## Supporting Information for:

## Stress-free two-way shape memory effect of poly(ethylene glycol)/poly(ε-caprolactone) semicrystalline networks

Nicoletta Inverardi,<sup>a,e,\*,†</sup> Maurizio Toselli,<sup>b,e</sup> Giulia Scalet,<sup>c,e</sup> Massimo Messori,<sup>d,e</sup> Ferdinando Auricchio,<sup>c,e</sup> and Stefano Pandini<sup>a,e</sup>

a. Department of Mechanical and Industrial Engineering, University of Brescia, via Branze 38, 25133, Brescia, Italy

b. Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale Risorgimento 4, 40136, Bologna, Italy

c. Department of Civil Engineering and Architecture, University of Pavia, via Ferrata 3, 27100, Pavia, Italy

d. Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy

e. INSTM, National Interuniversity Consortium of Materials Science and Technology, Via Giuseppe Giusti 9, 50121 Firenze, Italy

\*(N.I.) E-mail: n.inverardi003@unibs.it ; ninverardi@mgh.harvard.edu

†(N.I.) Present address: Department of Orthopaedic Surgery, Massachusetts General Hospital and Harvard Medical School, Boston, MA, USA



**Figure S1.** <sup>1</sup>H-NMR spectra of (*a*) hydroxyl terminated PCL10 and (*b*) dimethacrylate macromonomer after rection with 2-IEM and relative assignments.

•



**Figure S2.** <sup>1</sup>H-NMR spectra of (a) hydroxyl terminated PEG3 and (b) dimethacrylate macromonomer after rection with 2-IEM and relative assignments.



**Figure S3.** DSC cooling and second heating scans at 10 °C min<sup>-1</sup> of PCL-PEG networks with 2:1 and 1:2 weight ratio and different molecular weight of PEG macromonomers.



**Figure S4.** DSC scans of (*a*) PCL10 methacrylated macromonomer and (*b*) PCL10 network (after photocrosslinking).



**Figure S5.** DSC scans of PEG networks with different molecular weight of PEG macromonomers.



**Figure S6.** Stress versus strain curves measured under tensile conditions at 65 °C for PCL10PEG2 and PCL10PEG4 networks.



**Figure S7.** Results of the stress-free two-way shape memory response for PCL10PEG3 1:2 evaluated over three cycles and represented in terms of strain versus temperature curve a) along the whole test and b) with a magnification on the three cycles (black line: 1<sup>st</sup> cycle, green line: 2<sup>nd</sup> cycle, blue line: 3<sup>rd</sup> cycle). Dashed line represents the programming cycle and the end of the test.



**Figure S8.** Results of swelling experiments in distilled water at room temperature as water uptake at 24h *versus* weight content of the PEG phase in PCL10-PEG3 networks.