

Supplementary Information

Amphiphilic Block Copolymers Based on Cyclodextrin Host-Guest Complexes via RAFT-Polymerization in Aqueous Solution

Heike S. Köllisch,¹ Christopher Barner-Kowollik^{2*} and Helmut Ritter^{1*}

¹Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität, Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf (Germany), Fax: (+49) 211 811-5840, E-mail: h.ritter@uni-duesseldorf.de

²Institut für Technische Chemie und Polymerchemie, Lehrstuhl für Präparative Makromolekulare Chemie, Karlsruhe University/Karlsruhe Institute of Technology, Engesser Str. 18, Geb. 11.23, 76131 Karlsruhe (Germany), Fax: (+49) 721 608-5740, E-mail: christopher.barner-kowollik@polymer.uni-karlsruhe.de, Homepage: www.macroarc.de

Experimental Section

Materials: The RAFT agent, 3-benzylsulfanylthiocarbonyl-sulfanylpropionic acid (TTC) was synthesized as described previously.^[1] 6-Acryloylamino-hexanoic acid-1-adamantylamid (M_{ADA}) was synthesized according to known procedures. *N,N*-dimethylacrylamide (DMA) was distilled under reduced pressure.

2,2'-azobis(*N,N*-dimethylenisobutyramidine) dihydrochlorid (VA-044) (WAKO) and randomly methylated β -CD (me- β -CD, average degree of substitution \approx 1.8 mainly in 2- and 6-position of the glucose unit, CAVASOL®W7M, Wacker) was used as received.

Measurements: GPC analysis were performed with a Viscotek GPCmax VE2001, using DMF as the eluent at 60 °C (flow rate: 1 mL min⁻¹). Samples of 100 μ L were injected on the arrangement of columns consisting of one Viscotek TSK guard column HHR-H 6.0 mm(ID) x 4 cm (L) and two Viscotek TSK GMH_{HR}-M 7.8 mm(ID) x 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 with a molecular weight ranging from 580 to 1186000 g mol⁻¹ were used for universal calibration. The samples withdrawn from the reaction vessel for SEC-measurements were diluted with water, after addition of trifluoroacetic acid (TFA) the precipitated polymer was isolated and washed with water till pH-neutrality. The dry polymeric material was dialyzed, and freeze-dried. MALDI-TOF-MS was performed on a Bruker Ultraflex TOF mass spectrometer using a 337-nm nitrogen laser. The samples were dissolved in THF and analyzed in a 4-hydroxyazabenzene-2'-carboxylic acid (HABA) matrix (HABA/THF 1 : 2). The monomer conversion was measured using a Bio-Tek Kontron Instruments HPLC (high pressure liquid chromatograph) equipped with HPLC 540 Diode array detector. For HPLC measurements aliquots (250 μ L) of the polymerization solution were taken and diluted (1 : 40) with acetonitrile: water (8:2).

Preparation of Aqueous me- β -CD/6-acryloylamino-hexanoic acid-1-adamantylamid Solutions: Preparation and characterization of the me- β -CD/6-acryloylamino-hexanoic acid-1-adamantylamid complex has already been described.^[2,3]

RAFT Homopolymerization: Me- β -CD and M_{ADA} were dispersed in water, stirred and sonicated to give a clear homogenous solution of the host/guest complex. The water-soluble RAFT agent TTC and the radical initiator VA-044 were successively added to the aqueous me- β -CD/ M_{ADA} solution

and dissolved under stirring at room temperature. For all polymerizations the molar ratio of me- β -CD : M_{ADA} was 1.5 : 1 and the amount of me- β -CD was kept constant at 40 wt.%. The molar ratios of RAFT agent and initiator are given in Table S11, S12 and 1. All polymerizations were performed in Schlenk flasks equipped with a magnetic stirring bar and gas inlet. After degassing by purging with argon for 20 min the flask was sealed and immersed in a preheated oil bath at 45 °C. Samples were taken after pre-selected time intervals to evaluate the evolution of conversion and molecular weight by use of HPLC and GPC as well as MALDI-TOF MS. No precipitation of the formed PM_{ADA} was observed during the reaction. After the polymerization time the mixture was diluted with water, trifluoroacetic acid was added and the precipitated poly(M_{ADA}), was isolated by filtration.

Table S11. RAFT polymerization me- β -CD/ M_{ADA} complexes in water at 45 °C using a molar ratio of [TTC] : [VA-044] = 5 : 1 and [M_{ADA}] : [TTC] = 15 : 1.

Time / min	Conv. ^[a] / %	ln([M] ₀ /[M])	M_n ^[b] / g mol ⁻¹	M_n ^{theo [c]} / g mol ⁻¹	PD ^[b]
30	31	0.37	5800	1400	1.1
60	61	0.91	6100	2500	1.1
90	79	1.58	5900	3200	1.1
120	88	2.14	6900	3500	1.1

[a] Measured by use of HPLC [b] measured by use of MALDI-TOF MS (HABA) [c] calculated according to Eq. 1.

Table S12. RAFT polymerization me- β -CD/ M_{ADA} complexes in water at 45 °C using a molar ratio of [TTC] : [VA-044] = 10 : 1 and [M_{ADA}] : [TTC] = 5.4 : 1.

Time / min	Conv. ^[a] / %	ln([M] ₀ /[M])	M_n ^[b] / g mol ⁻¹	M_n ^{theo [c]} / g mol ⁻¹	PD ^[b]
30	29	0.35	4600	800	1.1
60	58	0.87	5200	1300	1.1
90	78	1.5	5500	1600	1.1
120	87	2.04	5800	1800	1.1

[a] Measured by use of HPLC [b] measured by use of MALDI-TOF MS (HABA) [c] calculated according to Eq. 1.

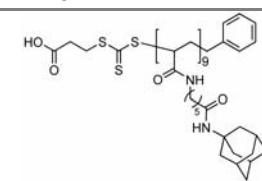
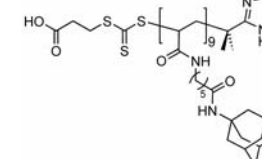
Table S13. RAFT polymerization me- β -CD/ M_{ADA} complexes in water at 45 °C using a molar ratio of [TTC] : [VA-044] = 10 : 1 and [M_{ADA}] : [TTC] = 15 : 1.

Time / min	Conv. ^[a] / %	ln([M] ₀ /[M])	M_n ^[b] / g mol ⁻¹	M_n^{theo} ^[c] / g mol ⁻¹	PDI ^[b]
10	2	0.02	4300	380	1.1
30	15	0.17	5300	1000	1.1
50	37	0.46	5800	2000	1.2
70	54	0.77	6100	2800	1.2
90	67	1.11	6300	3500	1.2
120	79	1.58	6700	4000	1.2
180	90	2.27	6800	4600	1.2
240	94	2.83	7100	4800	1.1

[a] Measured by use of HPLC [b] measured by use of MALDI-TOF MS (HABA) [c] calculated according to Eq. 1.

RAFT Block Copolymerization (Chain Extension): Me- β -CD (1.36 g, 1.04 mmol) and the PM_{ADA} macro CTA (158 mg, 0.06 mmol) were dissolved in chloroform to give a clear homogenous solution of the PIC, after evaporation of the solvent, the PIC was dissolved in water (5 g). The water-soluble monomer DMA (1.00 g, 10.1 mmol) and the radical initiator VA-044 (3.7 mg, 0.012 mmol) were successively added to the aqueous me- β -CD/ PM_{ADA} solution and dissolved under stirring at room temperature. After degassing by purging with argon for 20 min the flask was sealed with the argon inlet and immersed in a preheated oil bath at 45 °C. After the polymerization time the mixture was lyophilized and isolated by dialysis.

Table S14. Experimental and theoretical m/z values for the signals of the zoom spectrum in Figure 2b and their structural assignment.

Signal	$m/z_{\text{exp.}}$	m/z_{theo}	Assignment
A ⁹	3161.5	3161.5	
B ⁹	3181.5	3181.5	

- [1] M. H. Stenzel, T. P. Davis, *J. Polym. Sci. Polym. Chem.* **2002**, *40*, 4498.
- [2] H. Ritter, O. Sadowski, E. Tepper, *Angew. Chem. Int. Ed.* **2003**, *42*, 3171.
- [3] O. Kretschmann, Soo Whan Choi, M. Miyauchi, I. Tomatsu, A. Harada, H. Ritter, *Angew. Chem. Int. Ed.* **2006**, *45*, 4361.