

## Thermo-responsive peptide-based triblock copolymer hydrogels

Antoni Sánchez-Ferrer,<sup>a‡</sup> Venkata Krishna Kotharangannagari<sup>a,b‡</sup>, Janne Ruokolainen,<sup>c</sup> and Raffaele Mezzenga<sup>\*a</sup>

<sup>a</sup> ETH Zurich, Food & Soft Materials Science, Institute of Food, Nutrition & Health, Schmelzbergstrasse 9, LFO, E23-29, CH-8092 Zürich, Switzerland

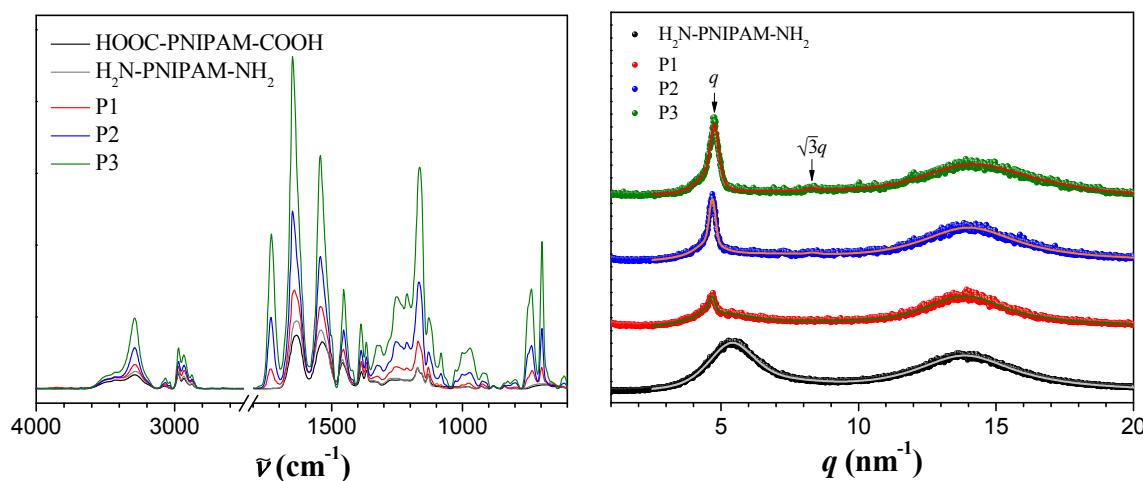
<sup>b</sup> Department of Physics and Frimat Center for Nanomaterials, University of Fribourg, Chemin du Musée 3, CH-1700 Fribourg, Switzerland.

<sup>c</sup> Department of Applied Physics, AALTO University, P.O. Box 15100, FI-00076 Helsinki, Finland.

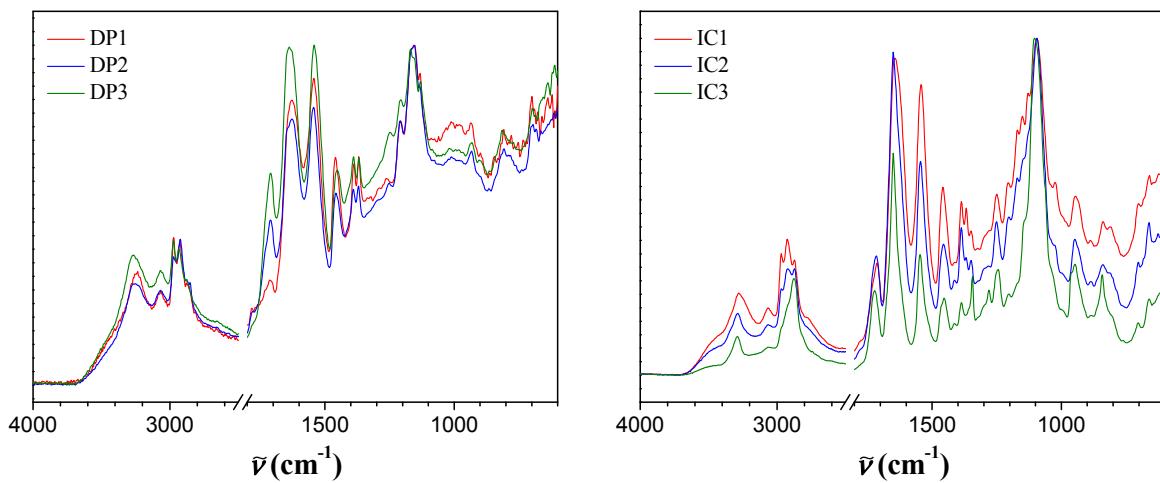
‡ The first two authors contributed equally to this study.

\* CORRESPONDING AUTHOR EMAIL ADDRESS ([raffaele.mezzenga@hest.ethz.ch](mailto:raffaele.mezzenga@hest.ethz.ch))

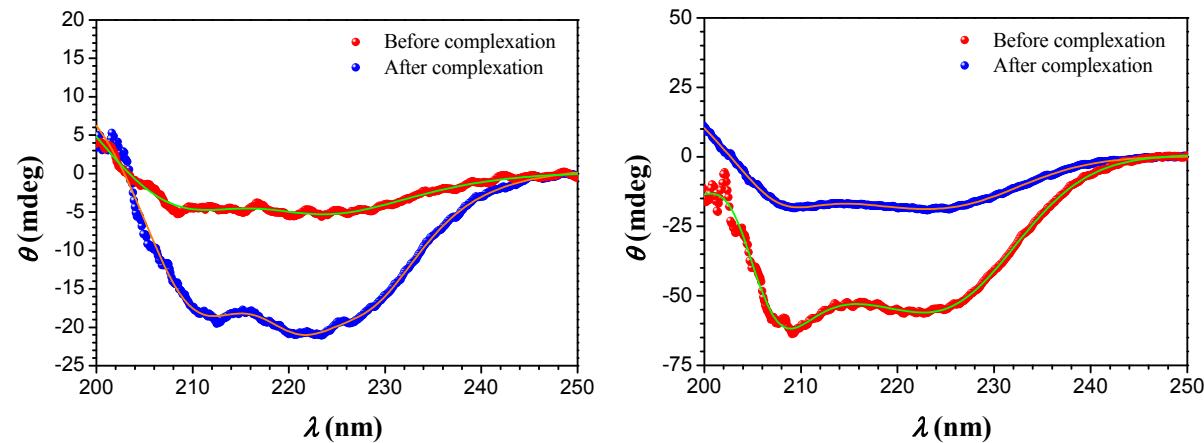
KEYWORDS: Stimuli-responsive, polypeptide, triblock copolymers, hydrogels.



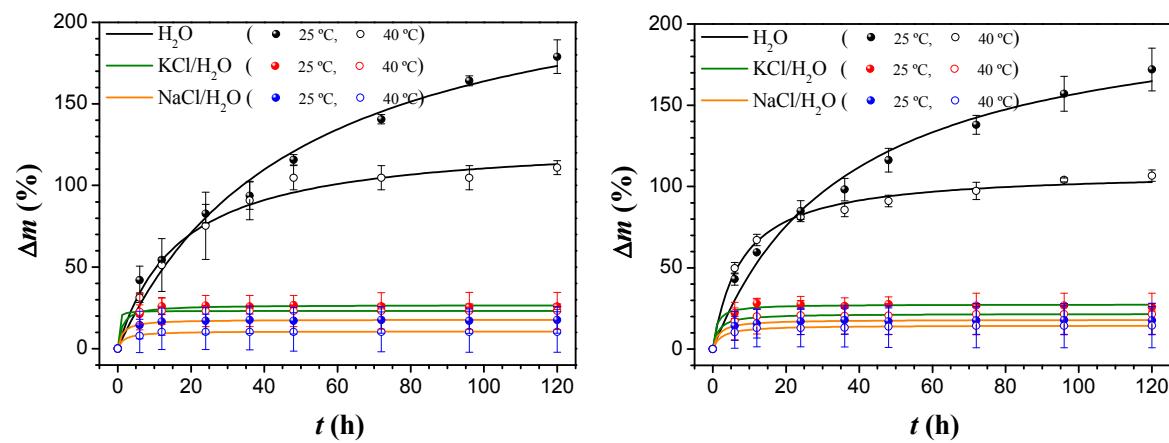
**Figure ESI-1.** FTIR spectra of the dicarboxy-terminated PNIPAM homopolymer, the diamino-terminated PNIPAM homopolymer, and the three PBLG-*b*-PNIPAM-*b*-PBLG triblock copolymers P1, P2 and P3 (left). WAXS patterns of the diamino-terminated PNIPAM homopolymer, and the three PBLG-*b*-PNIPAM-*b*-PBLG triblock copolymers P1, P2 and P3 (right).



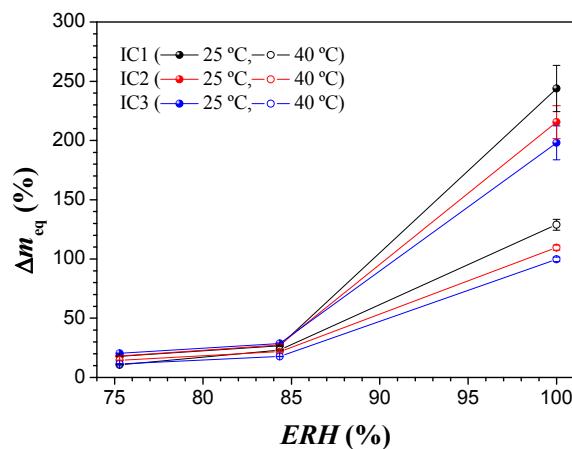
**Figure ESI-2.** FTIR spectra of the three PLGA-*b*-PNIPAM-*b*-PLGA triblock copolymers DP1, DP2 and DP3 (left), and FTIR spectra of the corresponding three ionic complexes IC1, IC2 and IC3 (right).



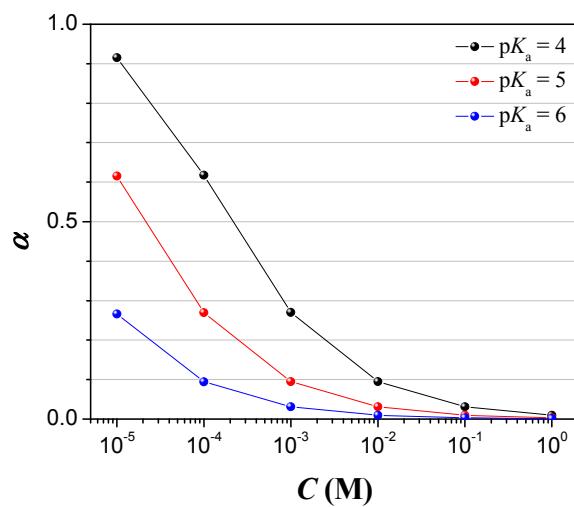
**Figure ESI-3.** Circular dichroism spectra of the two PLGA-*b*-PNIPAM-*b*-PLGA triblock copolymers DP1 (left) and DP2 (right) and their corresponding ionic complex IC1 (left) and IC2 (right).



**Figure ESI-4.** Swelling behaviour of the two ionic complexes IC1 (left) and IC2 (right) at 25 °C and 40 °C in water, KCl/water, and NaCl/water atmospheres.



**Figure ESI-5.** Absolute equilibrium swelling ratio ( $\Delta m_{eq}$ ) for the three ionic complexes IC1, IC2 and IC3 at 25 °C (filled symbols) and 40 °C (empty symbols) in water (black symbols), KCl/water (red symbols), and NaCl/water (blue symbols) atmospheres.



**Figure ESI-6.** Dissociation degree as function of the concentration for weak acids for different dissociation constants ( $pK_a$ ).

**Table ESI-1.** Equilibrium swelling ratio ( $\Delta m_{\text{eq}}$ ), swelling life time ( $\tau$ ), and swelling stretching factor ( $\beta$ ) for the three ionic complexes IC1, IC2 and IC3 at 25 °C and 40 °C in water atmosphere.

	$T = 25 \text{ } ^\circ\text{C}$			$T = 40 \text{ } ^\circ\text{C}$		
	$\Delta m_{\text{eq}} (\%)$	$\tau (\text{h})$	$\beta$	$\Delta m_{\text{eq}} (\%)$	$\tau (\text{h})$	$\beta$
IC1	$244 \pm 20$	$49.7 \pm 0.4$	$0.88 \pm 0.01$	$129 \pm 5$	$22.2 \pm 0.2$	$0.77 \pm 0.01$
IC2	$215 \pm 14$	$40.6 \pm 0.3$	$0.85 \pm 0.01$	$110 \pm 2$	$12.1 \pm 0.1$	$0.69 \pm 0.01$
IC3	$198 \pm 14$	$37.8 \pm 0.3$	$0.84 \pm 0.01$	$100 \pm 2$	$24.2 \pm 0.2$	$0.78 \pm 0.01$

**Table ESI-2.** Equilibrium swelling ratio ( $\Delta m_{\text{eq}}$ ), swelling life time ( $\tau$ ), and swelling stretching factor ( $\beta$ ) for the three ionic complexes IC1, IC2 and IC3 at 25 °C and 40 °C in KCl/water atmosphere.

	$T = 25 \text{ } ^\circ\text{C}$			$T = 40 \text{ } ^\circ\text{C}$		
	$\Delta m_{\text{eq}} (\%)$	$\tau (\text{h})$	$\beta$	$\Delta m_{\text{eq}} (\%)$	$\tau (\text{h})$	$\beta$
IC1	$26.7 \pm 0.5$	$1.95 \pm 0.03$	$0.51 \pm 0.01$	$23.2 \pm 0.1$	$1.95 \pm 0.03$	$0.52 \pm 0.01$
IC2	$27.5 \pm 0.5$	$1.48 \pm 0.03$	$0.49 \pm 0.01$	$21.7 \pm 0.2$	$2.33 \pm 0.04$	$0.53 \pm 0.01$
IC3	$28.7 \pm 0.4$	$3.3 \pm 0.1$	$0.56 \pm 0.01$	$17.7 \pm 0.2$	$1.90 \pm 0.03$	$0.51 \pm 0.01$

**Table ESI-3.** Equilibrium swelling ratio ( $\Delta m_{\text{eq}}$ ), swelling life time ( $\tau$ ), and swelling stretching factor ( $\beta$ ) for the three ionic complexes IC1, IC2 and IC3 at 25 °C and 40 °C in NaCl/water atmosphere.

	$T = 25 \text{ } ^\circ\text{C}$			$T = 40 \text{ } ^\circ\text{C}$		
	$\Delta m_{\text{eq}} (\%)$	$\tau (\text{h})$	$\beta$	$\Delta m_{\text{eq}} (\%)$	$\tau (\text{h})$	$\beta$
IC1	$17.8 \pm 0.2$	$2.00 \pm 0.04$	$0.52 \pm 0.01$	$10.7 \pm 0.2$	$2.71 \pm 0.04$	$0.54 \pm 0.01$
IC2	$18.1 \pm 0.2$	$2.71 \pm 0.04$	$0.54 \pm 0.01$	$14.5 \pm 0.2$	$3.80 \pm 0.05$	$0.57 \pm 0.01$
IC3	$20.4 \pm 0.3$	$3.00 \pm 0.05$	$0.55 \pm 0.01$	$11.5 \pm 0.1$	$2.91 \pm 0.05$	$0.55 \pm 0.01$