

Electronic Supporting Information

Adsorption *versus* aggregation of NIPAM nanogels: new insight into their behaviour at the air/water interface as a function of concentration

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1. Experimental

Neutron reflectivity, NR

The neutron reflectivity measurements were carried out by means of FIGARO reflectometer at ILL, Grenoble, Franceⁱ. Most structural information is in the lower Q region. At high Q the fit to the data for the higher concentrations are relatively poor because of off-specular contribution to the specular reflection. This contribution cannot be fully modelled in the specular data. This background contribution is from the in-plane structure (in-plane lateral structure) which has been observed in the Brewster Angle Microscopy (BAM) imagesⁱⁱ. For kinetic data (collected for 1 hour) fitting and calculations of adsorbed amount (Γ) data for nanogels in NRW were analysed in a reduced wavelength range of 4.5–14 Å (Q_z -range of 0.01–0.03 Å⁻¹, 1 layer fit, layer thickness of 20 Å and σ of 4 Å). To ascertain structural information on the adsorbed nanogels fitting over the full Q_z -range was carried out. It is worth to mention

that after 1 hour of equilibration data were collected over the period of another hour and are the average over this time (total measurements time 2 hours).

Ellipsometry

The data were recorded using a Picometer Light ellipsometer (Beaglehole Instruments, New Zealand) in the PSCM (Partnership for Soft Condensed Matter), Grenoble, France. The instrument was equipped with a HeNe laser at a wavelength of $\lambda = 632$ nm and the angle of incidence used was $\theta = 50^\circ$. Measurements are influenced by the change in polarisation of light reflected at an interface, where the relative amplitude and phase of the s- and p-polarised contributions change by different amounts. In this work, we simply modelled the measured phase shift $\Delta_{\text{surf}} = \Delta - \Delta_0$, where Δ_{surf} is the change in Δ from the nanogel at the interface, Δ is the measured value of the mixed solution and Δ_0 is the calibration value for pure water. Note that this subtraction minimises effects on the data from surface roughness.

To convert values of Δ_{surf} into the surface excess Γ , an optical matrix model may be applied, as explained in detail in the Supporting Information of ref. ⁱⁱⁱ.

$$\Gamma = \frac{(n_{\text{surf}} - n_{\text{water}})}{dn/dc} \cdot \frac{n_{\text{surf}}^2 \lambda}{g(\theta)(n_{\text{surf}}^2 - n_{\text{air}}^2)(n_{\text{surf}}^2 - n_{\text{water}}^2)} \cdot \Delta_{\text{surf}} \quad (1)$$

where n_{surf} is the refractive index of the surface layer, n_{water} is the refractive index of water, n_{air} is the refractive index of air, dn/dc is the refractive index increment of the nanogel, and $g(\theta)$ is a function that depends only on bulk properties and on the angle of incidence. In the thin film limit, the data may be modeled either with a layer of constant density (varying thickness) to produce a linear $\Gamma(\Delta_{\text{surf}})$ relation or a layer of constant thickness (varying density) to produce a quadratic $\Gamma(\Delta_{\text{surf}})$ relation. Input of the refractive index increment $dn/dc = 0.162$ cm³/g^{iv} and calculation of n_{surf} using the literature value of its density of 1.17 g/cm^{3 v} results in the following two relations:

$$\Gamma = 0.721 * \Delta_{\text{surf}} \text{ (constant density model)} \quad (2)$$

$$\Gamma = 0.925 * \Delta_{\text{surf}} - 0.0227 * \Delta_{\text{surf}}^2 \text{ (constant thickness = 4.5 nm model)} \quad (3)$$

Note that: (1) the parameters used in the model was those for NIPAM with the contribution of the MBA neglected, and (2) a thickness value of 4.5 nm was chosen in the latter model for

varying layer density based on the thickness of the near-surface layer determined in our previous study.^{iv}

Given the model determined from NR measurements that is discussed in Figure 4 of the main text, i.e. where at low nanogel concentrations the coverage of the near-surface layer increases and at higher concentrations the more diffuse layers increase in density, the latter relation for constant layer thickness was used for data involving bulk nanogel concentration of $< 5 \times 10^{-3} \text{ mg ml}^{-1}$ and the former relation for constant layer density was used for data involving higher concentrations.

Supporting data

Table S-1. Nanogel hydrodynamic diameter (d_H) and polydispersity (Pdl) as measured by DLS at 25°C.

MBA % conc.	NIPAM %conc.	sample	H nanogels		sample	D nanogels	
			d_H (nm)	Pdl		d_H (nm)	Pdl
10	90	10 MBA-H	9.6	0.28	10 MBA-D	7.5	0.27
20	80	20 MBA-H	11.8	0.22	20 MBA-D	10.8	0.25
30	70	30 MBA-H	16.8	0.28	30 MBA-D	15.9	0.26

d_H - nanogel hydrodynamic diameter via volume, *Pdl* - polydispersity index measured by DLS (SD not higher than 0.03)

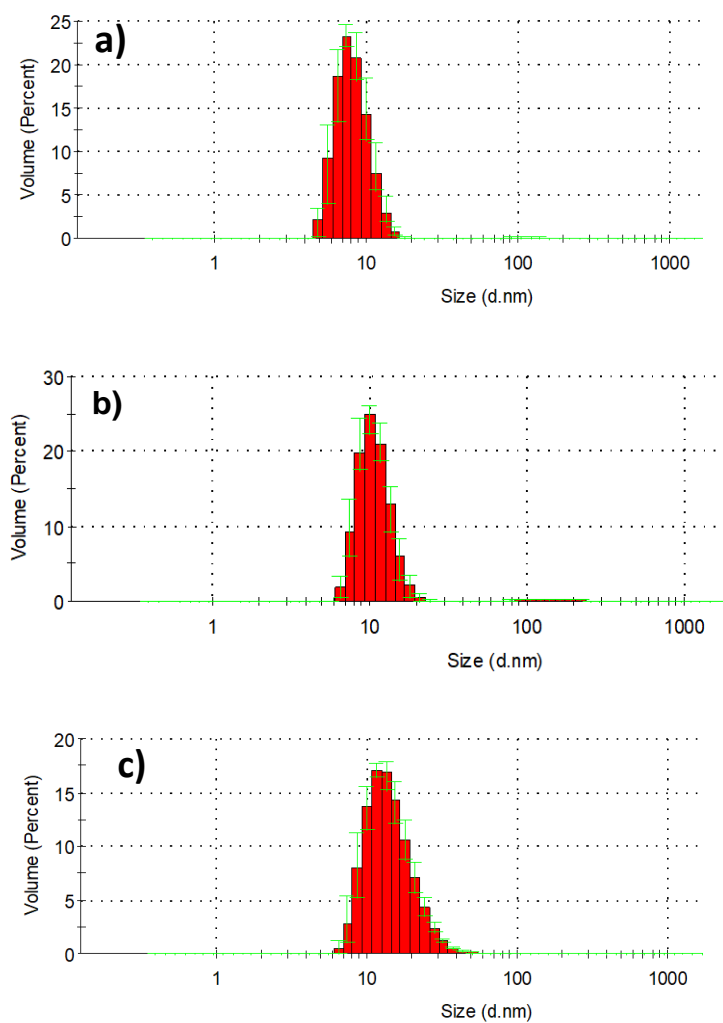


Figure S-1. Distribution of hydrodynamic diameter, d_H , of NIPAM-based nanogels with a) 10%, b) 20% and c) 30% of cross-linker at 25°C ($c=1.0 \text{ mg ml}^{-1}$) as measured by DLS

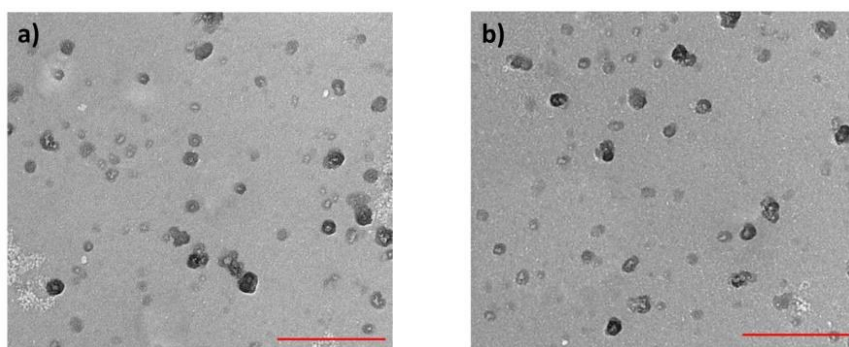


Figure S-2. TEM images of a) 20 MBA-H and b) 20 MBA-D nanogels. Scale bar equal to 200 nm.

Table S-2. Surface properties of NIPAM based nanogels at the air/water interface at 25°C.

sample	plateau conc. (mg ml ⁻¹)	γ_{plateau} (mN m ⁻¹)	dy/dlnc
10 MBA-H	2.1x10 ⁻³	45.2	6.3
20 MBA-H	3.0x10 ⁻³	47.8	7.4
30 MBA-H	4.5x10 ⁻³	49.7	7.9

plateau conc. – concentration at which plateau appears, γ_{plateau} – surface tension at plateau,
dy/dlnc – slope of the first part of surface tension curve

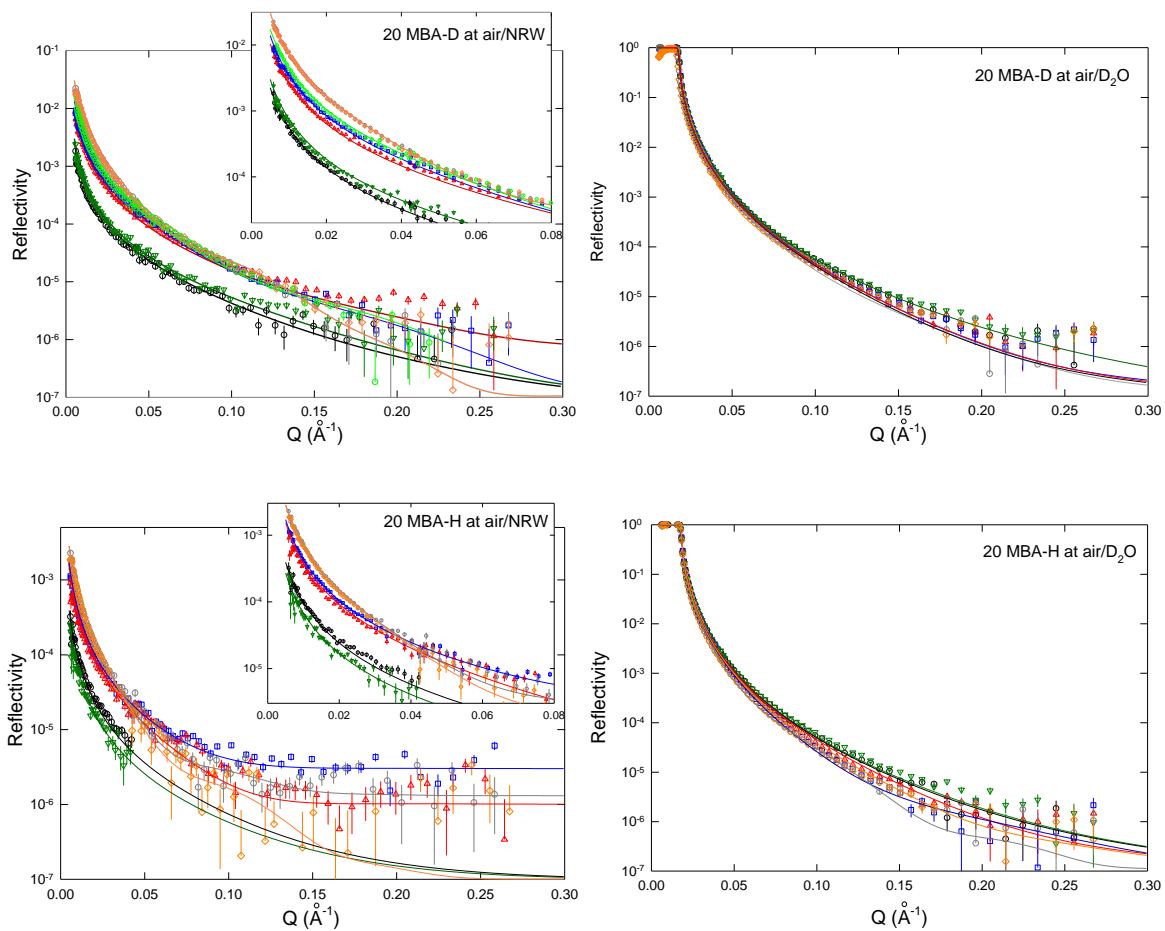


Figure S-3. Neutron reflectivity profiles of NIPAM (a) and NIPAM D (b) nanogels at the air/NRW (left panel) and air/D₂O (right panel) interfaces at different concentrations. The solid lines are fits to the data and inserts show zoom in on data at low Q .

Adsorption dynamics

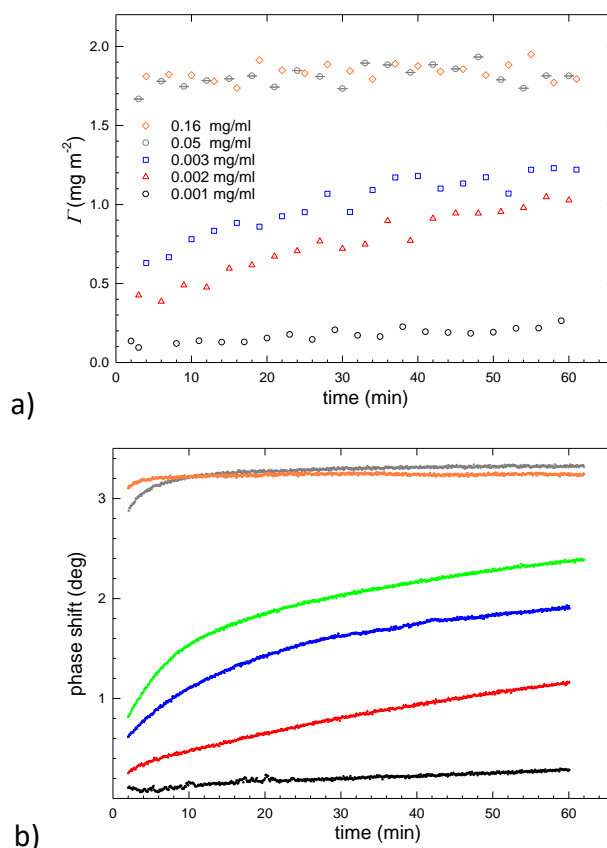
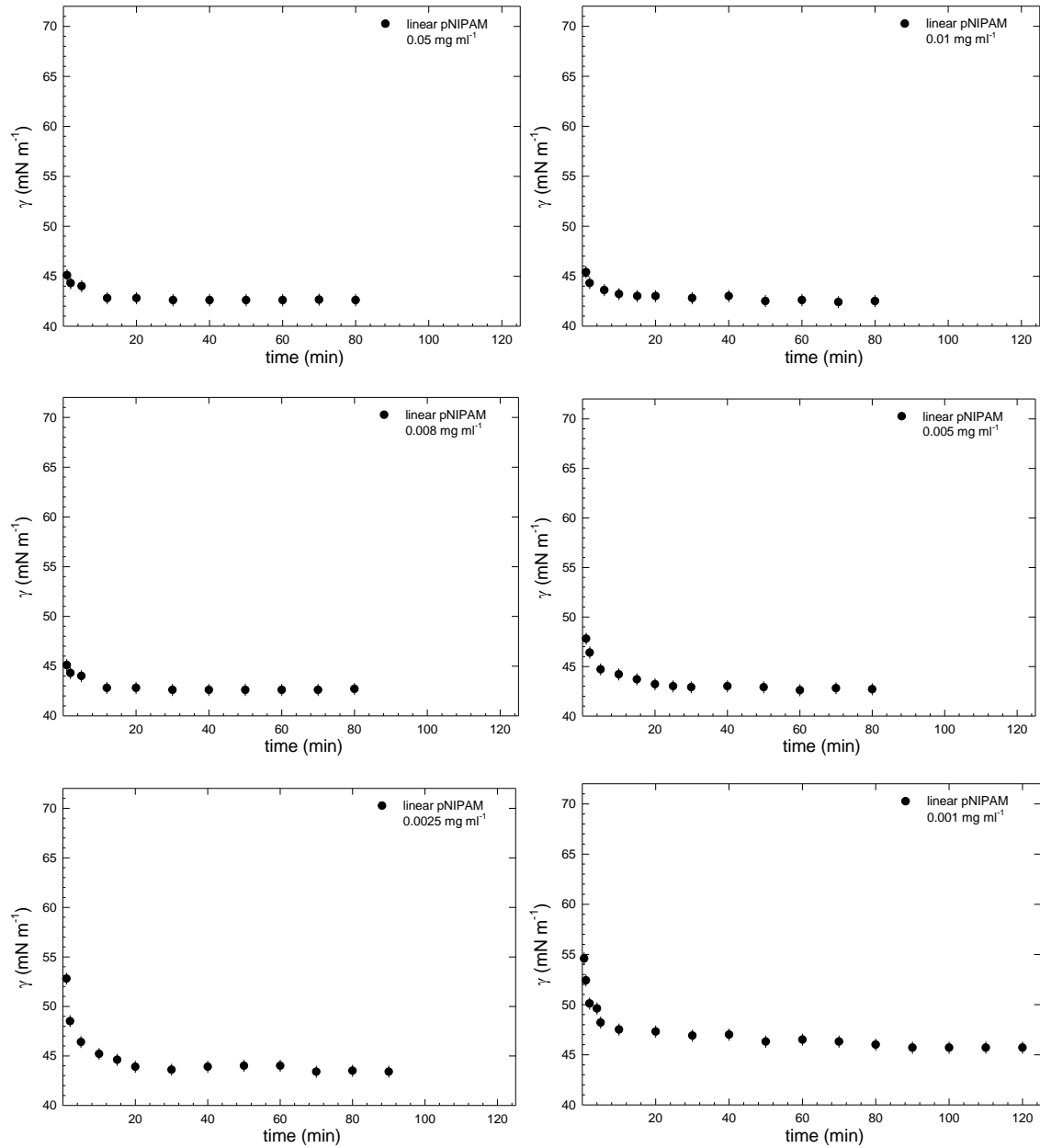


Figure S-4. The dynamic of NIPAM nanogel adsorption as measured by (a) NR and (b) ellipsometry as a function of concentration at 25 °C.

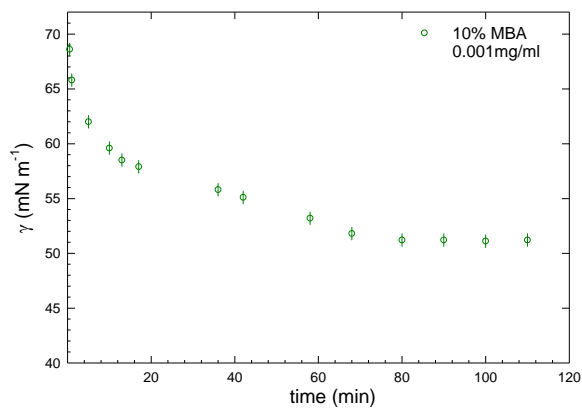
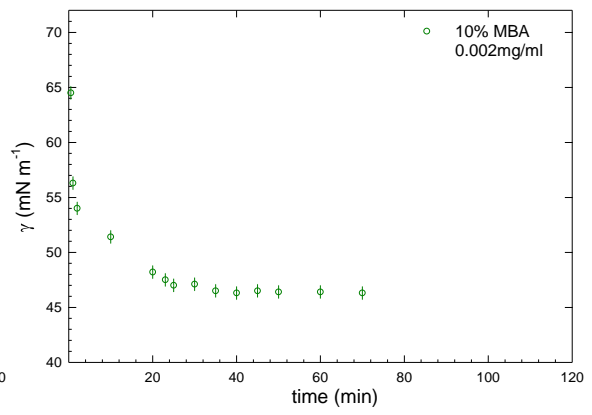
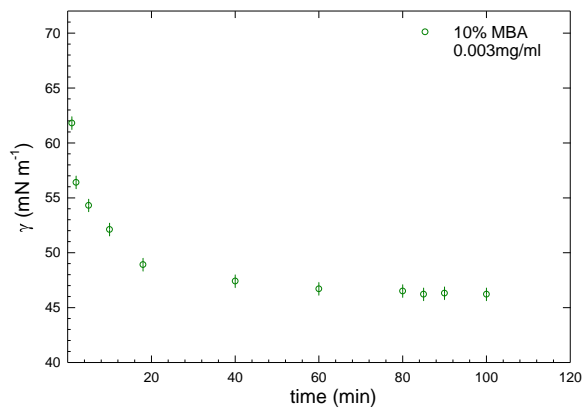
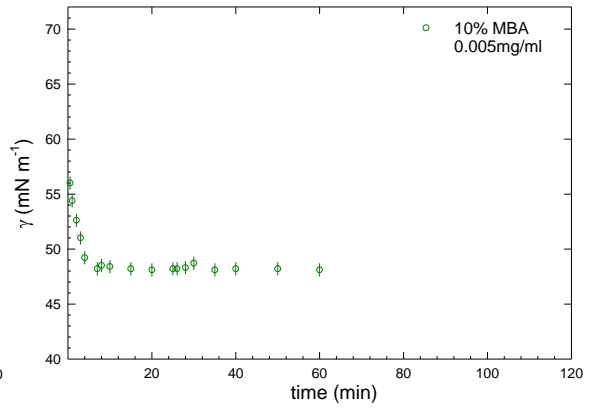
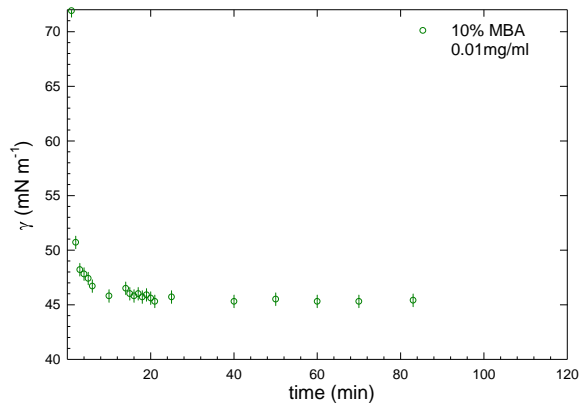
The adsorption dynamics of the nanogels was studied by means of ellipsometry, NR measurements and surface tension, results are shown in Figure S4 and S5 respectively. It is generally accepted that adsorption process of particles at the interfaces is divided into two stages: diffusion to a thin sublayer followed by the adsorption from the sublayer to the interface. In such a case adsorption will be governed by the slowest process – diffusion and can be described by Fick law. In case of gel particles adsorption is followed by reconfiguration of the particles at the interface (this includes unfolding of polymer chains to optimal conformation). This third step is the slowest one and will dominate the kinetic of the whole process. Combinations of surface tension data with ellipsometry and NR measurements support this assumption. The values of surface tension initially decrease rapidly and then relax to a final value. Similar trend is observed for ellipsometry and NR data though the time scale

of the process is much longer indicating processes (conformational changes) to which surface tension measurements are not sensitive.

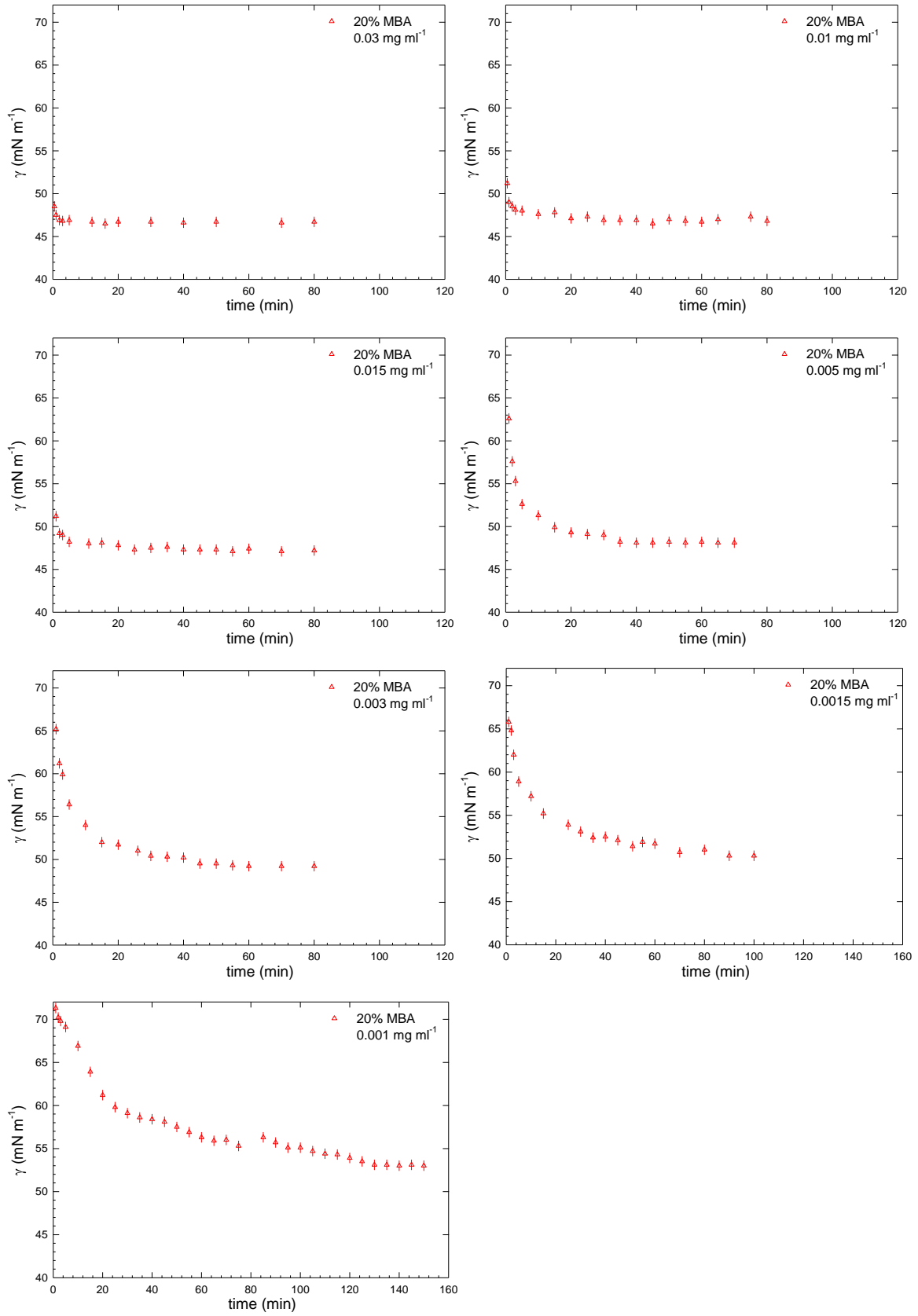
a)



b)



c)



d)

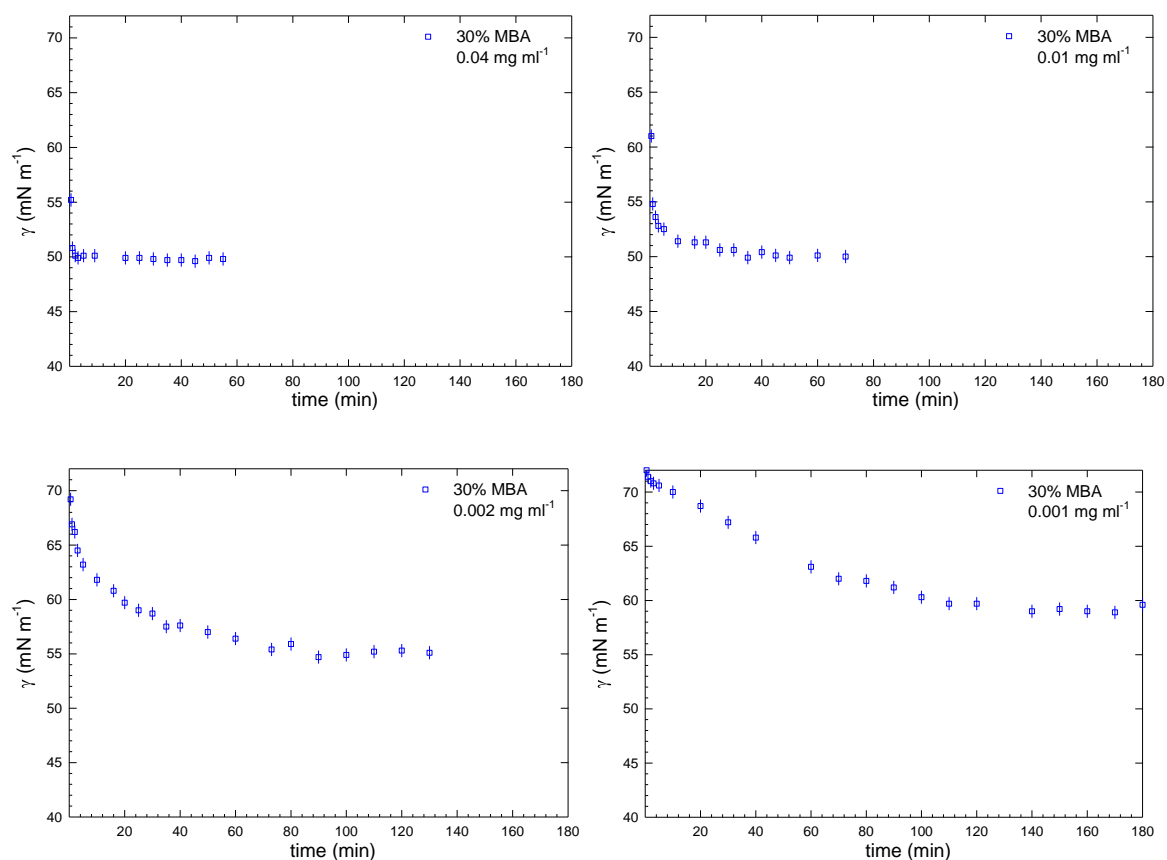


Figure S-5. Surface tension of a) linear polymer, pNIPAM and nanogels with b) 10%, c) 20% and d) 30% of cross-linker as a function of time at 25 °C.

ⁱ R. A. Campbell, H. P. Wacklin, I. Sutton, R. Cubitt, G. Fragneto, *Eur. Phys. J. Plus* **2011**, *126*, 107.

ⁱⁱ H. Sun, PhD thesis

ⁱⁱⁱ R. A. Campbell, J. C. Ang, F. Sebastiani, A. Tummino, J. W. White, *Langmuir* **2015**, *31*, 13535.

^{iv} K. Kubota, K. Hamano, N. Kuwahara, S. Fujishige, I. Ando, *Polym. J.* **1990**, *22*, 1051.

^v L. Arleth, X. Xia, R. P. Hjelm, J. Wu, Z. Hu, *J. Polym. Sci. Part B Polym. Phys.* **2005**, *43*, 849.