



Supporting Information

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Pseudo-LCST Behavior of Polymethacrylamides by Supramolecular Interactions with Cyclodextrin

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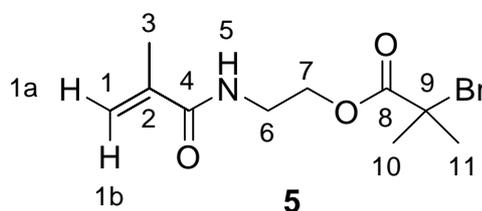
Materials and instruments

Methacryloyl chloride (ALDRICH), 2-aminoethanol (ALDRICH), 2-bromoisobutyryl bromide (ALDRICH) and randomly methylated β -cyclodextrin (β -CD) (WACKER) were used as received. All solvents were distilled before usage.

The structures of the synthesized monomers and polymers were proven by ^1H - and ^{13}C -NMR spectroscopy using a Bruker Avance DRX 500 spectrometer at 500.13 MHz for proton and 125.77 MHz for carbon, using CDCl_3 and DMSO-d_6 as solvents. Infrared spectra were recorded on a Nicolet 5SXB FT-IR spectrometer. MALDI-TOF analyses were performed using a Bruker Ultraflex TOF. Turbidity measurements were realized using a TP1 turbidity photometer and apendent corvette HELMA 110-QS 10 from TEPPER-Analytic. The measurements took place in the temperature range from 10 to 85°C with a heating/cooling rate of 1°C/ minute. The relative transmittance of the sample was determined by use of a power regulated semiconductor laser (wavelength of 670 nm) and a silicium photodiode.

2-(Methacrylamido)ethyl 2-bromoisobutyrate (5).

Elemental analysis: $C_{10}H_{16}NO_3Br$, calculated (%): C, 43.18; H, 5.79; N, 5.04. Found (%): C, 43.13; H, 5.92; N, 4.79. 1H -NMR (500 MHz, $[D_1]CHCl_3$, 25°C, TMS): δ 1.95 (s, 6H; 10-H, 11 H), 1.97 (s, 3H; 3-H), 3.66 (m, 2H; 6-H), 4.33 (m, 2H; 7-H), 5.35 (m, 1H; 1- H_a), 5.73 (m, 1H; 1- H_b), 6.32 (bs, 1H; 5-H) ppm. ^{13}C -NMR (500 MHz, $[D_1]CHCl_3$, 25°C, TMS): δ 18.65 (3-C), 30.65 (10-C, 11-C), 38.61 (6-C), 56.14 (9-C), 64.55 (7-C), 120.13 (1-C), 139.65 (2-C), 168.53 (8-C), 171.70 (4-C) ppm. FT-IR (diamond): $\tilde{\nu}$ [cm^{-1}] = 3332 [$\nu(NH)$]; 2977, 2957, 2928 [$\nu(CH)$]; 1734 [$\nu(C=O)$]; 1657 [$\nu(C=O)$], amide I], 1525 [$\delta(NH)$, amide II]; 1454 [$\delta(CH)$]; 1372, 1390 [$\delta(CH_3)$]; 1272, 1216, 1159 [$\nu(C-O)$]; 926 [$\gamma(CH)$]; 1619, 1461, 1107, 869, 809



Preparation of polymer 6

1H -NMR (500 MHz, $[D_1]CHCl_3$, 25°C, TMS): δ 1.02 (2H; $-CH_2-$), 1.97 (9H; $-CH_3$), 3.48 (2H; $-NH-CH_2-$), 4.25 (2H; $-O-CH_2-$), 6.23 (1H; $-NH-$) ppm. FT-IR (diamond): $\tilde{\nu}$ [cm^{-1}] = 3421 [$\nu(NH)$]; 2976, 2930 [$\nu(CH)$]; 1733 [$\nu(C=O)$]; 1662 [$\nu(C=O)$], amide I], 1516 [$\delta(NH)$, amide II]; 1390, 1371 [$\delta(CH_3)$]; 1274, 1161 [$\nu(C-O)$]; 1463, 1107

Job-Plot

The preferred stoichiometry of monomer β -CD complexes can be evaluated using Job's method ^[11,12] transferred to the NMR-spectroscopy by Blanda et al. ^[13]. Both methods are based on the so-called method of continuous variation. Different volumes of solutions of host and guest are mixed in a way that the total volume remains constant while the ratio $[Host]/[Guest]$ varies in small steps. The change in the chemical shift of defined guest protons of a host-/ guest-solution relative to the pure guest-solution ($\Delta\delta$) describes a linear function of the mole fraction (x) of each species under these conditions. A plot of the product $\Delta\delta * x(guest)$ against $x(host)$ yields a curve whose maximum determines the complex stoichiometry. Therefore the chemical shift of the six protons of the methyl groups

(-CBr(CH₃)₂) has been monitored. Job's plot is shown in figure 1a. For the measurement 3mmolar solutions of host and guest in D₂O were used.

2D-ROESY-NMR

The 2D-ROESY measurements indicate strongly the formation of structures "A" and "C" as schematically represented in figure 5. Furthermore, structure B should exist in a low probability, taking the magnetic interactions between β-CD and guest monomer 5 into account (figure 1b). Few magnetic interactions between β-CD and the protons next to the vinyl group (-C(CH₃)=CH₂) exist, which result in a minimal difference of chemical shift of $\Delta\delta = 0.035$ ppm with increasing amount of β-CD. However, the structures A and B represent the existence of a 1:2 complex while structure C illustrates a simple 1:1 complex. In conclusion, the formed complex should be intermediate. This is in accordance to the 1:1.5 average complex as calculated from the Job Plot (figure 1a).

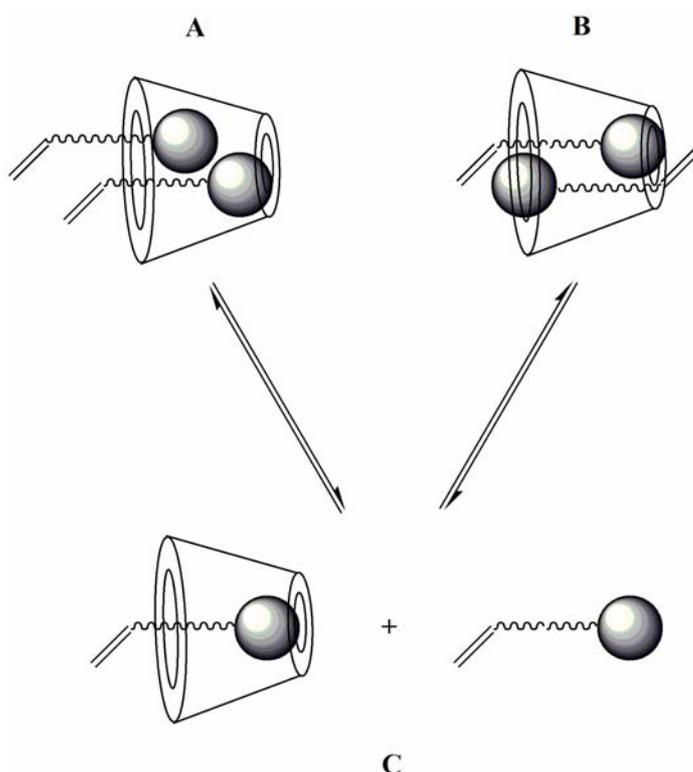


Figure 5. Postulated equilibrium in complex formation between a 1:2 - and a 1:1 - complex