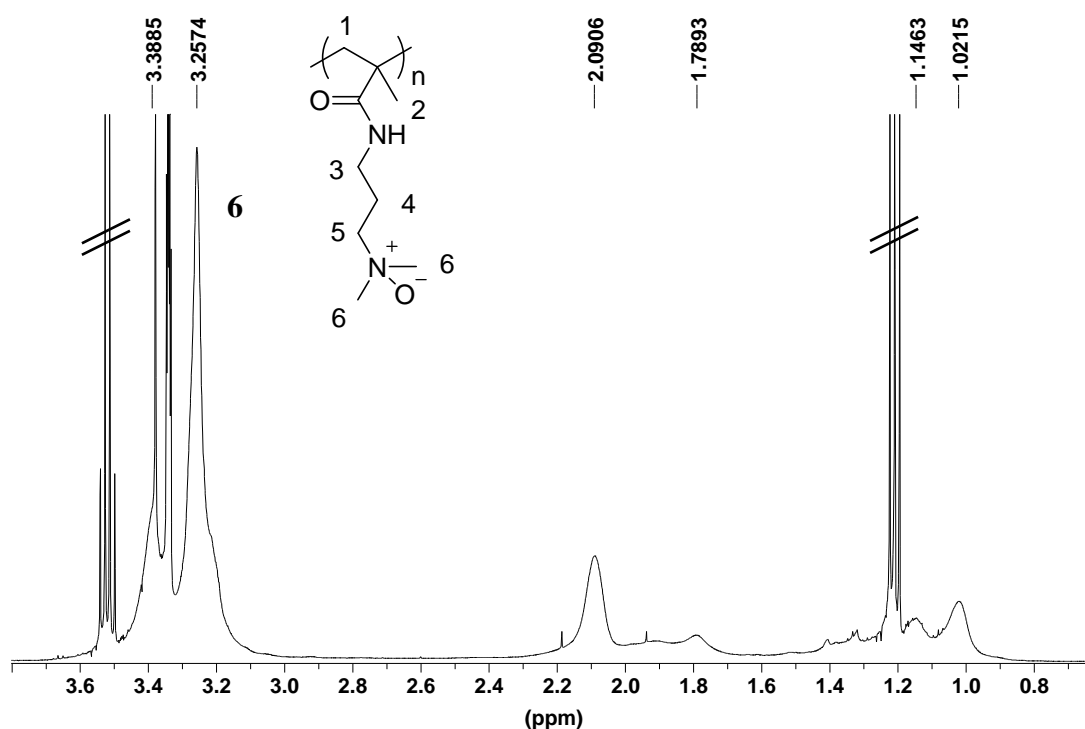


$^1\text{H-NMR}$ (500 MHz, $[\text{D}_1]\text{CHCl}_3$, 25 °C, TMS): δ [ppm] = 1.69 (bs, 4H; 4-H + 1-H), 2.1 (bs, 1H; 2-H) 2.25 (bs, 6H; 6-H), 2.34 (bs, 2H; 5-H), 3.18 (bs, 2H; 3-H)

FT-IR (diamond): $\tilde{\nu}$ [cm^{-1}] = 3281 [$\nu(\text{N-H})$], 2940 [$\nu(\text{C-H})$], 2860 [$\nu(\text{C-H})$], 2815 [$-\text{N}(\text{CH}_3)_2$], 2774 [$-\text{N}(\text{CH}_3)_2$], 1641 [$\nu(\text{C=O})$, amide I], 1539 [$\delta(\text{N-H})$, amide II], 1460 [$\delta(\text{C-H})$], 1376 [$\delta_s(-\text{CH}_3)$], 1261, 1233, 1039

Poly{N-[3-(dimethylamine oxide)propyl]methacrylamide} (8)

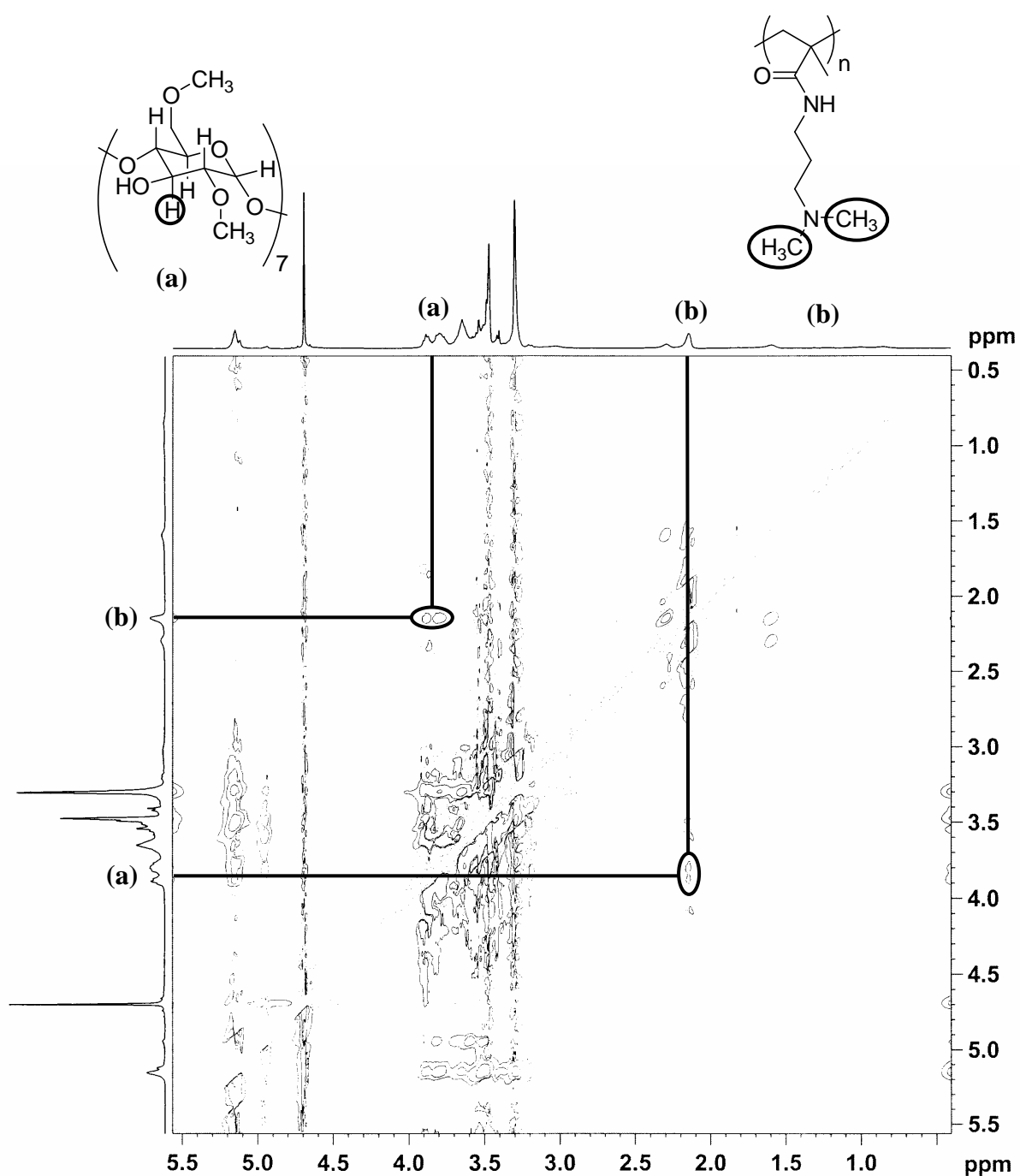
0.1 g of **6** were dissolved in 2 ml of methanol. 0.47 ml of H₂O₂ were added. After stirring for 2 days the solvent was removed in vacuum. The obtained polymer was dissolved in a small amount of methanol, poured into diethyl ether, filtered off and dried under reduced pressure. As the remaining polymer is not soluble in [D₁]CHCl₃, ¹H-NMR-spectra of **6** and **8** were measured in [D₄]MeOH to compare the shift of the signals. The signal of the CH₃-groups (**6**) shifted from 2.25 ppm (polymer **6**) to 3.26 ppm (polymer **8**) according to the conversion from tertiary amine to amine oxide.



¹H-NMR (500 MHz, [D₄]MeOH, 25°C): δ [ppm] = 1.02-1.15 (bd, 3H; 2-H), 1.79 (bs, 2H; 1-H), 2.09 (bs, 2H; 4-H), 3.26 (bs, 6H; 6-H), 3.39 (bs, 4H; 3-H + 5-H)

FT-IR (diamond): $\tilde{\nu} [\text{cm}^{-1}] = 3282 [\nu(\text{N-H})]$, 2954 $[\nu(\text{C-H})]$, 2801, 2155, 2029, 1629 $[\nu(\text{C=O})]$, amide I], 1528 $[\delta(\text{N-H})]$, amide II], 1475, 1455 $[\delta(\text{C-H})]$, 1390 $[\delta_s(-\text{CH}_3)]$, 1285, 1203, 1121, 963 $[\nu(\text{N-O})]$, 928

2D-ROESY-NMR of the polymer- β -CD-complex



Turbidity measurements

To determine the LCST of the polymers **6**, **7** and **8**, 0.5 weight-% solutions were prepared. Therefore 0.015 g of each polymer were dissolved in 2985 μl of water. The measurements were carried out in the temperature range from 10 to 80°C with a heating rate of 1°C/min.