Supporting Information

pH dependent thermoresponsive behavior of acrylamide-acrylonitrile UCSTtype copolymers in aqueous media

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Composition determination of poly(AAm-co-AN) synthesized via RAFT

Figure S1. A: FTIR spectrum of poly(AAm₈₇-*co*-AN₁₂) demonstrating the corresponding bands of AN (C=N vibration) at 2240 cm⁻¹ and AAm (C=O vibration) at 1653 cm⁻¹. B: ¹H NMR spectrum of (poly(AAm₈₇-*co*-AN₁₂)) in d_{6} -DMSO showing the characteristic signals of AAm and AN as well as these CMDT. The methyl group (-CH₃) at 0.85 ppm was used as reference.

Controlled RAFT polymerization of AAm and AN with CMDT as CTA

Table S1.	RAFT polymeri	zation of AAm	and AN (Mor	nomer:CTA i	ratio 200 :	1 at 70 °C) with AIB	N as initiat	or and
CMDT as	CTA.								

Entry	Time / min	AN / mol %	In(M ₀ /M _t)	M _{n,theo} / Da	Mn(GPC) / Da	Yield / %	Ð
1	45	15.0	0.41	5000	3000	29	1.4
2	90	13.2	0.62	6300	4800	40	1.3
3	150	12.3	1.14	9300	6700	58	1.3
4	270	11.8	1.27	9900	8500	66	1.2

In the present work CMDT was used as RAFT agent and the copolymerization process of AAm and AN was followed with kinetic studies. Figure S2A, shows a continuous increased of the polymer chains (150min), supported by a first order kinetic plot until 50 % conversion. The increase of the molecular weight with monomer conversion is displayed in Figure S2B. The GPC curves of all polymers were unimodal without chain aggregation (Figure S3).



Figure S2. A: First-order kinetic plots over 150 min of the RAFT polymerization of AAm and AN with the following conditions: monomer: CTA ratio 200:1, monomer ratio AAm : AN =170 : 30 at 70 °C, with 0.3 equiv. of AIBN. B: Molar masses and polydispersity as a function of time.



Figure S3. GPC (DMSO) curves of poly(AAm-*co*-AN) synthesized by RAFT polymerization (monomer: CTA ratio 200 : 1), monomer ratio AAm : AN =170 : 30 at 70 °C, with 0.3 equiv. of AIBN.

Characterization of HCl hydrolyzed samples (pH 0, 40 °C)

FTIR analysis were carried out before and after hydrolysis. The spectra confirmed the characteristic carbonyl stretching vibration at 1740 cm⁻¹, this peak appeared gradually with increasing hydrolysis of the polymers (Figure S4). The C≡N band at 2240 cm⁻¹ was observed in each spectrum as well as the amide band at 1600-1650 cm⁻¹. These results showed that polyacrylic acid is present in its protonated state.



Figure S4. FTIR spectra of non- and hydrolyzed poly(AAm₈₇-*co*-AN₁₂). Hydrolysis were carried out in HCl (pH 0) at 40 °C.

The acid catalyzed hydrolysis neither changed the characteristic backbone signals at 1.2-2.4 ppm nor the amide corresponding peak at 6.5-8 ppm. However, at 12 ppm a gradual formation and increase of the peak corresponding to the carboxylic acid proton, could be observed. In all solutions, DCE (8.6 mg/mL) was used as internal standard (Figure S5).



Figure S5. ¹H-NMR spectra in d_6 -DMSO of non- and hydrolyzed poly(AAm₈₇-co-AN₁₂) with DCE as internal standard. Hydrolysis were carried out in HCl (pH 0) at 40 °C.

Characterization of hydrolyzed samples in buffer solutions (RT)

Typical FTIR spectra of non- and hydrolyzed samples of poly(AAm₈₇-co-AN₁₂) are shown in Figure S6. Slight differences are observed in the shift of the amide C=O stretching bands to the left from 1651 to 1655 cm⁻¹. However, no signals corresponding to the COO stretching could be observed. An increase of the hydrolysis decreased the intensity of the nitrile C=N stretching band (2240 cm⁻¹). Further analysis of the samples were carried out by ¹H-NMR spectroscopy. The observed backbone signals at 1.2-2.4 ppm and the amide corresponding peaks at 6.5-8 ppm remained between non- and -hydrolyzed samples unchanged. In the case of the hydrolyzed polymer, the expected carboxylic acid proton at 12 ppm could not observed (Figure S7). In the case of NaOH hydrolyzed samples, no changes within the FTIR and NMR-spectra could be observed as well.



Figure S6. FTIR spectra of non- and hydrolyzed poly(AAm_{87} -*co*- AN_{12}). The hydrolysis was carried out in buffer solutions of pH 9 over 25 days.



Figure S7. ¹H-NMR spectra in d_6 -DMSO of non- and hydrolyzed poly(AAm₈₇-*co*-AN₁₂). The hydrolysis was carried out in buffer solutions of pH 9 over 25 days.

Characterization of NaOH hydrolyzed samples (pH 14, 40 °C)

Figure S8 compares the NMR spectra before and after hydrolysis. Since all signals of the hydrolyzed samples were influenced by the NaOH treatment, including the reference signal of the RAFT agent (–CH₃) at 0.85 ppm, the analysis was carried out using dichloroethane (DCE) as internal standard (10 mg/mL). Due to the presence of sodium polyacrylate salt, a defined content of deutero-HCl (15 μ L/mL) was added to achieve solubility in DMSO. As supposed, the amide peak between 6.5-8 ppm decreased with increasing hydrolysis. Due to the addition of deutero-HCl, inter polymer complexation between polyacrylamide and polyacrylic acid could be observed between 8.5-10 ppm for hydrolyzed samples. Hydrogen bonding proton signals shifted to lower field as presented in following NMR spectrum.¹



Figure S8. ¹H-NMR spectra in d_6 -DMSO of non- and hydrolyzed poly(AAm₈₇-*co*-AN₁₂) with DCE as internal standard. Hydrolysis was carried out in NaOH (pH 14) at 40 °C.

References

 P. L. Wash, E. Maverick, J. Chiefari and D. A. Lightner, J. Am. Chem. Soc., 1997, 119, 3802– 3806