The Hierarchical Bulk Molecular Structure of Poly(acrylamide) Hydrogels: Beyond the Fishing Net

Yvonne Gombert, Fabrice Roncoroni, Antoni Sanchez-Ferrer, and Nicholas D. Spencer

Supporting Information

1. UV/vis Absorbance Spectrum of pAAm Hydrogel

Absorbance of electromagnetic radiation in the UV/vis range takes place only for wavelengths below 340 nm (Figure 1). The spectrum shows a characteristic peak at 287 nm, independent of the amount of cross-linker (*bis*-AAm) in the hydrogel sample.

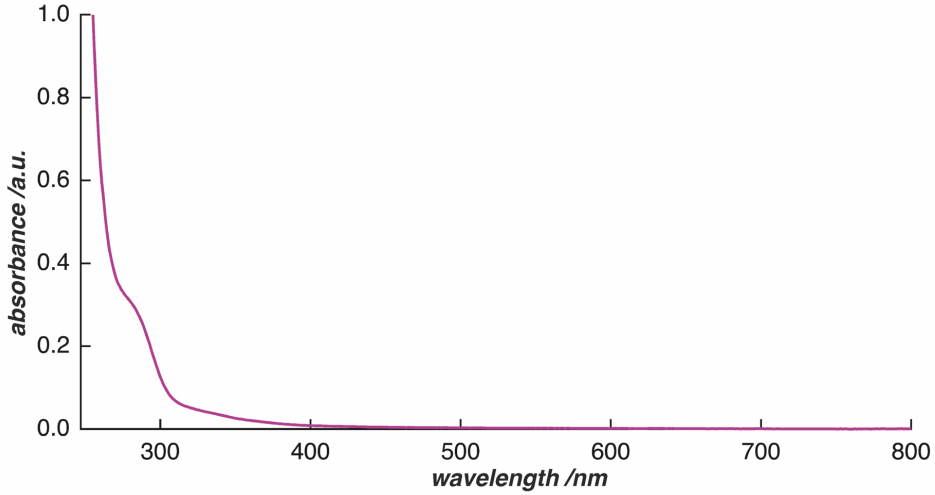

Figure 1: The absorbance spectrum of a pAAm01 (0.1 wt % *bis*-AAm) hydrogel shows no interaction with light. Significant absorbance is only observed below 340 nm.

2. Calculations for the Polymer-Domain-Size Approximation

2.1. The Domain Volume Concentration Φ_p

The radius of polymer domains in the hydrogel was calculated based on the sample turbidity as follows:

$$T = \frac{I}{I_0} = e^{-L\tau} = e^{-L\frac{N}{V}C_{sca}} =$$

$$= e^{-\frac{24\pi^3 V_d^2 L n_m^4}{\lambda^4}\frac{N}{V_S}\left(\frac{\left(\frac{n_P}{n_m}\right)^2-1}{\left(\frac{n_P}{n_m}\right)^2+2}\right)^2} = e^{-\frac{24\pi^3 V_d L n_m^4 \Phi_P}{\lambda^4}\left(\frac{\left(\frac{n_P}{n_m}\right)^2-1}{\left(\frac{n_P}{n_m}\right)^2+2}\right)^2}$$

This equation includes the volume concentration of domains in the sample, Φ_p. In order to estimate this parameter, some approximations were made regarding the monomer sizes of AAm and *bis*-AAm and assumptions about their quantitative distribution in the polymer network.

As discussed in this work, polymer domains are composed of agglomerated polymer clusters. For this reason, it is possible to estimate Φ_p through an estimation of the volume concentration of clusters in the sample, $\Phi_p \approx \Phi_{cluster}$.

Available values for an estimation of $\Phi_{cluster}$ were the total concentration of both monomers in solution and the diameter of a cluster, ε, from the data analysis of the SAXS measurements.

Polymer clusters that polymerize during the pre-gel reaction, were considered spherical. Thus, their volume, V_{cl}, could be calculated as:

$$V_{cl} = \frac{4}{3}\pi\left(\frac{\xi}{2}\right)^3$$

An estimation of the number of clusters in solution, n_{cl}, was possible through the total concentration of monomers. In a first step, the volumes of individual monomers were determined through their bond lengths and angles and by approximating

them as spherical (Figure 2..a).[1, 2] Here, the volume of AAm monomers was approximated from single spheres while the volume of *bis*-AAm monomers, V_{bis}, was approximated as the sum of three spheres (Figure 2.b.): twice the volume of AAm monomers plus the volume of the C-bridge in between (the bond length of N-C was approximated as 1.47 Å).

To obtain n_{cl} from the volume data calculated above, two assumptions were made based on the polymerization behavior of the monomers. First, the majority of monomers polymerizing in the pre-gel reaction are *bis*-AAm molecules. Only a reduced proportion of AAm molecules is active in this first polymerization phase (section 2.2. in paper). Therefore, the composition of the clusters was set to a 9:1 ratio of particle number of *bis*-AAm to AAm monomers. Second, as stated by Okay *et al.*, approximately 80 % of the total amount of *bis*-AAm monomers in the reaction solution polymerize into polymer clusters during the pre-gel reaction.[3]

Taking the first assumption into account, the number of *bis*-AAm molecules per cluster, $n_{bis}(cl)$, can be calculated as

$$n_{bis}(cl) \ : \ n_{AAm}(cl) \ = \ 9 \ : \ 1$$

$$V_{cl} = \ n_{bis}(cl) \ V_{bis} \ + \ n_{AAm}(cl) \ V_{AAm}$$

$$V_{bis} \ = \ 3.0528 \ * \ V_{AAm}$$

Taking the second assumption into account, the number of polymer clusters that form in solution can be calculated as

$$n_{cl} = \frac{0.8 \ \frac{m_{bis}}{M_{bis}} \ N_A}{n_{bis}(cl)}$$

Here, m_{bis} is the total mass of *bis*-AAm monomers in the reaction solution, M_{bis} is the molecular weight of *bis*-AAm, M_{bis} = *154.17 g mol*$^{-1}$, and N_A is the Avogadro constant.

This yields the volume fraction of clusters to be

$$\Phi_p \approx \ \Phi_{cl} = \frac{n_{cl} \ V_{cl}}{V_s}$$

with V_s being the swollen hydrogel volume.

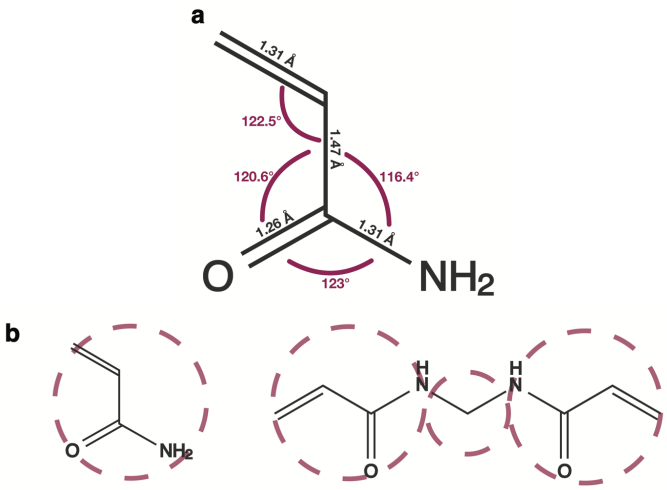

Figure 2: The bond lengths and angles of AAm monomers (a) were used to approximate the volumes of AAm and *bis*-AAm monomers (b). Schematics are not to scale.

2.2 The Refractive Index n_p of Acrylamide

For the refractive index, n_p, of acrylamide, various values can be found in literature between n_p = 1.3365 and n_p = 1.5.[4-6] For this work, refractive indices were used as determined by Hecht *et al.* in a study with polymer concentrations similar to our own sample series.[7] Their study predicted a linear dependence of the refractive index on cross-linker concentration according to

$$n_p(\omega) = 1.3292 + 0.1826\omega$$

with ω being the polymer weight fraction in the sample. This dependence was applied to hydrogels of this study, resulting in values for n_p as given in Table 1. The refractive index of water, n_m, was set as n_m = 1.333.

Table 1: The volume concentration of polymer domains, Φ_p, was approximated by the volume concentration of polymer clusters in the hydrogel. This approximation was based on the polymer cluster size, ξ, and the total concentration of *bis*-AAm in solution.

sample name		pAAm003	pAAm01	pAAm03	pAAm05	pAAm08
cluster diameter, ε (SAXS)	nm	2.3	2.7	3.7	3.6	3.6
cluster volume, V_{cl}	nm^3	6.4	10.3	26.5	24.4	24.4
# *bis*-AAm/cluster, $n_{bis(cl)}$		159.3	257.7	663.3	611.0	611.0
# cluster/volume, n_{cl}	mL^{-1}	$0.6*10^{16}$	$1.2*10^{16}$	$1.4*10^{16}$	$2.6*10^{16}$	$4.1*10^{16}$
volume concentration, Φ_p	%		$1.3*10^{-3}$	$3.8*10^{-2}$	$6.3*10^{-2}$	$9.9*10^{-2}$
refractive index		1.3430	1.3431	1.3435	1.3438	1.3444

3. Measurement & Calculation Results

Table 2: All spectroscopic and mechanical measurement results discussed in this paper are listed by the amount of cross-linker in the polymer network. In addition to the indication of the amount of cross-linker in wt %, the composition of the pAAm hydrogels is listed in %T and %C, a formerly well-established classification method for hydrogel compositions.

sample name				pAAm003	pAAm01	pAAm03	pAAm05	pAAm08
monomer concentrations	amount cross-linker		wt %	0.03	0.1	0.3	0.5	0.8
	total monomer concentration *	%T	%	7.53	7.6	7.8	8.0	8.3
	proportion of cross-linker **	%C	%	0.40	1.32	3.85	6.25	9.64
SAXS	cluster diameter	ε	nm	2.3	2.7	3.7	3.6	3.6
	domain diameter	d	nm	80	48	42	30	27
SEM	pore diameter	d	nm	772 ± 107	664 ± 94	499 ± 107	513 ± 100	
Swelling	swelling ratio	Q	-	36.8 ± 0.3	26.7 ± 0.1	17.5 ± 0.0	15.2 ± 0.1	14.1 ± 0.1

$* \ \%T = \frac{m(AAm)+m(bis-AAm)}{V_{H_2O}} * 100$; $** \ \%C = \frac{m(bis-AAm)}{m(bis-AAm)+m(AAm)} * 100$

Table 3: All results calculated and discussed in this chapter for chain lengths are listed by the amount of crosslinker in the polymer network.

sample name				pAAm003	pAAm01	pAAm03	pAAm05	pAAm08
average molecular weight	domain structure	$\overline{M_c}$	g mol^{-1}	78,820	31,905	14,264	9,544	8,790
cross-linker functionality	domain diameter	d	nm	2.3	100	100	1000	1000
	functionality	ϕ	-	56	149,000	149,000	1,490,000	1,490,000

Table 4: Material-specific parameters used for calculations in this work.

density pAAm	ρ_{pAAm}	1.30	g mL^{-1}	molar volume H_2O	V_1	18.07	mL mol^{-1}	molecular weight monomers	M_{AAm}	71.08	g mol^{-1}
specific density pAAm [8, 9]	$\bar{\nu}_{pAAm}$	0.77	mL g^{-1}	Flory interaction parameter[10]	χ	0.495			$M_{bis\text{-}AAm}$	154.17	g mol^{-1}

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