

## SUPPLEMENTARY INFORMATION

### Supplementary Experimental Section

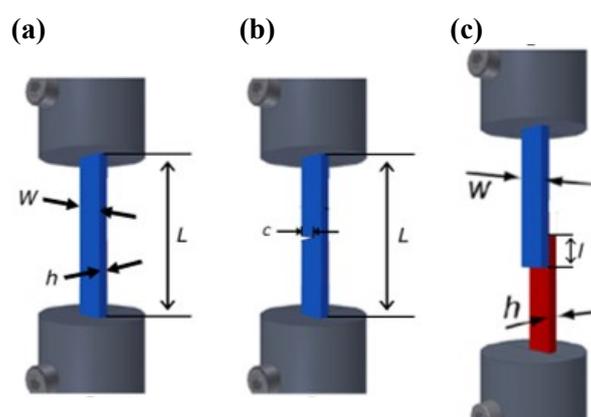
**Synthesis of PNIPAm macromonomers.** The synthesis involved a two-step process:

#### *1) Synthesis of Amino-Terminated Telomers*

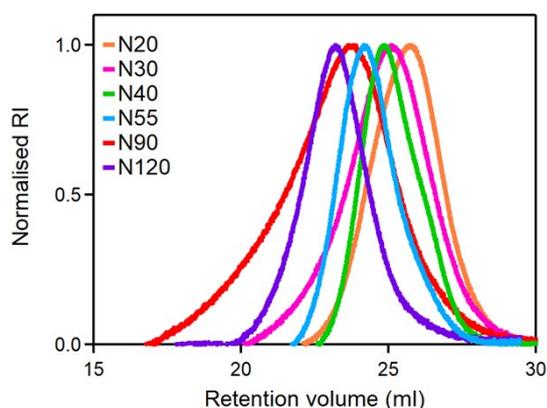
The synthesis of functional chains was achieved by radical polymerization using 2-Amino-ethane-thiol hydrochloride (AET.HCl,  $\geq 97\%$ , Aldrich) as chain transfer agent. This telomerization allows controlling the end group of the polymer as well as its molar mass. In a three necked flask, 100 mmol of PNIPAm monomers was dissolved in 100 mL of water and the solution was deoxygenated for 1 h with nitrogen bubbling. The redox initiators, KPS (1.0 mmol) and AET·HCl (2.0 mmol), were separately dissolved in 10 mL of water and deoxygenated for 30 min before adding to the monomer solution. The reaction was allowed to proceed in an ice bath, in order to avoid the phase separation of the reaction medium in the case of PNIPA. SEC was applied to monitor the polymerization process. After 4 h, no monomer was left according to SEC, and an appropriate amount of sodium hydroxide was added to neutralize the hydrochloride ions and the polymer was recovered by dialysis against pure water (membrane cut-off=3.5 kDa) for one week and freeze-dried. The telomers were obtained with a yield of 70 wt%.

#### *2) Synthesis of linear macromonomers*

Typically for the PNIPAm macromonomer, 6.0 g of amino-terminated telomers (about 0.26 mmol) and 0.29 g of AA (4 mmol) were initially dissolved in 50 mL of NMP at room temperature. After dissolution, 0.8 g of DCCI (4 mmol), initially dissolved in a minimum of NMP, was introduced rapidly and the reaction was allowed to proceed overnight under stirring at room temperature. After dilution with 100 mL of water, the polymer was purified by dialysis against pure water (membrane cut-off=3.5 kDa) for one week, and the aqueous solutions were filtered and freeze dried. The reaction was almost quantitative and the PNIPAm macromonomer was obtained with a yield of 95 wt%.

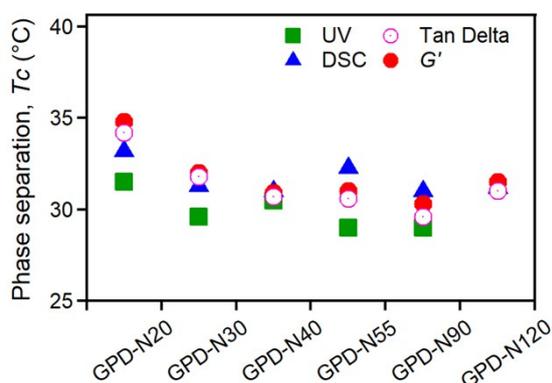
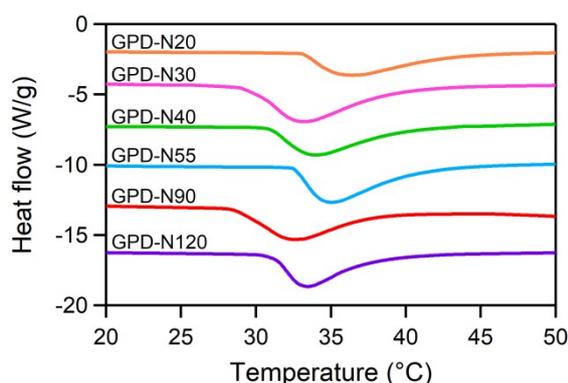


**Supplementary Figure S1.** Geometries used for large strain mechanical testing (a) Uni-axial tensile test geometry; (b) Fracture test geometry with  $c$  being the initial crack length; (c) Lap-joint geometry.

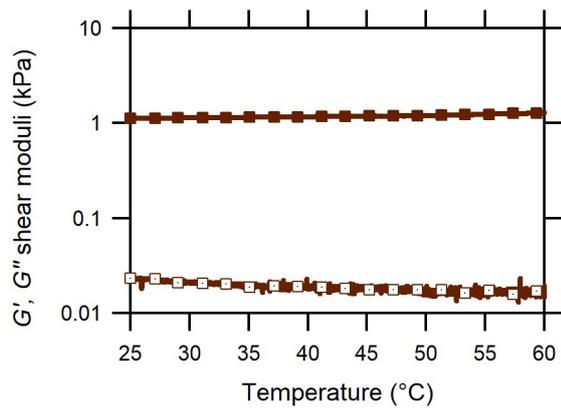


Macromonomer	$M_n$ (kg/mol)	$M_w$ (kg/mol)	DP <sub>n</sub>	$\bar{D}$
PNIPAm-N20	18.9	22.4	170	1.2
PNIPAm-N30	32.9	48.2	290	1.5
PNIPAm-N40	39.3	52.8	350	1.3
PNIPAm-N55	54.9	73.9	485	1.4
PNIPAm-N90	87.2	123.3	770	2.4
PNIPAm-N120	121.0	177.2	1070	1.5

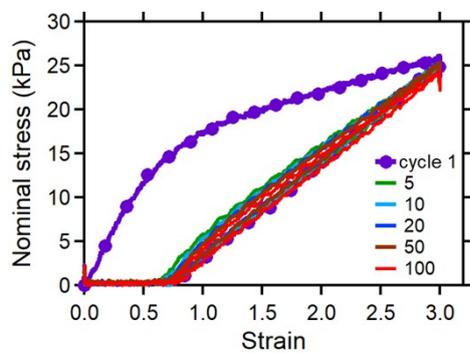
**Supplementary Figure S2.** PNIPAm macromonomers characteristics determined by Size Exclusion Chromatography



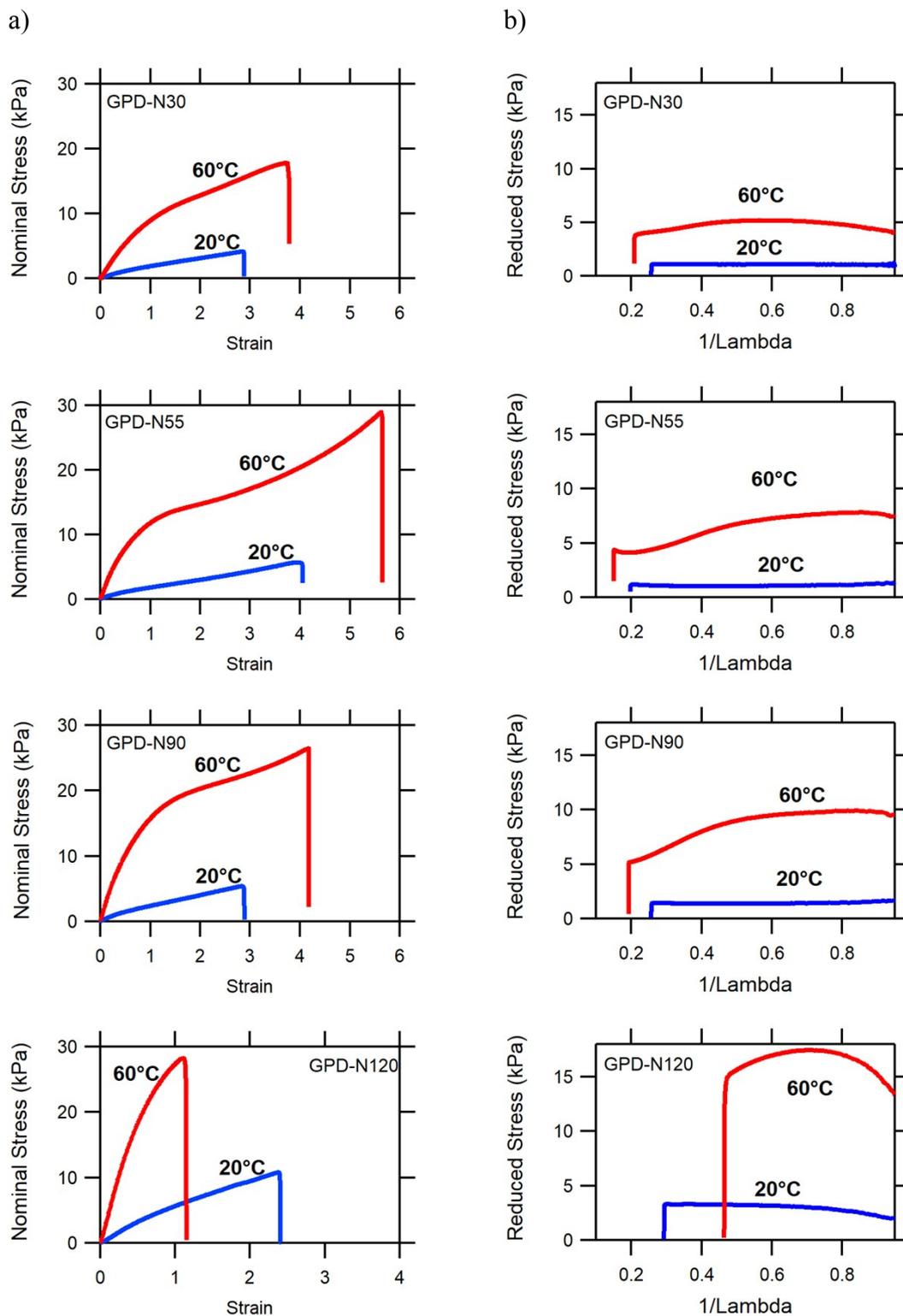
**Supplementary Figure S3. a)** Endotherms obtained by differential scanning calorimetry upon heating reflects the phase-transition undergone by PNIPAm side-chains forming microdomains. **b)** Comparison of phase-separation temperature,  $T_c$  determined by turbidimetry (UV-vis), Differential Scanning Calorimetry (DSC) and linear rheology ( $G'$  and  $\tan \delta$ )



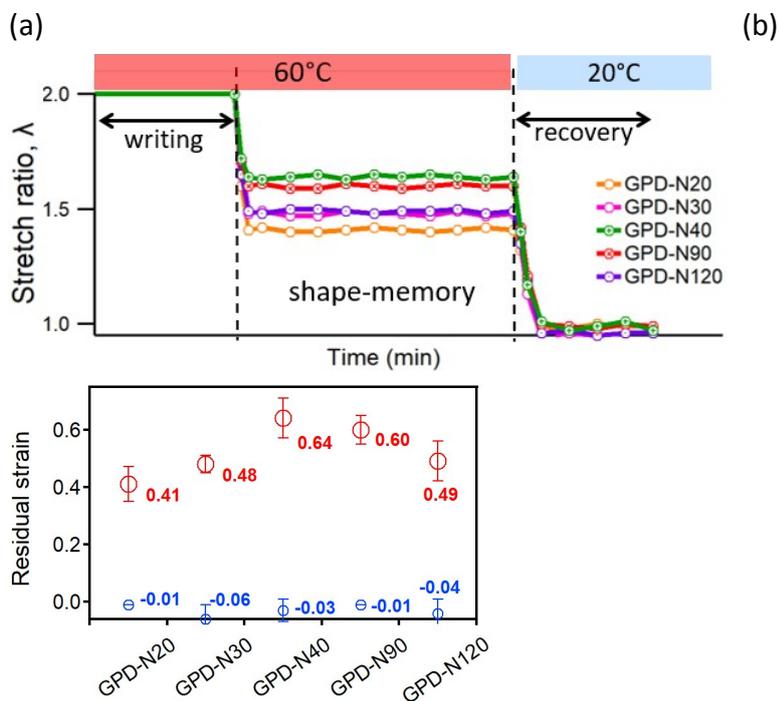
**Supplementary Figure S4.** Dynamic shear elastic (or storage) modulus  $G'$  (filled symbols) and loss modulus  $G''$  (open symbols) for a homo-PDMA gel.



**Supplementary Figure S5.** Fatigue test in tensile mode for GPD-N55 at 60 °C, 100 consecutive cycles were applied at 60 °C. Note that hundreds of consecutive cycles present almost closed-loops and an overlapping mechanical response, with no loss in stiffness or creeping phenomena over time



**Supplementary Figure S6.** Large strain behavior of GPD-Nx gels. **(a)** Tensile stress-strain curves of GPD-Nx at 20 °C and 60 °C. **(b)** Corresponding stress-strain curves plotted as reduced stress as a function of  $1/\lambda$ . This representation enhances the deviations from the classical rubber elasticity model displayed by the gel at 60 °C: a strong hardening is observed at the early stages of deformation followed by softening above 50% of strain. The GPD-Nx behavior at 20 °C is given as a guideline and follows the theoretical rubberlike behavior.



**Supplementary Figure S7.** Shape-memory curves of GPD-Nx series. **(a)** First, the gels were stretched to  $\lambda=2$  at 20 °C prior to be heated at 60 °C to perform the “writing” procedure during 3 minutes. After writing for 3 min, stress was released, and the residual stretched ratio was measured over time. Finally, the gels were cool down at 20 °C to fulfil the “recovery” process. **(b)** Summary of the residual strain at 60 and 20 °C after the “writing” and the “recovery” processes, respectively.