Supporting Information

Multiscale Surface-Attached Hydrogel Thin Films

with Tailored Architecture

Benjamin Chollet,[1]** Mengxing Li,[1]** Ekkachai Martwong,[1]

Bruno Bresson,[1] Christian Fretigny,[1] Patrick Tabeling,[2] Yvette Tran[1]*

[1] École Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI), ParisTech, PSL Research University, Sciences et Ingénierie de la Matière Molle, CNRS UMR 7615, 10 rue Vauquelin, F-75231 Paris cedex 05, France. Sorbonne-Universités, UPMC Univ Paris 06, SIMM, 10 rue Vauquelin, F-75231 Paris cedex 05, France.

[2] Institut Pierre-Gilles de Gennes (IPGG), 6-12 rue Jean Calvin, 75005 Paris, France.

* Address correspondence to Yvette.Tran@espci.fr

** B. Chollet and M. Li contributed equally to this work.

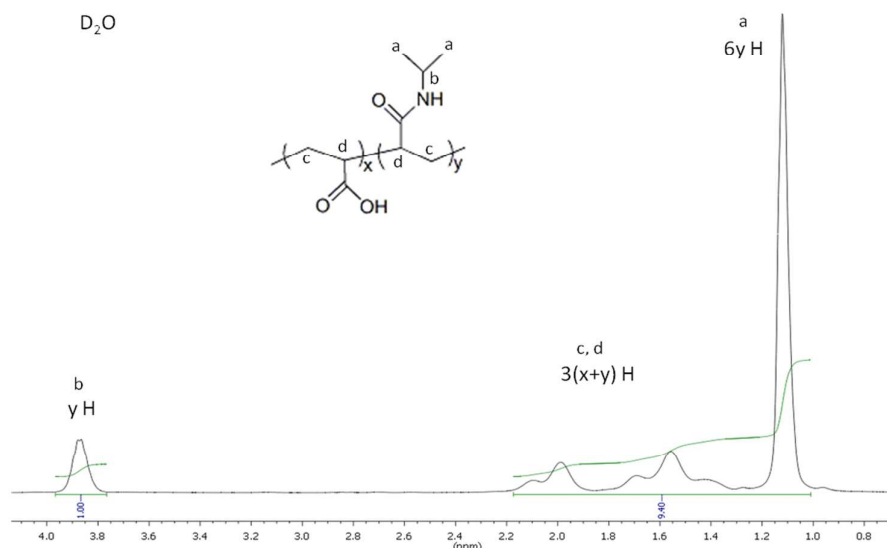## Table of Contents

1. Characterization of ene-functionalized polymers

Figure S1. ^1H *NMR spectrum of P(AA-co-NIPAM) copolymer synthesized by free radical polymerization. The ratio of acrylic acid in the P(AA-co-NIPAM) chains can be calculated.*

The P(NIPAM-*co*-AA) copolymer is characterized by SEC chromatography and ^1H NMR spectroscopy. SEC provides the weight-average molar mass (Mw) and polymer dispersity index (PDI) of the copolymer, while ^1H NMR gives the ratio of AA in the copolymer. The characteristics are shown in Table S2. The weight-average molar masses (M_W) obtained are quite close to the expected value. For example, 254 kg/mol and 195 kg/mol are found when 250 kg/mol was targeted. The polymer dispersity index (PDI) of the copolymer is quite low, around 2, and even lower than 2 for copolymers with molar mass higher than 200 kg/mol. The ^1H NMR spectrum shown Figure S1 is an example of spectra obtained with P(NIPAM-*co*-AA) copolymers in D_2O. The peak at 1.0-1.2 ppm corresponds to the protons on the methyl group (marked as "a"), the peak at 3.8-4.0 ppm to the proton connected to the secondary carbon of the isopropyl group (marked as "b") and the peaks at 1.3-2.2 ppm to the protons connected to the carbon on the main chain (marked as "c" and "d"). The ratio of AA in the polymer can be determined by comparing the integral of the peak. We found here a ratio of AA in the copolymer equal to 9%.
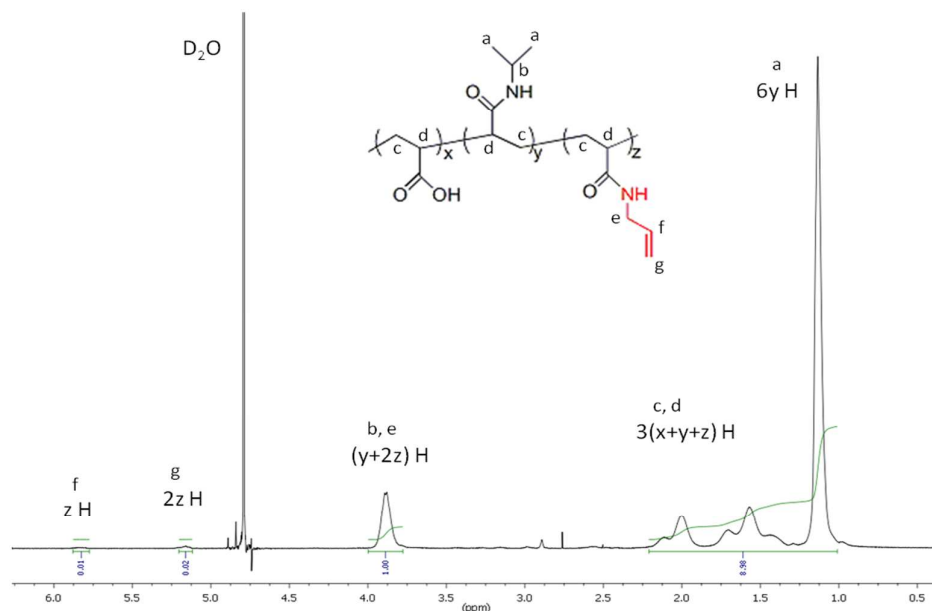
Figure S2. *¹H NMR spectrum of ene-functionalized copolymers obtained by peptide bond using allylamine. The ratio of ene-functionalization can be calculated.*

The ¹H NMR spectrum shown Figure S2 is an example of spectra obtained with ene-modified PNIPAM in D_2O. The peak at 1.0-1.2 ppm corresponds to the protons on the methyl group (marked as "a"), the peak at 3.8-4.0 ppm to the proton connected to the secondary carbon of the isopropyl group and the one connected to the primary carbon on the allyl group (marked as "b" and "e" respectively), the peaks at 1.3-2.2 ppm to the protons connected to the carbon on the main chain (marked as "c" and "d") and the peaks at 5.8 ppm and 5.2 ppm to the protons on the ene group (marked as "f" and "g" respectively). The ratio of ene-functionalization can be determined by comparing the integral of the peak. We found here a ratio of AA in the copolymer equal to 2%. The ratios of ene-groups for most of polymers are equal to 2% (see Table S1).

Table S1. *Characteristics of ene-functionalized PNIPAM. PDI is the polymer dispersity index, defined as Mw/Mn ratio.*

Mw (kg/mol)	PDI*	Ratio of AA		Ratio of ene-groups
		expected	obtained	
681	1.9	10%	11%	2%
669	1.6	10%	10%	2%
629	1.8	10%	10%	1%
474	1.8	5%	5%	3%
405	1.8	10%	12%	2%
254	1.8	5%	6%	2%
195	2.2	10%	9%	2%
66	2.2	10%	12%	2%

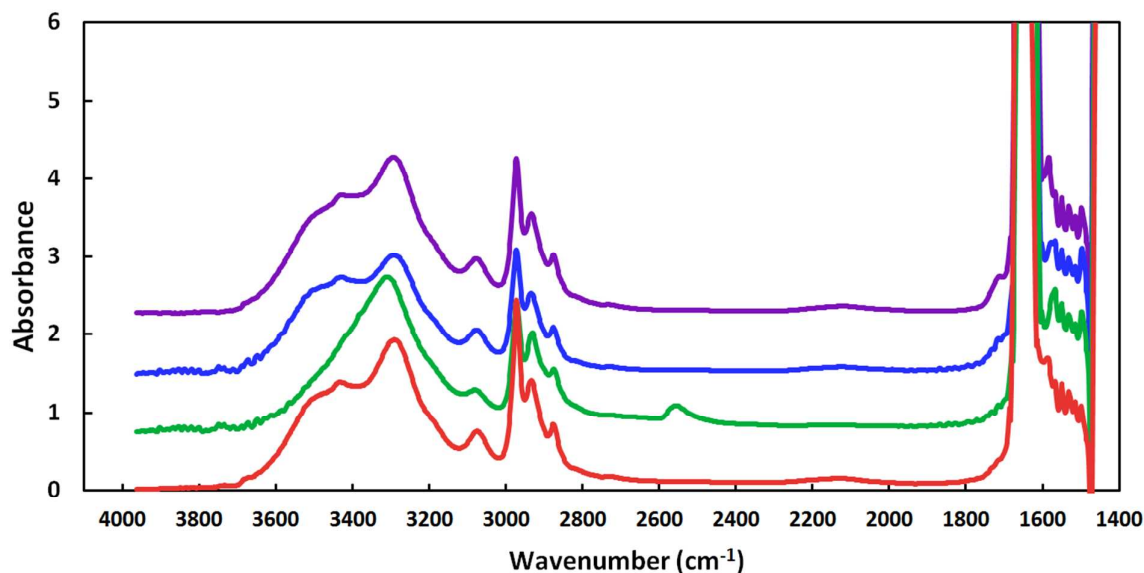## 2. Characterization of PNIPAM hydrogel films

Figure S3. *FTIR-ATR spectra of PNIPAM films. The absorption spectra are obtained with PNIPAM films at the surface of silicon prisms (waveguides): spin-coated film containing PNIPAM (red), spin-coated film containing PNIPAM and dithioerythritol (green), PNIPAM hydrogel film after 24 hours thermal activation (blue), PNIPAM hydrogel film after 2 hours UV irradiation (purple).*

Figure S3 shows FTIR-ATR spectra of PNIPAM films. Are compared four absorption spectra: spin-coated film containing only PNIPAM (spectrum a), spin-coated film containing PNIPAM and dithioerythritol cross-linkers (spectrum b), PNIPAM hydrogel film after grafting and cross-linking of chains by thiol-ene reaction either by thermal activation (spectrum c) or by UV irradiation (spectrum d). As silicon substrates are used as (infrared) waveguides, it is difficult to quantitatively analyze the wave number range below 1600 cm^{-1} due to the high absorbance of the substrates (O-H, Si-O, Si-Si bonds). There is some interesting information that could be extracted from 4000 – 1600 cm^{-1} range. The absorption bands between 3100 and 2800 cm^{-1} are characteristics of asymmetric and symmetric stretching vibrations of CH, CH_2 and CH_3 groups. The absorbance is the same for the four spectra as expected. The loss of the peak at 2500 cm^{-1} attributable to dithiol cross-linkers (S-H stretch) for spectra (c) and (d) is explained by the thiol-ene reaction and the removal of dithiol in excess. It is also consistent with the high increase of the absorption band at 3300 cm^{-1} characteristics of O-H (due to H bonds) found in the spectrum b (because of the presence of dithioerythritol in excess), this broad and high band even hiding the peak at 3430 cm^{-1} characteristics of N-H amide groups. As expected, it is not possible to quantify the thiol-ene reaction for two main reasons. First, the absorption peak which is characteristics of S-C bond is at very low wave number (around 700 cm^{-1}). Second, the thiol-ene ratio is weak with a maximum of 2%, the ratio of ene groups measured by ^{1}H NMR being around 2%.

3. Synthesis of hydrogel films

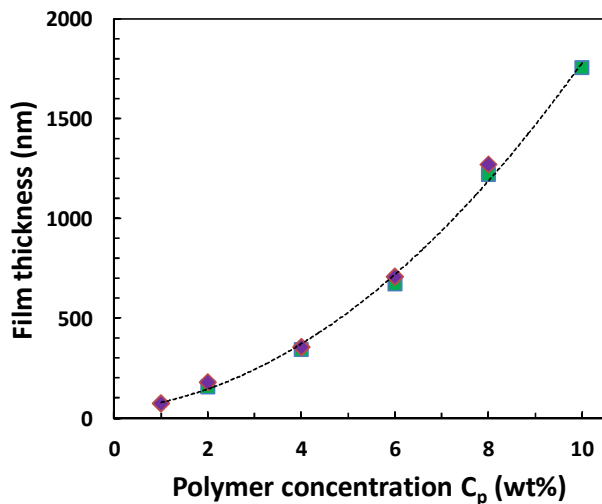### *Synthesis of PAA hydrogel films by thermal activation*

Figure S4. Dry thickness of the hydrogel film as function of the concentration of polymer in the solution for spin-coating for PAA (purple markers) and PNIPAM (green markers) with the similar average molar mass equal to 250 kg/mol for PAA and 254 kg/mol for PNIPAM.

Figure S4 shows the dry thickness of PNIPAM and PAA hydrogels films as function of the concentration of polymer in the solution for spin-coating for similar average molar mass (254 kg/mol for PNIPAM and 250 kg/mol for PAA). The variation of thickness is the same for both PNIPAM and PAA hydrogels.

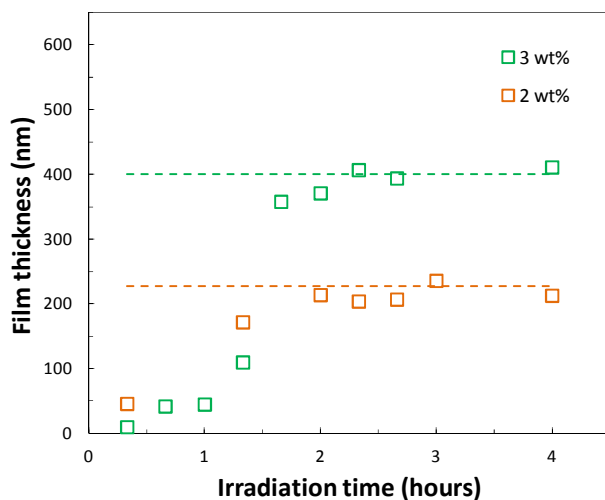### *Synthesis of PAA hydrogel films by UV-irradiation*

Figure S5. Dry thickness of PAA hydrogel film as function of UV-irradiation time for various concentrations of polymer in the solution for spin-coating (with average molar mass equal to 250 kg/mol), the lines corresponding to the maximum thickness of the hydrogel film which is also obtained by heating activation.

Figure S5 shows the dry thickness of the PAA hydrogel film as function of UV-irradiation time. The data are given for two different concentrations of polymer in the solution for spin-coating (the average molar mass is 250 kg/mol). The maximum thickness reached for each concentration is the same than that obtained by heating activation at 120°C for 24 hours. The maximum is reached after 2 hours irradiation. It is obtained for both PAA and PNIPAM hydrogel films.

4. Synthesis of hybrid hydrogel films

Table S2. *Formulation of silica-PNIPAM hybrid gel films. The volume fraction of silica particles is calculated considering the density of silica is 2.3 g/cm^3 and of PNIPAM is 1.1 g/cm^3 (water content of 10 % in the hybrid film in air is taken into account).*

Mw of polymer (kg/mol)	Concentration of polymer (wt%)	Silica/polymer ratio (wt/wt)	Volume fraction of silica particles	Thickness in air (nm)
66	1.0%	0	0	70
		5/1	63.4%	198
	2.0%	0	0	90
		2/1	44.0%	277
		5/1	63.4%	420
	5.0%	0	0	200
		1/100	0.4%	230
		1/50	0.9%	251
		1/20	2.1%	293
		1/10	4.1%	340
		1/5	7.8%	352
		1/2	17.3%	400
		1/1	29.1%	455
681	1.0%	0	0	80
		5/1	63.4%	237
	2.0%	0	0	170
		1/50	0.9%	178
		1/20	2.1%	201

Table S2 shows all the hybrid gel films synthesized. The hybrid gel films are stable, i.e. the particles are stably trapped inside the mesh of the surface-attached network (the thickness measured in air remains the same after numerous steps of washing in water). The thickness of the hybrid gel film increases with the molecular weight of PNIPAM chains and the concentration of polymers in the solution for spin-coating (or the viscosity of the spinning solution). It also increases with the volume fraction of silica particles.