Supporting Information for:

Improved Stimuli-Response and Mechanical Properties of Nanostructured Poly(*N*isopropylacrylamide-co-dimethylsiloxane) Hydrogels Generated through Photopolymerization in Lyotropic Liquid Crystal Templates

Bradley S. Forney, Céline Baguenard and C. Allan Guymon*

Department of Chemical and Biochemical Engineering

The University of Iowa

Iowa City, IA 52242

*Corresponding author: Telephone: +1 319 335 5015. Fax: +1 319 335 1415. E-mail: allanguymon@uiowa.edu. **Appendix S1: Conversion of Double Bonds.** The rate of polymerization of a monomer *i* was obtained from heat flow *Q* as follow:

$$R_p(t) = \frac{Q(t) \cdot MW_i}{m_i \cdot n_i \cdot \Delta H_{p_i}} = Q(t) \cdot E_i$$
(1)

where *MW* is the molecular weight, *m* the mass, *n* the number of double bonds and ΔH_p the enthalpy of polymerization of the double bond of the analyzed monomer.¹ The theoretical value of the enthalpy of acrylamide double bond and acrylate double bond polymerizations are 18.5 kcal/mol and 13.1 kcal/mol. For the case of 3 different monomers, the equation becomes:

$$R_p(t) = \frac{Q(t)}{\frac{1}{E_1 + \frac{1}{E_2} + \frac{1}{E_3}}}$$
(2)

Finally, as $R_{p(t)} = -\frac{dp}{dt}$, with p being the double bond conversion, the conversion is obtained as a function of time by integration of $R_p(t)$. The results are shown on figures A1 and A2 for samples of two different PDMS concentrations.



Figure S-1. DSC experiments: heat flow against time (a) and conversion of double bonds vs time (b) of samples containing 6.7% PDMS (\blacksquare) and 33.3% PDMS (\Box).

Appendix S2: Polarized Light Microscopy. All samples have been observed by polarized light microscopy before and after polymerization. Figure S-2 shows the PLM picture of the sample containing 12.5% PDMS, before and after polymerization. This pattern is characteristic of the normal hexagonal phase, especially if the sample contains macromers (macromolecular monomer) such as PDMS crosslinker. The PLM also shows the similar nature of the system before and after polymerization indicating significant retention of nanostructure. All other examined samples exhibit similar patterns using PLM before and after polymerization.



Figure S-2. Polarized light microscopy picture for the sample containing 12.5% PDMS before (a) and after (b) polymerization.

Appendix S3: Evolution of the Nanostructure as the Amount of PDMS Increases. In SAXS profiles, the q value of the primary peak is related to the distance between discontinuous domains, as $q = 2\pi/d_{100}$. In the normal hexagonal phase, the distance between the centers of cylinders is equal to the lattice parameter *a* which is obtained using the equation: $a = 2/\sqrt{3} \cdot d_{100}$. As the amount of PDMS increases, the primary peak shifts to lower q (as shown in Figure S-3a and Figure S-4a, respectively before and after polymerization), implying that the distance between the centers of PDMS cylinders increases. For clarity, the q value of the primary peak maximum and the lattice parameter *a* were plotted against the amount of PDMS contained in the sample (Figure S-3b and Figure S-4b). While the resolution of the SAXS prevents differentiation of *q* and *a* at some concentrations , the graphs clearly show that q decreases and a rises as the PDMS amount increases.



Figure S-3. (a) Primary peak of the SAXS profiles for 0% PDMS (\blacksquare), 12.5% PDMS (\bigcirc) and 33% PDMS (\blacktriangle), before polymerization. (b) Evolution of the q (\blacksquare) value and the lattice parameter *a* (\Box) calculated from the primary peak's top, plotted against the amount of PDMS, before polymerization.



Figure S-4. (a) Primary peak of the SAXS profiles for 0% PDMS (\blacksquare), 12.5% PDMS (\bigcirc) and 33% PDMS (\blacktriangle), after polymerization. (b) Evolution of the q (\blacksquare) value and the lattice parameter *a* (\Box) calculated from the primary peak's top, plotted against the amount of PDMS, before polymerization.

1. M. A. DePierro, K. G. Carpenter and C. A. Guymon, *Chem. Mater.*, 2006, 18, 5609-5617.