Homogeneous Poly(acrylamide) Hydrogels Made by Large Size, Flexible Dimethacrylate Cross-linkers

Supporting Information

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Experimental Procedure

Acrylamide (AAm, Fluka), ammonium persulfate (APS, Fluka), N,N,N',N'-tetramethylethylenediamine (TEMED, Fluka), ethylene glycol dimethacrylate (DMA-1, Fluka), diethylene glycol dimethacrylate (DMA-2, Aldrich) tetraethylene glycol dimethacrylate (DMA-4, Fluka), and polyethylene glycol dimethacrylates of molecular weights 550 and 750 g/mol (DMA-9 and DMA-14, respectively, Aldrich) were used as received. Stock solutions of APS and TEMED were prepared by dissolving 0.500 g APS and 0.100 mL TEMED separately in 10 mL of water.

Reaction solutions were prepared by dissolving AAm (1.0 g) and DMA-*x* crosslinker of various amounts in about 9 mL distilled water for 30 min. After addition of the stock solutions of APS (0.20 mL) and TEMED (0.25 mL), the volume was completed to 10 mL with water. For the rheological experiments, portion of this solution was transferred between the parallel plates of the rheometer. For the swelling measurements, the solution was transferred into plastic syringes of 1 mL volumes. For the light scattering measurements, the gelation reactions were carried out in the light scattering vials. All glassware was kept dustfree by rinsing in hot acetone prior using. The solutions were

filtered through membrane filters (pore size = 0.2 μm) directly into the vials. This process was carried out in a dustfree glovebox. All the gels subjected to light scattering measurements after a reaction time of 24h were clear and appeared homogeneous to the eye. For the calculation of excess scattering, the polymerization was repeated under the same experimental condition except that the crosslinker DMA-*x* was not used.

Rheological experiments

Gelation reactions were carried out at 25°C between the parallel plates of the rheometer (Gemini 150 Rheometer system, Bohlin Instruments) equipped with a Peltier device for temperature control. The upper plate (diameter 40 mm) was set at a distance of 500 μm before the onset of the reactions, i.e., during the induction period. During all rheological measurements, a solvent trap was used to minimize the evaporation.

Swelling measurements

The hydrogel samples taken out of the syringes were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at 25°C. In order to reach swelling equilibrium, the hydrogels were immersed in water for one month replacing water several times. The swelling equilibrium was tested by weighing the gel samples. The interpretation of the swelling measurements was made on the basis of the relative weight swelling ratio of gels, m_{rel}, which was calculated as $m_{rel} = m/m_0$, where m is the mass of the equilibrium swollen gel sample in water, and m_o is its mass after preparation.

Static light scattering measurements

The scattered light intensities were measured at 25°C using a commercial multi-angle light scattering DAWN EOS (Wyatt Technologies Corporation) equipped with a vertically polarized 30mW Gallium-arsenide laser operating at λ = 690 nm and 18 simultaneously detected scattering angles. The light scattering system was calibrated against a toluene standard. The scattered light intensities were recorded from angles θ = 14.5° to 152.5° which correspond to the scattering vector q range $3.1\text{x}10^{-4} - 2.4\text{x}10^{-3}$ A° $^{-1}$, where $q = (4\pi n/\lambda)\sin(\theta/2)$.

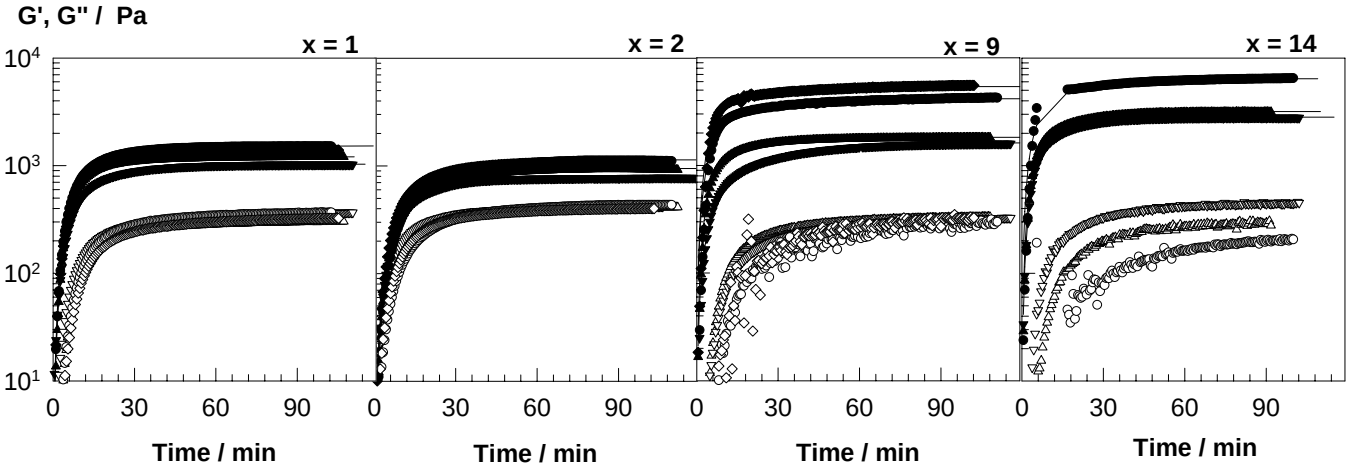

Figure S1. *G'* (filled symbols) and *G''* (open symbols) of the reaction system in the presence of DMA-*x* crosslinker shown as a function of the reaction time. The chain length *x* of the crosslinker is indicated. DMA-*x* = 0.5 (▼), 1.0 (▲), 2.0 (●), and 2.5 mol % (◆).

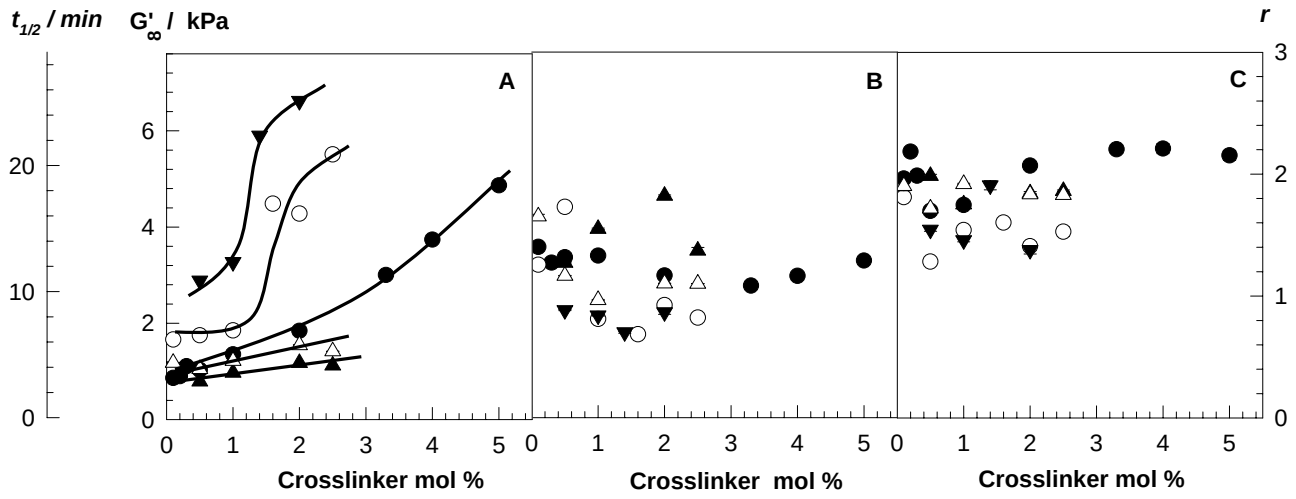

Figure S2: The final modulus of the hydrogels G'_∞ (A), half-gelation times $t_{1/2}$ (B) and the coefficient *r* of eq 1 (C) shown as functions of the crosslinker concentration. x = 1 (△), 2 (▲), 4 (●), 9 (○), and 14 (▼).

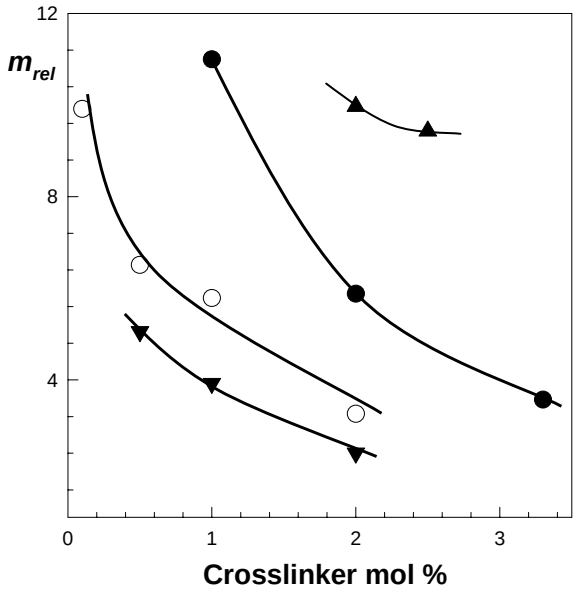

Figure S3. Relative weight swelling ratio m_{rel} of the hydrogels in water plotted against the crosslinker concentration. The solid curves are guide to the eye. x = 2 (▲), 4 (●), 9 (○), and 14 (▼). Gels with lower crosslinker contents were too weak to withstand the swelling tests.

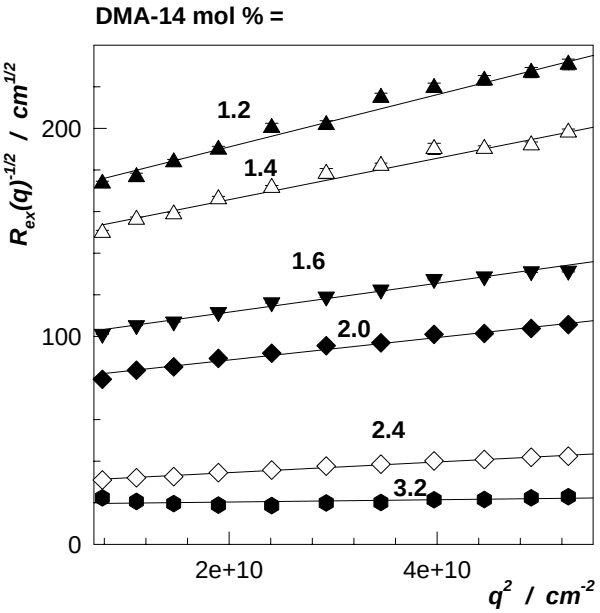

Figure S4: Debye - Bueche plots for PAAm gels prepared using DMA-14 crosslinker. The crosslinker concentration is indicated.

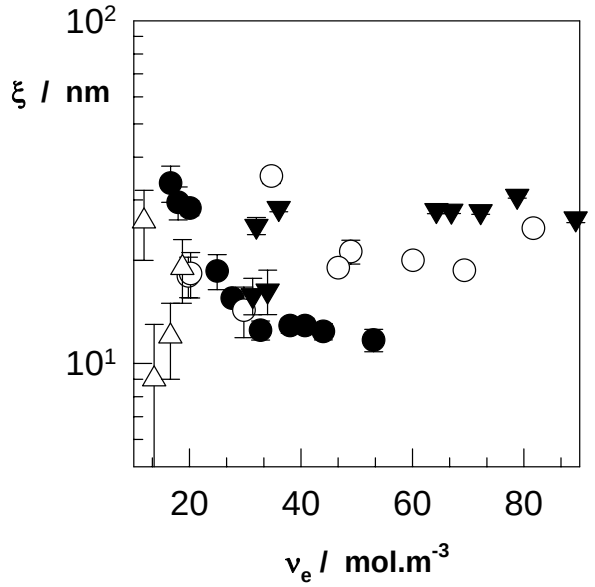

Figure S5. The correlation length ξ of the scatterers plotted against the crosslinker concentration. x = 1 (△), 4 (●), 9 (○), and 14 (▼).