

Supporting information for

UCST behavior of polyampholytes based on stoichiometric RAFT copolymerization of cationic and anionic monomers

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Experimental details

Materials and Instrumentation

All chemicals and solvents are commercially available and were used as received unless otherwise stated. Methacrylic acid (MAA), 2-(dimethylamino)ethyl methacrylate methanol, ethanol, isopropanol, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA) and diethyl ether were obtained from Sigma Aldrich. Deuterium oxide is supplied by Eurisotop.

¹H NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer using D₂O as solvent. Chemical shifts (δ) are given in ppm relative to TMS.

Size-exclusion chromatography (SEC) characterization for the copolymers was performed on a Agilent 1260-series HPLC system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler (ALS), a thermostatted column compartment (TCC) at 50°C equipped with a PSS Gram30 column in series with a PSS Gram1000 column, a 1260 diode array detector (DAD) and a 1260 refractive index detector (RID). The used eluent was DMA containing 50mM of LiCl at a flow rate of 0.6 ml/min. The spectra were analyzed using the Agilent Chemstation software with the GPC add on. Molar mass and PDI values were calculated against Varian PMMA standards.

Gas chromatography was performed on a 7890A from Agilent Technologies with an Agilent J&W Advanced Capillary GC column (30 m, 0.320 mm, and 0.25 μm). Injections were performed with an Agilent Technologies 7693 auto sampler. Detection was done with a FID detector. Injector and detector temperatures were kept constant at 250 and 280 $^{\circ}\text{C}$, respectively. The column was initially set at 50 $^{\circ}\text{C}$, followed by two heating stages: from 50 $^{\circ}\text{C}$ to 100 $^{\circ}\text{C}$ with a rate of 20 $^{\circ}\text{C}/\text{min}$ and from 100 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ with a rate of 40 $^{\circ}\text{C}/\text{min}$, and then held at this temperature for 0.5 minutes. Conversion was determined based on the integration of monomer peaks using DMA as internal standard.

Turbidity measurements were performed on a Cary 300 Bio UV-Visible spectrophotometer at a wavelength of 600 nm. The samples were first heated to a suitable temperature to fully dissolve the copolymer (5 mg ml^{-1}), after which the sample was placed in the instrument and cooled to 2 $^{\circ}\text{C}$. The transmittance was measured during at least two controlled cooling/heating cycles with a cooling/heating rate of 1 $^{\circ}\text{C min}^{-1}$ while stirring in PS cuvettes controlled by block temperature probe. Cloud point temperatures (T_{CpS}) were calibrated to adjust for differences between block temperature and sample temperature.

Dynamic light scattering (DLS) was performed on a Zetasizer Nano-ZS apparatus (Malvern Instruments Ltd) using disposable cuvettes. The excitation light source was a He-Ne laser at 633 nm, and the intensity of the scattered light was measured at 173 $^{\circ}$. This method measures the rate of the intensity fluctuation and the size of the particles is determined through the Stokes-Einstein equation

$$d(H) = kT / (3\pi\eta D)$$

where $d(H)$ is the mean hydrodynamic diameter, k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the dispersing medium, and D is the apparent diffusion coefficient. All samples were filtered through Millipore membranes with pore sizes of $0.2 \mu\text{m}$ prior to measurement.

Synthesis and characterization

For a typical RAFT copolymerization, methacrylic acid (MAA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid and V-70 were first dissolved in a DMF/DMA solvent mixture (80/20 vol) in a schlenk vial. The concentration of monomer was fixed at 2M. After degassing the solution three times by freeze-vacuum-thaw cycles, the schlenk vial was filled with argon and immersed in an oil bath preheated at $70 \text{ }^\circ\text{C}$ while stirring. Conversion of the monomers was followed by GC with DMA as internal standard. The reactions were stopped by immersing the schlenk vial into a dry ice/isopropanol bath as long as the charge-neutral copolymers were obtained according to GC. The resulting polymer was isolated by precipitation in ether for three times followed by drying under reduced pressure at room temperature. Size exclusion chromatography was used to evaluate number average molar mass (M_n) and dispersity (Đ) of the obtained copolymers. For kinetic studies, samples were withdrawn from the polymerization mixture under a flow of argon at different times.

Table S1 Characterization data for the RAFT polymerization of polyampholytes

Code	Polymers	Feeding (mmol)				Conversion by GC /%		
		MAA	DMAEMA	PEGMA	CTA	MAA	DMAEMA	PEGMA
PA1	MAA ₂₂ DMAEMA ₂₄	12.5	5	0	0.15	26.5	72.5	N/A
PA2	MAA ₂₈₇ DMAEMA ₂₈₈	22	10	0	0.02	26.1	57.5	N/A
PA3	MAA ₃₈ DMAEMA ₃₈ PEGMA _x	9	5	2.5	0.1	42.1	75.1	Not determined

Supporting Figures:

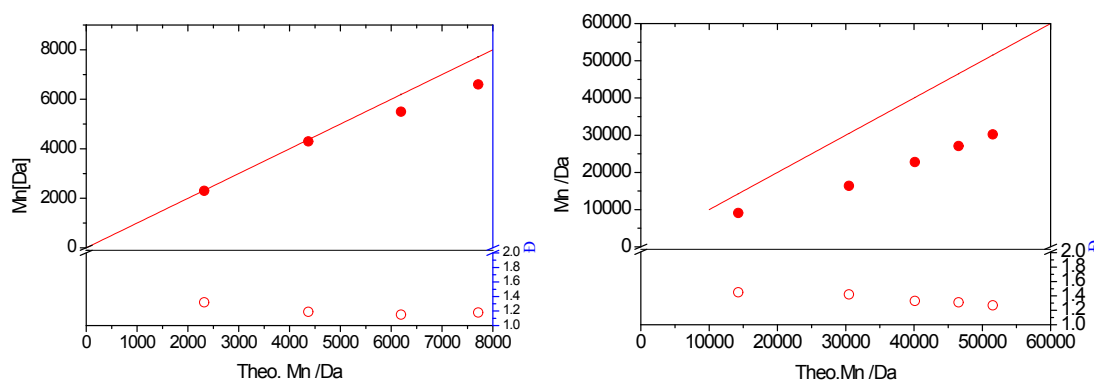


Figure S1. Plots of the experimental number-average molar mass (M_n) and dispersity (\bar{D}) versus theoretical M_n for the RAFT copolymerizations of MAA and DMAEMA with feed ratios of MAA: DMAEMA: CTA: V70 at a) 100: 40: 1: 0.1 and b) 733: 200: 1: 0.2, performed at 40 °C with V70 as initiator. The dotted lines represent the identical value of the experimental and theoretical M_n ; the underestimation of the experimental M_n at high molecular weight range can be ascribed to the collapse of the polymer globules with high M_n due to the strong intra-chain interaction leading to smaller hydrodynamic radius compared to the PMMA standard.

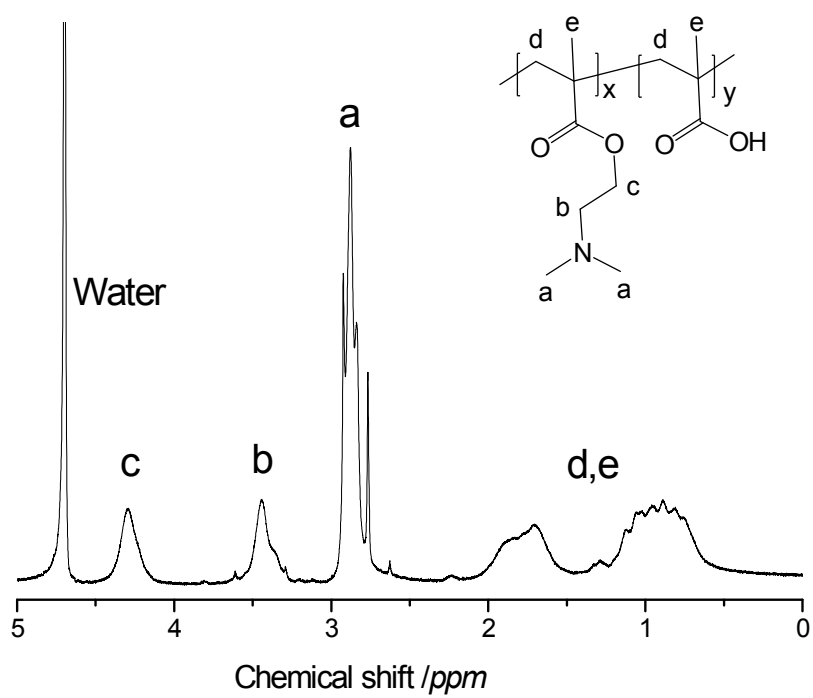


Figure S2 ^1H NMR spectrum of PA1 in D_2O

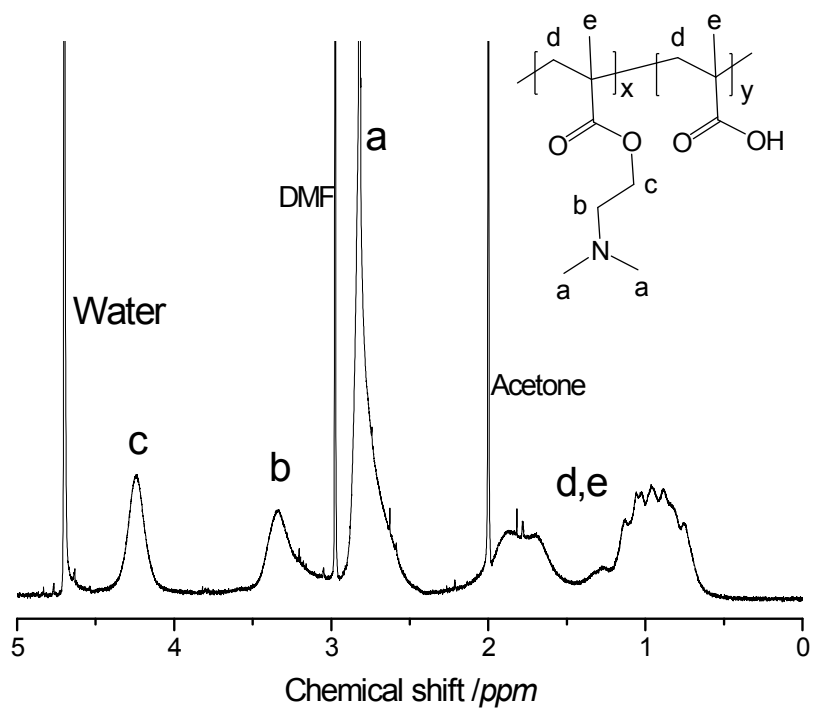


Figure S3 ^1H NMR spectrum of PA2 in D_2O

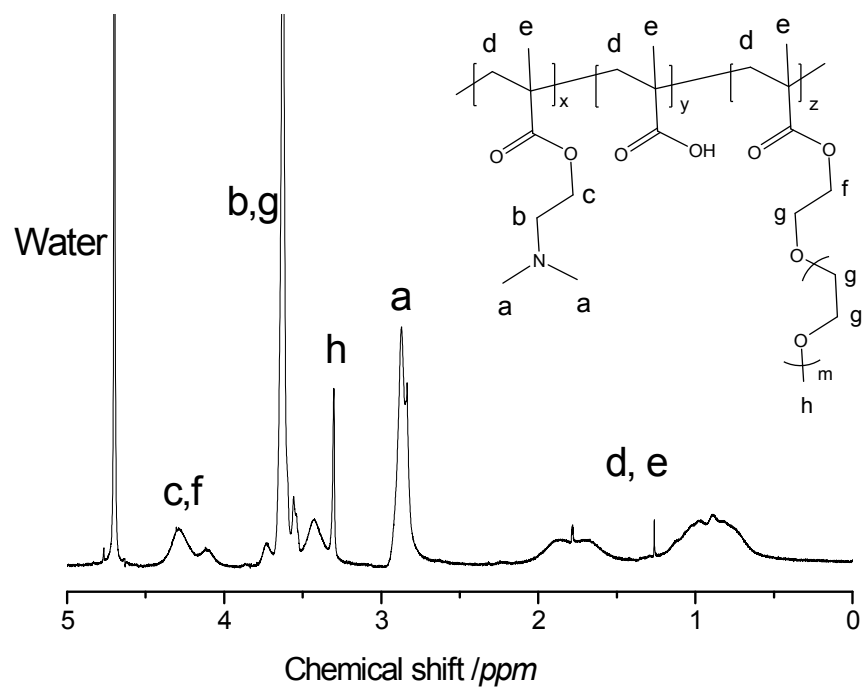


Figure S4 ^1H NMR spectrum of PA3 in D_2O