Formation of Physical Hydrogels via Host−Guest Interactions of *β*-Cyclodextrin Polymers and Copolymers Bearing Adamantyl Groups

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ABSTRACT: In this paper, we would like to present a novel system of host−guest hydrogels. By polymerizing adamantyl containing acrylamide monomers (**12**−**15**) with water soluble comonomers, we synthesized various copolymers bearing guest components. As host system we applied easily accessible *β*-cyclodextrin polymers with M_n values of about 30K−100K g mol^{-1}. The viscosity of the resulting hydrogel could be influenced by the concentration of both substances, by the length of the carbon spacer chain of the guest monomer, by the pH value or by the conformation of the *β*-cyclodextrin polymers. Moreover, the hydrogels stayed stable in solutions of starch hydrolyzing enzyme taka-diastase from *Aspergillus oryzae*.

Introduction

In recent years cyclodextrins (CDs) achieved increasing importance in various fields of chemical applications, for example drug delivery systems,[1] polymerization of hydrophobic monomers in water via polymer-inclusion complexes[2−15] and functional hydrogels.[16−19]

We have recently reported about switchable hydrogels obtained by host−guest interaction of adamantyl-containing copolymers with cyclodextrin dimers.[20] Wenz et al. investigated the building of physical hydrogels by host−guest interaction of main chain cyclodextrin-polymers with suitable guest copolymers.[21−23] Futhermore, the synthesis of hydrogels based upon epichlorohydrin cross-linked cyclodextrin polymers and diadamantyl-PEO[24−27] or poly{*N*-[tris(hydroxymethyl)methyl]-acrylamide}[28] has been shown. Thus, the host−guest interaction of cyclodextrins with suitable guests is an ideal system to prepare fast and easily non covalently cross-linked, physical hydrogels.

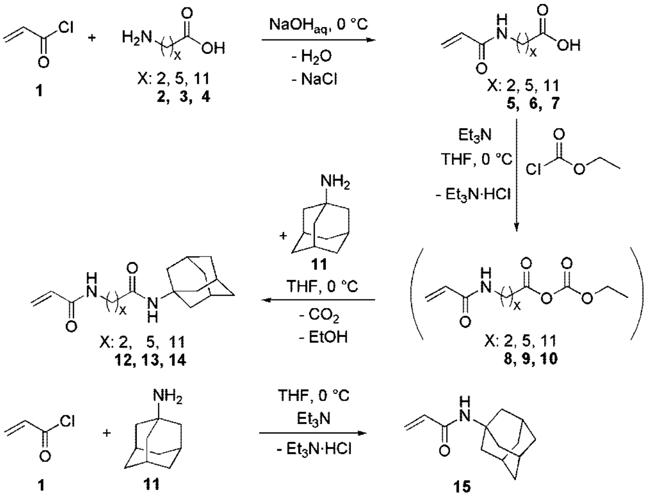
In this paper, we wish to present a novel route to obtain hydrogels based on polymeric-cyclodextrins and adamantane-containing guest copolymers.

Results and Discussion

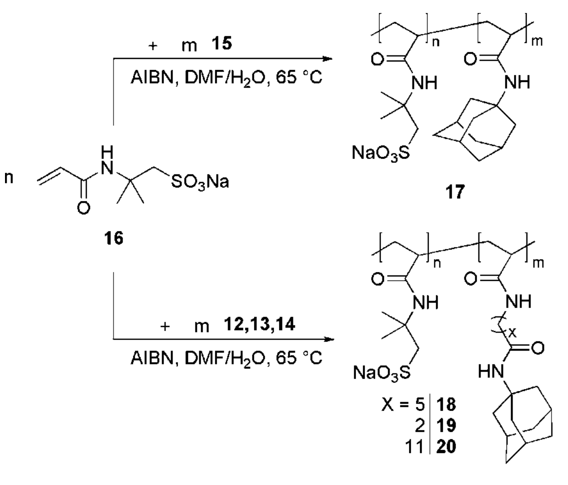
Acrylamide monomers **12**−**15** containing adamantyl moieties were synthesized[8,29] and polymerized. Typically, a copolymer was obtained with M_n = 125K g/mol via radical polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS-Na) (**8**) and adamantyl-containing monomers **6**, **7** (Schemes 1 and 2).

The cyclodextrin (CD) polymer as potential host component for copolymers **17**−**20** is easily accessible via a reaction of native *β*-CD and epichlorohydrin **22** in a sodium hydroxide solution. Dialysis (MWCO 8000) was carried out to separate the CD polymer from unreacted substances and smaller CD oligomers. It was possible to obtain a maximum yield of 65% of CD polymer **23** cross-linked with 5 mol % **22** after dialysis. The molecular weight and the size of the CD polymers are influenced by the amount of cross-linker **22**. It was possible to synthesize water soluble CD polymers **23** by adding 2−5 mol % cross-linker **22** to the *β*-CD solution. Lower amounts of cross-linker yielded only CD oligomers which were fully removed by dialysis.

Scheme 1. Synthesis of Adamantyl-Containing Acrylamide Monomers 12, 13, 14, 15



Scheme 2. Synthesis of Guest-Polymers 17, 18, 19, 20 with a Molar Ratio of Both Monomers *m*/*n* = 1/9



Furthermore, we tried to design the CD polymers in two different pathways. By adding toluene in a first step of the reaction to the CD solution, we synthesized preferentially linear CD polymers **23**. The steric hindrance of the CD−toluene

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Scheme 3. Synthesis of Linear Host CD Polymer 23 and Globular Host CD Polymer 24

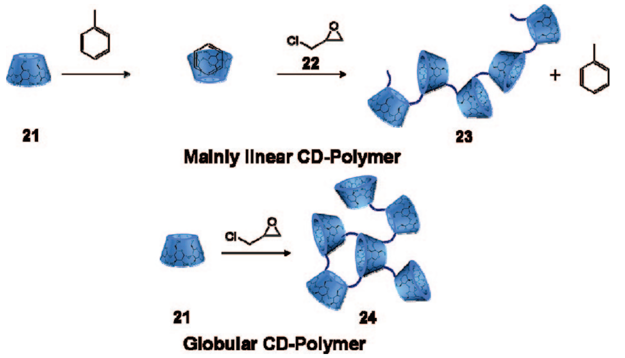


Table 1. Molecular Weight Measured by AFFF (Asymmetric Field Flow Fractionation)/LS (Light Scattering) and Hydrodynamic Diameter Measured by DLS (Dynamic Light Scattering) of Both Types of CD Polymer 23, 24 in Dependence of Addition of Cross-Linker during Synthesis

	M_n /gmol^{-1}		hydrodynamic diam/nm	
addition of cross-linker/mol %	linear CD polym **23**	globular CD polym **24**	linear CD polym **23**	globular CD polym **24**
2	30K	28K	3.12	3.12
3	37K	30K	4.85	4.19
4	96K	43K	5.61	4.85
5	106K	100K	8.72	6.5

complex mainly supports linear linking. In contrast, without toluene, we obtained globular CD polymers **24**, with a maximum yield of 50% by application of 5 mol % cross-linker **22**. (Scheme 3). Both structures of CD polymer types could be confirmed by a comparison between molecular weight and hydrodynamic radius. CD polymers, which are synthesized without the addition of toluene, show at higher molecular weights a smaller hydrodynamic diameter compared to samples prepared in the absence of toluene[30] (Table 1).

The final hydrogel is formed easily by mixing aqueous solutions of host CD polymer **23**,**24** and guest polymer **18**. The rheological properties of the emerging hydrogels were measured and compared. In the following experiments, we used host CD polymers, which are synthesized with 5 mol % epichlorohydrin **22** as cross-linker. Figure 1 shows that mixing of both components (**18** and **23**) in aqueous solution leads to a drastic increase of the viscosity. Both guest copolymer **18** and host CD polymer **23** behave like Newtonian fluids with zero shear viscosity η_0 = 0.01 Pa•s (**18**) and η_0 = 0.003 Pa•s (**23**) respectively. As expected, the hydrogel shows shear thinning behavior even at low shear rates, as the physical host–guest relationship between host CD polymer and the adamantyl side chain of the guest copolymer is disturbed by the increasing mechanical stress. Nevertheless, the aqueous mixture of **18** and **23** shows a dramatic difference in its rheological behavior with η = 400 Pa•s at a shear rate of ca. 0.12 s^{-1}. The addition of a competitive guest monomer, like adamantanecarboxylate, to the hydrogel also leads to a breakdown of the physical network.

The stability of the hydrogel network depends on the concentration of both host CD polymer **23** and guest polymer **18**, as the viscosity first increases with increasing concentration and passes a maximum for the host at a concentration of 25 mg mL^{-1} and for the guest at 50 mg mL^{-1} (Figure 2a/b). The maximum in both curves corresponds to a host–guest stoichiometry of 1:1, i.e. the hydrogel then consists of the same amount of linked CD units and adamantyl groups. At higher concentrations of **18** or **23** physical cross-linking is suppressed. By varying the concentration, the viscosity of the system is easily adjustable.

Moreover, the viscosity or the host–guest interaction of these hydrogels can be influenced by the length of the adamantyl side chain. In Figure 3 flow curves of four different hydrogels are displayed. At lower shear rates all hydrogels nearly behave like Newtonian fluids with a shear thinning behavior at higher shear rates. The zero shear viscosity η_0 of the hydrogel with guest polymer **17** bearing adamantyl directly next to the polymer backbone is ca. 3.63 Pa•s and increases up to ca. 1007 Pa•s at guest polymer **19** with a 3-C-atom spacer between the backbone and the adamantyl group (6C polymer **18** 354.8 Pa•s, 12C polymer **20** 138.3 Pa•s). The spacer length between the polymer backbone and the adamantyl groups influences the complexation with **23**. In the case of no spacer, the polymer backbone of **17** prevents an easy complexation with the host CD polymers **23**. With a 3-C-atom spacer the adamantyl groups of **19** are accessible the best for **23**. With increasing spacer length the flexibility of the spacer also increases, thus, it is possible to build moieties of adamantane in the polymer coil, which results in worse complexation and less viscosity of the hydrogel network.

Furthermore, the hydrogel is also influenced by the relative amount of the adamantyl groups assembled into the polymer backbone. The zero shear viscosity η_0 of the hydrogel rises up to 1247 Pa•s when the adamantyl monomer **6** is assembled into the backbone with a stoichiometry of 4:1 [(AMPS-Na **16**):(adamantylacrylamide **6**)], decreases to 354.8 Pa•s (9:1) and finally to 62.3 Pa•s (19:1). At a 4:1 stoichiometry the shear thinning effect earlier initiates at a shear rate of ca. 0.3 s^{-1} and decreases more drastically than at the other hydrogels (Figure 4), i.e. the physical network is linked at more points but is easier affected by outside influences. Moreover, by changing the stoichiometry of the adamantyl groups in the polymer backbone, the total molar ratio of adamantane in the whole system is modified. That means the driving force for a complexation is influenced by the amount of adamantane. Thus, this is another possibility to influence the hydrogel characteristics in an easy way to find a perfect match with the desired properties.

A variation of the amount of cross-linker **22** used for the CD polymer synthesis also has an influence on the hydrogels. In Figure 5 it is shown that the hydrogel formation with high viscosities can only be realized with higher concentrations of epichlorohydrin **22**. A satisfactory hydrogel formation is primarily obtained by usage of linear 4 mol % cross-linked CD polymers **23**. The viscosity of hydrogels built by mainly linear linked CD polymers **23** is always higher. Thus, the single CD units of the CD polymers more easily include the adamantyl groups of the corresponding copolymer **19**. Moreover, a satisfying hydrogel formation could be realized only by CD polymers with molecular weights above 90K g/mol, i.e. CD polymers consisting of ca. 80 cyclodextrin units.

A variation of the pH value of the hydrogel has also an effect on the viscosity of the system (Figure 6). At lower pH values from 4 to 8 the hydrogel shows nearly the same zero shear viscosities. By changing the pH value to 10, the zero shear viscosity is doubled. At higher pH values the most acidic 2-OH of the CDs will be deprotonized. But this has nearly no effect on the size of the polymeric CD **24**, as the hydrodynamic diameter just shrinks a bit from 5.62 nm at pH 6 to 4.85 nm at pH 10 due to the salt effect. On the other hand, the hydrodynamic diameter of the guest polymer **18** increases from 3.12 nm at pH 6 to 6.5 nm at pH 10. In alkaline environments the guest polymer is totally deprotonized, which leads to an expansion of the polymer coil. Thus, even more adamantyl groups of the guest copolymer can be complexed by the polymeric cyclodextrin, i.e. the aggregation of the physical hydrogel network will increase.

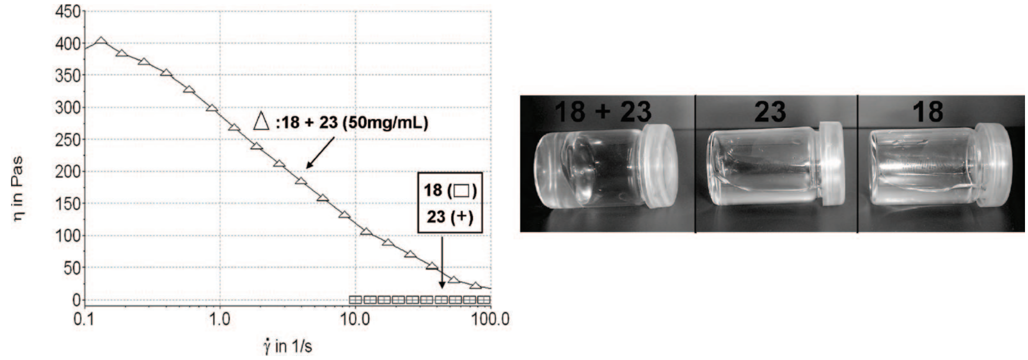


Figure 1. Viscosity of an aqueous solution **18** (50 mg·mL^{-1}) and **23** (50 mg·mL^{-1}) as well as aqueous solutions of the single components (50 mg mL^{-1}) in dependence on the shear rate (T = 20 °C, pH = 7) (left). Rotated, aqueous solutions of a mixture of **18** + **23** and the single components **18** and **23** (50 mg mL^{-1}) after 30 s (right).

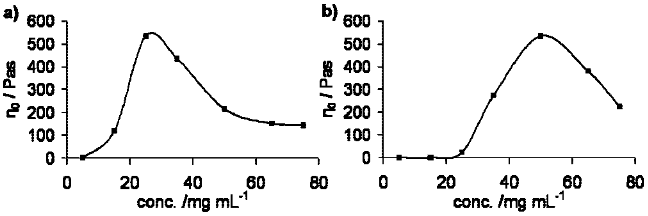


Figure 2. (a) Zero shear viscosity η_0 versus concentration of **23** at constant concentration of **18** (50 mg mL^{-1}) in an aqueous solution (T = 20 °C, pH = 7). (b) Zero shear viscosity η_0 versus concentration of **18** at constant concentration of **23** (25 mg mL^{-1}) in an aqueous solution (T = 20 °C, pH = 7).

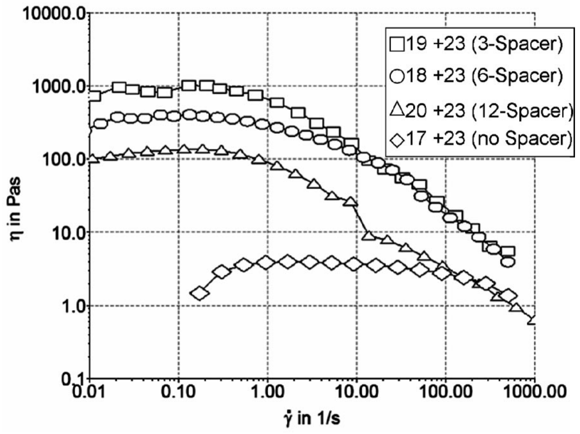


Figure 3. Flow curves of different guest polymers (50 mg mL^{-1}) with varying adamantyl side chains and host CD polymers (50 mg mL^{-1}) in aqueous solution (T = 20 °C, pH = 7).

Adding an amyloglucosidase taka-diastase from *Aspergillus oryzae* has nearly no effect on the physical network, as the flow curve after one week of stirring hydrogel and enzyme does not strongly differ from the unaffected solution (Figure 7). Moreover, an aqueous solution of **23** at pH 4 was not affected by the enzyme, as its particle size distribution (DLS) measured after a week of enzymatic treatment did not differ from the former. Because of its specially dense linked structure, the CD polymer **23** could not be decomposed into its α-D-glucopyranoside units.

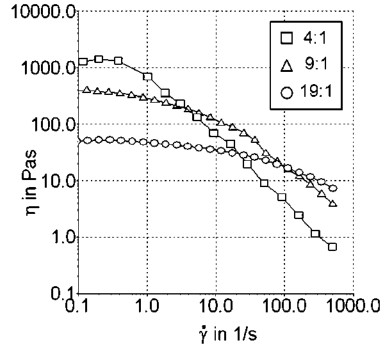
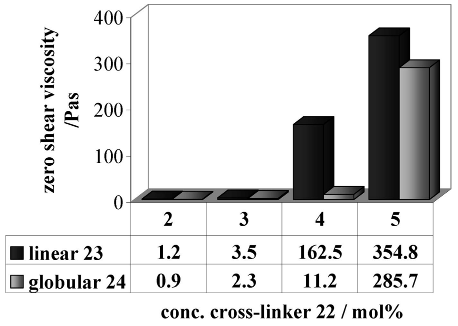


Figure 4. Flow curves of different guest polymers **18** (50 mg mL^{-1}) with varying monomer stoichiometries [(AMPS-Na **16**):(adamantyl-acrylamide monomer **6**)] and CD polymer **23** (50 mg mL^{-1}) in aqueous solution (T = 20 °C, pH = 7).



	2	3	4	5
■ linear 23	1.2	3.5	162.5	354.8
▨ globular 24	0.9	2.3	11.2	285.7

Figure 5. Zero shear viscosity vs cross-linker **22** concentration of an aqueous solution (T = 20 °C, pH = 7) of guest polymer **18** (50 mg mL^{-1}) and variously cross-linked CD polymers **23**, **24** (50 mg mL^{-1}).

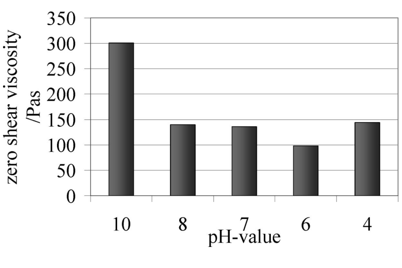


Figure 6. Zero shear viscosities of an aqueous hydrogel consisting of **18** (50 mg mL^{-1}) and **24** (50 mg mL^{-1}) at different pH values.

Conclusion

In this paper we present a novel and easy route to design physical hydrogels. By using only polymerizable guest-monomers **12**−**14** it is possible to apply this system on various hydrophilic polymer systems to synthesize copolymers bearing adamantyl groups or to vary the relative amount of these adamantyl groups in the copolymer very easily. The hydrogels are formed by mixing aqueous solutions of CD polymers and hydrophilic guest copolymers. The application of mainly linear CD polymers **23** or globular CD polymers **24** has an influence

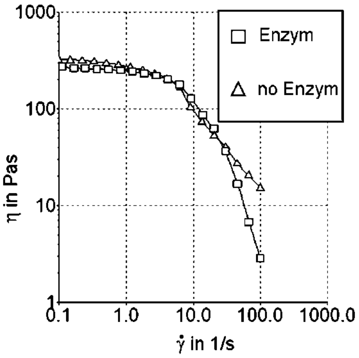


Figure 7. Flow curves of guest polymer **18** (50 mg mL^{-1}) and CD polymer **23** (50 mg mL^{-1}) in aqueous solution ($T = 20$ °C) before (△) and after (□) addition of sugar decomposing enzyme taka-diastase. The solution was stirred for one week after enzyme addition at pH 4.

on the viscosity of the hydrogel. These hydrogels are stable at pH values from 6 to 10, at lower shear rates and could not be decomposed by enzymatic treatments. Thus, we present a novel system to build a flexible, easy manipulable physical hydrogel in a two component system. By separately mixing fluid solutions it is possible to create very viscous hydrogels in a two step application at every desired place even through small capillaries.

Experimental Section

All the reagents used in our experiments were of analytical purity and were used without further purification.

The identity of synthesized compounds was confirmed by mass spectrometry, NMR and IR measurements. ^{1}H NMR and ^{13}C NMR were performed using a Bruker Advance DRX 500 spectrometer at 500.13 MHz for proton and 125.77 MHz for carbon in DMSO-d_6 and $CDCl_3$ as solvent. The δ-scale relative to TMS was calibrated to the deuterium signal of the solvent as an internal standard.

Molecular weights and molecular weight distributions were measured by asymmetric field flow fractionation (AFFF) and static light scattering (SLS) with a Wyatt ECLIPSE2 (AFFF) in combination with a Wyatt OPTILAB rex as refractive index detector and a Wyatt miniDAWN TREOS for SLS.

Dynamic light scattering (DLS) experiments are carried out with a Malvern Zetasizer Nano: Nano ZS ZEN 3600 at a temperature of 20 °C. Poly(styrene) disposable sizing cells are used. The particle size distribution is derived from a deconvolution of the measured intensity autocorrelation function of the sample by the General Purpose Mode (non-negative least-squares) algorithm included in the DTS software. Each experiment is performed at least five times. The hydrodynamic diameter of the particle is calculated from a sigmoidal fit of measured diameters.

Viscosities were measured with a Thermo scientific HAAKE Mars viscosimeter via plate−plate configuration using a MP35 plate and a PP35Ti plate.

***N*-Adamantylacrylamide (15).** 7.56 g (50 mmol) of 1-adamantylamine and 7.66 mL (55 mmol) triethylamine are dissolved in 150 mL of THF (abs) and are cooled less than 5 °C. Within 30 min, 4.47 mL (50 mmol) of acryloyl chloride in 50 mL of THF (abs) were added dropwise. The mixture was stirred for another 2 h in the cold and subsequently at room temperature for 12 h. The precipitate was filtered and the solvent was removed by rotary evaporation. The white solid was purified by flash chromatography in chloroform/acetone v/v 25/1 and dried in vacuum. Yield: 9.17 g (89%). thin layer chromatography: $R_f = 0.51$ (chloroform/acetone 25/1). ^{1}H NMR δ/ppm (500 MHz, $CDCl_3$) = 1.69 (m, 6H); 2.05 (m, 6H); 2.09 (m, 3H); 5.24 (br.s, 1H); 5.56 (dd, 1H); 6.02 (dd, 1H); 6.22 (dd 1H). ^{13}C NMR δ/ppm (125 MHz, $CDCl_3$) = 29.44; 36.36; 41.62; 52.1; 125.57; 132.18; 164.51. MS EI: 205 [M]$^+$ for $C_{13}H_{19}NO$.

3-Acrylamidopropanoic Acid (5)/6-Acrylamidohexanoic Acid (6)/11-Acrylamidoundecanoic Acid (7). 3.87 mL (45.7 mmol) of acryloyl chloride in 10 mL of THF were added dropwise into a solution of 5 g (38.1 mmol) of 6-aminohexanoic acid in 30 mL of 1.27 N aqueous sodium hydroxid at 0 °C. After 2 h stirring at 0 °C, the solution was acidified to pH 3 with 1 N hydrochloric acid. Afterward, the mixture was poured on ice water and extracted with ethyl acetate. The organic phase was washed with water and dried over magnesium sulfate. The solvent was then removed via rotary evaporation. The crude product was purified by recrystallization in hexane/ethyl acetate. Yield: 4.17 g (59%). thin layer chromatography: $R_f = 0.43$ (dichloromethane/methanol 9/1). ^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 1.28 (m, 2H); 1.43 (m, 2H); 1.51 (m, 2H); 2.21 (t, 2H); 3.12 (pseudo-q, 2H); 5.57 (dd, 2JH = 2.2 Hz, 3JH = 10.1 Hz, 1H); 6.07 (dd, 2JH = 2.3 Hz, 3JH = 17.0 Hz, 1H); 6.21 (dd, 3JH(trans) = 17.4 Hz, 3JH(cis) = 10.1 Hz, 1H); 8.07 (br.s, 1H); 12.03 (br.s, 1H). ^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 25.15; 26.95; 29.73; 34.52; 39.30; 125.70; 132.82; 165.34; 175.37. MS EI *m*/*z*: 185 [M]$^+$ for $C_9H_{15}NO_3$.

3-(Acrylamido)-*N*-propaneamide (12), 6-(Acrylamido)-*N*-adamantylhexaneamide (13), 11-(Acrylamido)-*N*-undecaneamide (14). A solution of 1.85 g (10 mmol) of 6-acrylamidohexanoic acid in 50 mL of THF (abs) was mixed with 1.39 mL (10 mmol) of triethylamine and cooled in an ice bath less than 0 °C. Subsequently, 0.96 mL (10 mmol) of ethyl chloroformate was added dropwise with stirring. After 40 min of stirring, 1.51 g (10 mmol) of 1-adamantylamine was added to the solution, and the mixture was stirred for another 2 h at 0 °C. Thereafter, the ice bath was removed and the mixture was stirred for another 16 h at room temperature. The solution volume was reduced to ca. 20 mL, and 50 mL of diethyl ether was added. After 24−48 h the product recrystallized in the refrigerator. In case of impurities, the product was again recrystallized in THF/diethyl ether. Yield: 1.66 g (52%). thin layer chromatography: $R_f = 0.36$ (dichloromethane/methanol 95/5). ^{1}H NMR δ/ppm (500 MHz, DMSO-d_6) = 1.24 (m, 2H); 1.44 (m, 4H); 1.62 (m, 6H); 1.92 (m, 6H); 2.00 (m, 5H); 3.11 (pseudo-q, 2H); 5.57 (dd, 2JH = 2.2 Hz, 3JH = 10.1 Hz, 1H); 6.07 (dd, 2JH = 2.2 Hz, 3JH = 17.1 Hz, 1H); 6.21 (dd, 3JH(trans) = 17.1 Hz, 3JH(cis) = 10.1 Hz, 1H); 7.21 (br.s, 1H); 8.06 (br.s, 1H). ^{13}C NMR δ/ppm (125 MHz, DMSO-d_6) = 26.12; 26.96; 29.73; 37.01; 39.37; 41.96; 51.38; 125.64; 132.84; 165.32; 172.38. MS EI *m*/*z*: 318 [M]$^+$ for $C_{19}H_{30}N_2O_2$.

Synthesis of Polymers (17, 18, 19, 20). A solution of the adamantyl-containing monomers (**12**−**15**) in 40 mL of DMF was mixed with the adequate amount of an aqueous 58 wt % solution of 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS-Na) (**8**) and was flushed for 30 min with argon. Thereafter, 0.5 mol % AIBN was added and the solution was stirred at 65 °C for 12 h. The crude polymer was precipitated in acetone, washed several times with acetone and dried under reduced pressure.

CD Polymer (23, 24). 10 g (8.81 mmol) of β-CD is dissolved by stirring for at least 2 h in 15 mL of a 15 wt % aqueous sodium hydroxide solution at 35 °C. Subsequently, 2 mL (8.81 mmol) of toluene was added to synthesize **23** or one continues without an addition to synthesize **24**. After an additional 2 h of stirring at 35 °C, the accordant amount of epichlorohydrin was added to the mixture. After 3 h of stirring, the solution was added to 200 mL of isopropanol and the precipitate was filtered. The raw product was dissolved in water, neutralized with diluted hydrochloric acid and dialyzed for 7 days (MWCO 8000). The product was isolated via lyophilization. Yield: Maximum 65% (**23**) or 50% (**24**) 5 mol % epichlorohydrin.

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