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Thermoresponsive Toughening in LCST-Type Hydrogels with Opposite Topology: From Structure to Fracture Properties

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1 Thermo-responsive Toughening in LCST-type
2 Hydrogels with Opposite Topology: From
3 Structure to Fracture Properties

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23 **ABSTRACT**

24 The challenge of this work was to investigate the role of topology in LCST hydrogels that
25 strongly and reversibly thermo-reinforce their mechanical strength under isochoric conditions.

26 To achieve this, two different hydrogels with opposite topologies were designed on the basis
27 of grafted architectures using equal amounts of water-soluble chains (poly(*N,N*-
28 dimethylacrylamide) = PDMA) and LCST polymer chains (poly(*N*-isopropylacrylamide) =
29 PNIPA). By working under isochoric conditions, with almost 85 wt% of water in the whole
30 temperature range (20 to 60 °C), we were able to clearly highlight the impact of the phase
31 transition of PNIPA on the mechanical reinforcement of the gel without any interference of
32 the volume transition. These graft hydrogels, designed with PNIPA in the backbone (GPN-D)
33 or as pendant chains (GPD-N), have been studied more specifically by tensile tests and 2D
34 neutron scattering at rest and under deformation. From these complementary techniques, we
35 show that PNIPA side-chains in GPD-N self assemble above their transition temperature into
36 a micellar network greatly interfering with the covalent PDMA frame. While the elastic
37 modulus increases reversibly more than ten times throughout the phase transition, other
38 properties like elongation at break and fracture resistance are greatly enhanced with
39 temperature. At high temperature and under extension, SANS data highlight the affine
40 deformation of PNIPA domains. By comparison, the opposite topology with PNIPA forming
41 the cross-linked backbone undergoes a similar phase separation with temperature and gives
42 rise to a bicontinuous structure that aligns under loading. The collapsed phase being
43 topologically defined as the load bearing phase, GPN-D displays remarkable fracture
44 toughening with crack bifurcation at high temperature whereas GPD-N gels fracture in a more
45 conventional way.

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47 **Keywords:** poly(*N*-isopropylacrylamide), hydrogels, nanostructure, responsive toughening,
48 crack bifurcation.

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69 **INTRODUCTION**

70 During the last decades, covalent hydrogels have received considerable attention due to their

71 important potential as biological containers or mechanical transducers. They are actually used

72 in many bio-applications¹⁻⁴ such as superabsorbents, contact lenses, drug delivery systems or
73 scaffolds for tissue engineering but they intrinsically suffer from their poor mechanical
74 strength. More recently, new challenges have emerged in this field such as the reinforcement
75 of the mechanical properties in order to elaborate smart and innovative polymer-based
76 materials. On one hand, one can find original covalent architectures like double networks,⁵
77 slide-ring gels⁶ or tetra-PEG gels,⁷ which have been shown to strongly improve the
78 mechanical properties in terms of stiffness, fracture toughness or stretchability. On the other
79 hand, a more versatile approach consists in introducing physical interactions into the covalent
80 network. In this case, the reinforcement of mechanical properties has been nicely
81 demonstrated with nanocomposite⁸ and hybrid networks,⁹ which develop reversible
82 interactions between the polymer matrix and inorganic nanofillers like clay platelets or silica
83 nanoparticles. In these examples, hybrid hydrogels showed improved mechanical response
84 with an increase of modulus, dissipation and fracture properties. This idea to mix both
85 reversible and covalent cross-links within the same structure to get tough hydrogels has been
86 extended afterwards to other physical interactions. We can mention for instance
87 hydrophobically modified hydrogels,¹⁰⁻¹² which show a large increase of their extensibility
88 and resistance to crack propagation due to a “costly” deformation of hydrophobic associations
89 under stress, or other mixed systems involving complex formation like calcium alginates
90 embedded in a cross-linked polyacrylamide network¹³ or polyampholyte hydrogels.¹⁴ With
91 these examples, it is clearly shown that the mechanical behavior of hydrogels can be
92 dramatically reinforced by introducing secondary interactions in the covalent structure, but in
93 these architectures the transient character of the physical network cannot be finely and
94 reversibly tuned using simple environmental triggers.

95 Now, from a fundamental point of view, as well as for specific applications, it could be
96 interesting to switch on/off the association process in response to environmental triggers.

97 Moreover, such systems would offer the possibility to investigate the exact contribution of
98 physical interactions to the mechanical properties of the swollen network and/or to develop
99 hydrogels with responsive toughness. In order to tackle this problem, one can immediately
100 think about *stimuli* responsive polymers that are currently used as transducers in smart
101 polymeric systems. In this regard, a physical trigger like temperature is very appealing and
102 thermo-responsive polymers obviously appear as a natural choice of building blocks to
103 prepare polymer networks with responsive mechanical properties. During the last three
104 decades, thermo-responsive polymers have been widely investigated as they provide
105 technological answers for industrial or medical applications that require materials or complex
106 fluids with improved or responsive properties above/below a given temperature. However,
107 since the pioneering work of Tanaka et al.¹⁵ describing the volume phase transition of
108 responsive hydrogels, most of academic studies on responsive polymer networks were
109 dedicated to the swelling/deswelling behavior of hydrogels in order to develop smart systems
110 able to respond reversibly under external *stimuli*. Even for hybrid systems which demonstrate
111 excellent mechanical properties, like nanocomposite gels based on poly(*N*-
112 isopropylacrylamide) (PNIPA), almost all the studies were carried out at low temperature, in
113 the swollen state. The main issue when crossing the transition threshold is that in most cases
114 the polymer network concurrently undergoes a large volume transition that dominates the
115 macroscopic properties. It is then difficult to draw a direct comparison of the mechanical
116 behavior before, during and after the transition in order to achieve a complete understanding
117 of the structure/properties relationships. In this framework, we have to mention the pioneering
118 work of Shibayama et al.¹⁶ that have reported a large increase of dynamic storage modulus in
119 PNIPA hydrogels under isochoric conditions when crossing the transition temperature.
120 However, this study was mainly focused on low deformation properties of isolated PNIPA-
121 based networks in their collapsed state with consequently a low water content. Recently,

122 Gong et al.¹⁷ have expanded this concept of gel toughening induced by phase separation using
123 polyacrylamide (PAM) gels collapsed in water/dimethylformamide mixtures. In this study,
124 the comparison between phase separated PAM gels and homogeneous samples, studied at the
125 same polymer concentration, clearly demonstrates the consequence of the formation of a
126 highly concentrated segregated phase, mostly glassy in this case, upon the improvement of the
127 mechanical behavior. Nevertheless, the polymer concentration in the gel was again very high
128 (more than 40 %) and the liquid medium was almost organic in this case. Clearly, if one
129 wants to take benefit of the phase separation in gels to improve the mechanical behavior,
130 while keeping a reasonable level of swelling, it is important to reconsider the primary
131 structure and the topology of the network. To the best of our knowledge, there are only a
132 couple of papers where the authors have tried to reduce the volume phase transition in
133 PNIPA-based hydrogels by adjusting the hydrophilic/hydrophobic balance of the network.
134 Nevertheless, while they succeeded on this point, the mechanical properties were not strongly
135 modified by the phase transition.^{18, 19}

136 By exploring original topologies of covalently cross-linked gels, we have recently
137 demonstrated²⁰ the remarkable asset represented by the phase-separation process on the
138 fracture properties of PNIPA network grafted with hydrophilic side-chains. Beyond the
139 excellent fatigue resistance, self-healing and high fracture energies, phase-separated gels
140 studied under isochoric conditions highlighted a thermo-toughening with systematic crack
141 bifurcation, unreported so far in gels. The impact of polymer topology seems to be crucial as
142 also preliminary reported on thermo-responsive grafted copolymers on self-assembling and
143 rheological properties in aqueous solutions.²¹ The main objective of the present project was to
144 investigate more systematically the structure/properties relationships of thermo-responsive
145 hydrogels under isochoric conditions and more especially on the effect of network topology.
146 To achieve this goal, the “LCST/hydrophilic” balance was set with equal amounts of LCST

147 and water-soluble polymers; namely poly(*N*-isopropylacrylamide) (PNIPA) and poly(*N,N*-
148 dimethylacrylamide) (PDMA). Working with fixed polymer concentrations and
149 PNIPA/PDMA ratio, the impact of the network topology has been addressed by preparing two
150 grafted networks designed with opposite topologies (see **Figure 1**).

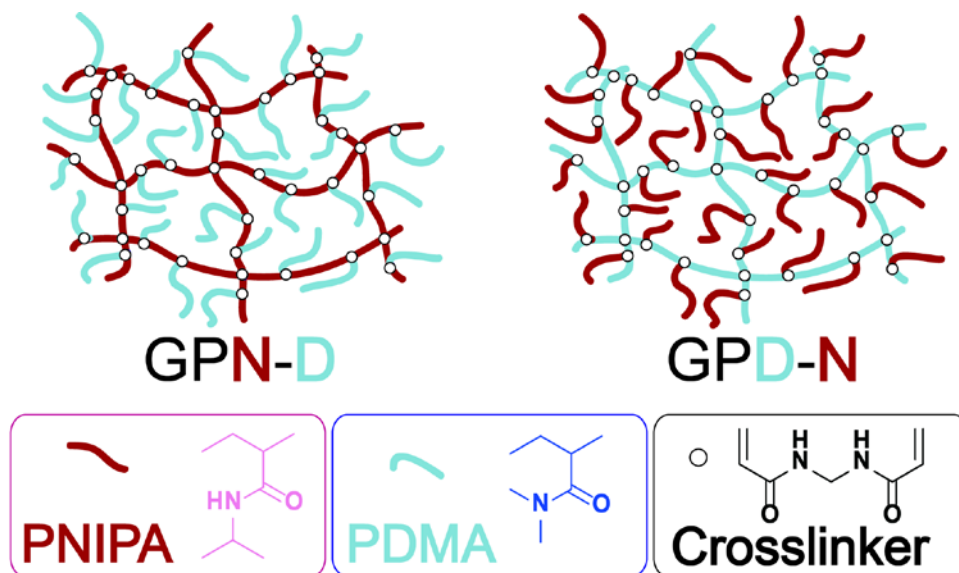


Figure 1. Schematic primary structure of thermo-responsive grafted hydrogels
GPN-D (**left**) and GPD-N (**right**) exhibiting opposite topologies.

151
152 GPD-N is a hydrophilic PDMA network (referred as GPD) grafted with thermo-responsive
153 PNIPA side-chains (denoted as -N), while GPN-D has the exact inverse topology with a
154 thermo-responsive PNIPA network (denoted as GPN) grafted with hydrophilic PDMA side-
155 chains (denoted as -D).

156 The structure and macroscopic properties of these hydrogels have been investigated as a
157 function of temperature by classical characterization methods like swelling experiments,
158 Differential Scanning Calorimetry, and rheology, and more specifically by tensile tests and
159 2D small angle neutron scattering performed at rest and under deformation. This
160 comprehensive set of analyses clearly highlights that under isochoric conditions, the phase

161 separation of PNIPA is responsible for a strong and reversible mechanical reinforcement of
162 hydrogels with a large impact of the topology.

163

164 **EXPERIMENTAL SECTION**

165 **Materials**

166 *N*-isopropylacrylamide (NIPA, Aldrich), *N,N*-dimethylacrylamide (DMA, Aldrich),
167 cysteamine hydrochloride (AET·HCl, Fluka), potassium peroxydisulfate (KPS, Aldrich),
168 acrylic acid (AA, anhydrous > 99%, Fluka), dicyclohexylcarbodiimide (DCCI, Aldrich), *N,N'*-
169 methylenebisacrylamide (MBA, Aldrich) and tetramethylethylenediamine (TEMED, Aldrich)
170 were used as received. All organic solvents were analytical grade and water was purified with
171 a Millipore system combining inverse osmosis membrane (Milli RO) and ion exchange resins
172 (Milli Q) for synthesis and purification.

173 **Synthesis of polymer precursors**

174 The synthesis of PDMA and PNIPA macromonomers was performed as previously
175 described^{20, 21} using a telomerization process with cysteamine hydrochloride followed by
176 modification of the amino end-group with acrylic acid in order to get the vinyl function. The
177 absolute characterization of macromonomers by size exclusion chromatography gives similar
178 average molar masses for the two polymers: $M_n=36$ kg/mol ($\mathcal{D}=1.4$) for PNIPA and $M_n=39$
179 kg/mol ($\mathcal{D}=1.3$) for PDMA. These polymerizable precursors are used afterwards to prepare
180 graft copolymer networks.

181 **Synthesis of hydrogels**

182 The same procedure was followed to prepare both grafted networks. Monomer, cross-linker
183 (stock solution of MBA) and macromonomer were initially dissolved in a given amount of

184 water under nitrogen bubbling; the temperature of the reactor being controlled with an ice
 185 bath. Stock solutions of KPS and TEMED were separately prepared under nitrogen
 186 atmosphere and after 30 min aliquots were added into the reaction medium. After fast mixing
 187 (2 min), the final formulation was rapidly transferred between glass plates of 2 mm width
 188 under nitrogen atmosphere and the reaction was left to proceed overnight in the fridge (4 °C).
 189 The resulting hydrogels were then cut with a die-cutter of rectangular or round shape and
 190 directly used for DSC and swelling experiments or stored into paraffin oil before mechanical
 191 testing in order to avoid any change in hydrogel composition induced by swelling or drying.
 192 For both topologies, the weight ratio “monomer/macromonomer/water” was constant, equal to
 193 1/1/10, and the molar ratio “monomer/MBA/KPS/TEMED” was set equal to 100/0.1/1/1. The
 194 details are reported in **Table 1**.

195

Table 1 Formulation of thermo-responsive grafted hydrogels								
	Monomer g	MBA mg	Macromonomer g	M_n kg/mol	\bar{D}	KPS mg	TEMED mg	Water g
GPN-D	1	1.36	1	39	1.3	23.9	10.3	10
GPD-N	1	1.56	1	36	1.4	27.3	11.7	10

196

197 **Gel composition and swelling experiments**

198 The swelling degree of the gel, Q , was defined as the weight ratio of the hydrated gel over the
 199 dried gel. Samples, originally in their preparation state ($Q_0=6$), were weighted and placed at a
 200 given temperature in a large excess of pure water. Water was changed every day and the
 201 swelling was determined with time until equilibrium (Q_e) was reached.

202 **Differential Scanning Calorimetry (DSC)**

203 The phase transition of PNIPA-based hydrogels was investigated by Differential Scanning
204 Calorimetry using a DSC Q200 from TA instrument. Gel samples (around 80 mg),
205 equilibrated with a reference filled with the same quantity of solvent, were submitted to
206 temperature cycles between 10 and 70 °C. The heating and cooling rates were fixed at 2
207 °C/min.

208 **Rheology**

209 The viscoelastic properties of hydrogels in their preparation state (discs with 4 cm diameter
210 and 2 mm thickness) were studied using a stress-controlled rheometer (AR 1000 from TA
211 Instruments) equipped with a plate/plate geometry (diameter 40 mm). The experiments were
212 performed in the linear regime and the temperature was controlled by a high power Peltier
213 system. The experimental conditions were fixed at constant frequency (1 Hz) and shear stress
214 (2 Pa). A particular care was taken to avoid the drying of the sample by using a homemade
215 cover which prevents from water evaporation during experiment. In these conditions,
216 dynamic moduli (G' and G'') were recorded between 20 and 70 °C by applying heating and
217 cooling scans of 0.5 °C/min.

218 **Large strain mechanical behavior: tensile, cycling, fracture and shape-memory** 219 **properties.**

220 Tensile tests were performed on a standard tensile Instron machine, model 5565, equipped
221 with an environmental chamber especially designed for the study and allowing for a precise
222 control of the swelling state. The device used a 10 N load cell (with a relative uncertainty of
223 0.16 % in the range from 0 to 0.1 N) and a video extensometer which follows the local
224 displacement up to 120 mm (with a relative uncertainty of 0.1 % at full scale).

225 The gel samples are cut with a punch and their final dimensions are $L_0 = 30$ mm, $w_0 = 4.9$ mm
226 and $t_0 = 2$ mm. The gauge length was taken constant ($L \cong 20$ mm). For high temperature or
227 long-term experiments, in order to prevent the samples from evaporation, tests were
228 conducted in an environmental chamber consisting of a temperature controlled paraffin oil
229 bath surrounding the sample. As a control experiment we verified the total immiscibility of
230 the paraffin oil with the gel within the temperature range investigated in this study.

231 All tensile experiments were carried out at a strain rate of 0.06 s^{-1} , which corresponds to an
232 initial velocity of 1.2 mm/s , with at least three tests per sample to check the reproducibility.
233 During the test, time (t), force (F) and displacement (L) were recorded while the nominal
234 stress ($\sigma = F/S_0$), the strain ($\varepsilon = (L - L_0)/L_0$) and stretch ratio λ ($\lambda = L/L_0$) were calculated.

235 Loading-unloading experiments were performed in order to characterize the recovery
236 processes. Measurements were carried out on hydrogels of similar size, using the same
237 conditions as described previously at $60 \text{ }^\circ\text{C}$. First, the loading process was performed with
238 given deformation and a waiting gap of 3 min was applied before unloading to initial
239 deformation. Between cycles, a waiting gap of another 3 min was applied for the recovery.

240 Fracture energy data were obtained using the single edge notch geometry. A notch of about 1
241 mm length was made in the middle of the sample strip, whose total width was 5 mm . The
242 fracture energy (G_C) was calculated using the following expression:²² $G_C = (6 \cdot W \cdot c) / \sqrt{\lambda_c}$, with c
243 the length of the initial notch, $\lambda_c = L_c/L_0$ the deformation rate at break in single edge notch
244 experiment and W the strain energy density calculated by integration of the stress versus
245 engineering strain of un-notched samples, until ε_c ($\varepsilon_c = \lambda_c - 1$).

246 The shape-memory properties were investigated by first stretching the gel to a certain nominal
247 stretch ratio at $20 \text{ }^\circ\text{C}$, and then immersing it at $60 \text{ }^\circ\text{C}$ during 3 minutes . Gel was then unloaded
248 (i.e. at zero external force) by removing the clamps. The gels were kept waiting at $60 \text{ }^\circ\text{C}$ for 6

249 minutes. Strain recovery was followed by cooling down the gel at 20 °C for another 6
250 minutes. The gel length was measured overtime.

251 **Small Angle Neutron Scattering (SANS)**

252 SANS experiments were performed at Laboratoire Léon Brillouin (CEA-Saclay, France) on
253 the PAXY spectrometer dedicated to anisotropic measurements. Two experimental
254 configurations at the sample-to-detector distance $D=2.5$ and 4.7 m, with respective incident
255 neutron wavelengths of $\lambda_0 = 4.5$ and 12 \AA , provide a scattering vector modulus
256 $q = (4\pi / \lambda_0) \sin(\theta/2)$ ranging between 3.10^{-3} and $5.10^{-1} \text{ \AA}^{-1}$ (where θ is the scattering angle).
257 For SANS experiments, gel plates of 2-mm thick were specially synthesized in D_2O to
258 intensify the scattering contrast between the polymer network and the solvent.

259 For isotropic analyses, the gel discs (diameter = 14 mm and thickness = 2 mm) punched from
260 plate samples in their preparation state were fit inside a ring spacer hermetically sandwiched
261 between two quartz slides. The gel samples were then placed in a temperature controlled
262 autosampler and let to equilibrate at least during 30 min at a given temperature (between 15
263 and 60 °C) prior to scattering experiments.

264 For anisotropic measurements performed with hydrogels under uni-axial deformation, a
265 special device has been developed as described in a previous paper (see **Figure S1** in
266 Supporting information).²³ With this setup, the hydrogel strip, immersed into the thermostated
267 chamber filled with perfluorodecalin, can be studied for hours without any risk of drying. In
268 the following, all the anisotropic scattering experiments have been carried out during at least
269 1 hour for each sample in a given deformation state. For all the analyses, the efficiency of the
270 detector cell was normalized by the intensity delivered by a pure water cell of 1-mm thickness
271 and absolute measurements of the scattering intensity $I(q)$ (cm^{-1} or 10^{-8} \AA^{-1}) were obtained
272 from the direct determination of the incident neutron flux and the cell solid angle. Finally, the

273 coherent scattering intensity of the gel was obtained after subtracting the contribution of the
274 solvent used, as well as perfluorodecalin for samples studied in the oil environment. For 2D
275 SANS experiments, the incident neutron flux recorded on a two dimensional detector built up
276 with 15500 cells of 25 mm², is directly transformed into a 2D image with a color code. After
277 sector averaging (see details in supporting information), the data have been quantitatively
278 analyzed in terms of diffusion pattern.

279

280 **RESULTS AND DISCUSSION**

281 **Transition temperature and swelling behavior**

282 As illustrated in **Figure 2a**, both gels feature an endothermic peak upon heating which is
283 related to the overall energy balance of hydrogen bonds disruption/re-formation between
284 amide groups and water molecules. The phase transition of graft hydrogels occurs more
285 readily when PNIPA is located in the backbone instead of the side-chains, as already observed
286 with linear graft copolymers,²¹ and the endothermic process starts at about 30 °C for GPN-D;
287 almost 2-3 °C below the transition of GPD-N. Upon heating, PNIPA chains have to balance
288 two opposite and competing effects: the enthalpic contribution, due to intra-molecular
289 hydrogen bonds and hydrophobic interactions that stabilizes the globular conformation, and
290 the entropic elasticity that goes against the coil-globule transition.

291

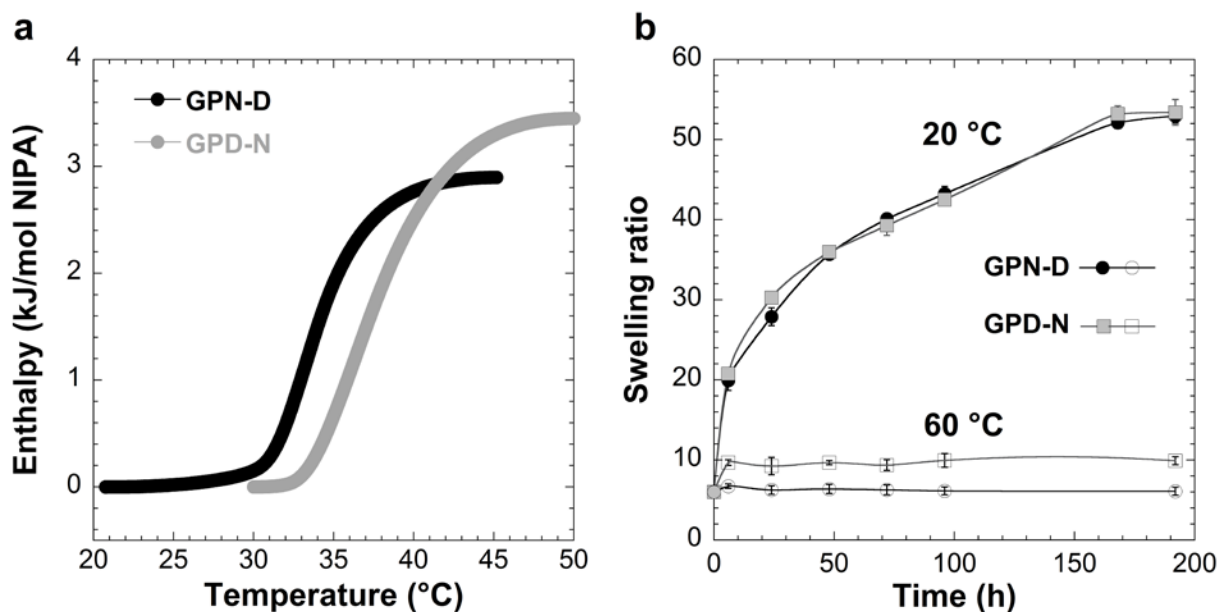


Figure 2. **a)** Thermograms of GPN-D (black) and GPD-N (grey) hydrogels (heating rate=2 °C/min). **b)** Swelling behavior of GPN-D (●○) and GPD-N (■□) hydrogels in pure water at 20 (filled symbols) and 60 °C (empty symbols).

292

293 Above the critical temperature, the polymer-polymer attractions prevail, and the resulting
 294 collapse and aggregation of macromolecular chains are generally accompanied by a large
 295 volume phase transition of the macroscopic network. Nevertheless, it is well known that the
 296 level of deswelling strongly depends on the hydrophobic/hydrophilic balance of the
 297 macromolecular structure. As shown in **Figure 2b**, the introduction of hydrophilic PDMA
 298 chains inside the copolymer network improves the macroscopic volume stability of GPD-N
 299 and GPN-D, especially at high temperature. In these experiments, the swelling properties
 300 were determined well below (20 °C) and far above (60 °C) the transition temperature
 301 previously determined by DSC. At low temperature, both hydrogels swell similarly with time
 302 and reach their equilibrium after one week at about $Q_e \approx 53$; well above the initial swelling
 303 corresponding to the preparation state ($Q_0=6$). No significant difference is observed between
 304 the two hydrogels and this is quite reasonable if we take into account that GPN-D and GPD-N

305 have been prepared with the same PNIPA, PDMA, MBA and water concentrations and if we
306 assume that at 20 °C PNIPA and PDMA have similar hydrophilicity. At high temperature (60
307 °C), the swelling at equilibrium remains a little higher than the initial swelling preparation state. The
308 higher value obtained for GPD-N ($Q_e=10$) compared to GPN-D ($Q_e=6.1$) emphasizes the impact of
309 topology on the volume transition with a lower efficiency for swelling when the LCST
310 polymer belongs to the cross-linked backbone. These swelling experiments point out that, if
311 the gel samples are isolated from water environment and kept in their preparation state, they
312 will be able to retain their initial swelling ($Q_0=6$) and consequently their initial volume over
313 the whole range of temperatures, i.e. well below and above the phase transition. Obviously,
314 these isochoric conditions obtained for GPD-N and GPN-D hydrogels with a relatively high
315 water content (almost 85 wt%) are the result of a prospective work based on various hydrogel
316 samples prepared by either changing the PNIPA/PDMA ratio or their relative concentrations
317 during the synthesis.

318

319 **Phase-separated structure at rest and linear viscoelasticity response**

320 Both hydrogels with opposite topologies, GPN-D and GPD-N, were studied by small angle
321 neutron scattering (SANS) in order to investigate the nanostructure of the polymer network as
322 a function of the temperature, first in static mode.

323 As confirmed in a previous study,²¹ the replacement of H₂O with D₂O does not induce
324 significant modification of the transition temperature in linear graft copolymers
325 PNIPA/PDMA. Therefore, all the gel samples have been studied in pure D₂O in order to
326 enhance the scattering contrast arising from the phase separation. The results are presented in

327 **Figure 3.**

328

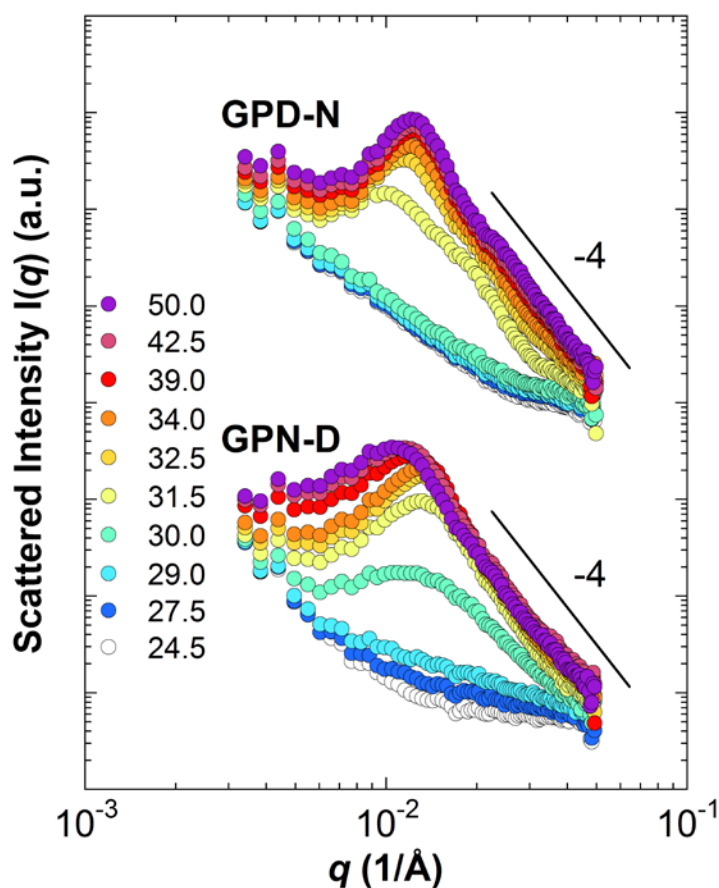


Figure 3. Scattered intensities in log-log scale of GPD-N (up) and GPN-D (down) hydrogels prepared in D₂O as a function of temperature. The intensities have been shifted for clarity.

329

330 From a general point of view, the SANS data obtained with the gels are qualitatively very
 331 similar to those already described for weakly charged PNIPA gels²⁴ and recently reported for
 332 homologous linear graft copolymers.²¹ For both hydrogels, the scattered intensity dramatically
 333 increases during the heating process on the whole q -range investigated. As observed from
 334 DSC, the transition temperature starts around 30 °C for GPN-D and above 31 °C for GPD-N
 335 in agreement with the departure of the phase transition of PNIPA chains forming the
 336 backbone or the side-chains, respectively. This phase transition of PNIPA chains induces an
 337 increase of the scattered intensity over the whole q -range with the appearance of a correlation
 338 peak at low q value, typically between $q=0.01$ and 0.02 \AA^{-1} , figuring fluctuation

339 concentrations between rich- and poor-PNIPA phases. We also observe that the correlation
 340 peak is narrower for GPD-N, compared to GPN-D, in relation with a better ordered biphasic
 341 structure when the phase transition arises from the side-chains rather than the backbone. At
 342 high temperature, the scattered intensity of both hydrogels decays in the high- q regime with
 343 the same Porod law $I(q)\sim q^{-4}$, characteristic of a sharp interface. Moreover, **Figures 3** clearly
 344 shows that the position of the correlation peak, q_{peak} , varies differently during the phase
 345 transition for both hydrogels and their respective evolutions are highlighted in **Figure 4**.

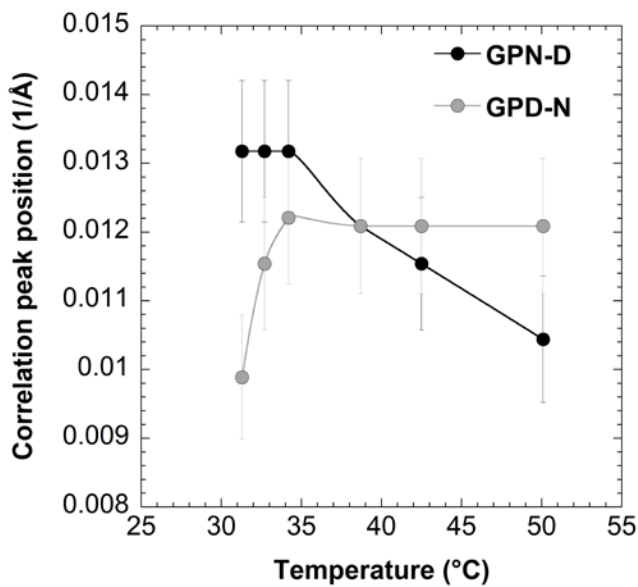


Figure 4. Evolution of the correlation peak position for both hydrogels as a function of the temperature.

346 In the case of GPN-D, the position of the correlation peak, $q_{\text{peak}}=0.0132 \text{ \AA}^{-1}$, corresponding to
 347 a characteristic distance ($d_c=2\pi/q_{\text{peak}}$) of 480 \AA , is rather constant between 31 and $34 \text{ }^\circ\text{C}$; i.e.
 348 just above the transition threshold. At higher temperatures, the position of q_{peak} subsequently
 349 shifts to lower q values, indicating larger fluctuations with further development of the
 350 microphase separation. On the other hand, the wavelength of the correlation peak in GPD-N
 351 gradually increases at the beginning of the phase separation, below $34 \text{ }^\circ\text{C}$, and finally remains
 352 constant up to $50 \text{ }^\circ\text{C}$ ($q_{\text{peak}} = 0.012 \text{ \AA}^{-1}$; $d_c \cong 520 \text{ \AA}$), indicative of a maintained microphase-
 353 separated structure for GPD-N.

354 Beside this qualitative description, a more quantitative analysis can be done by using adequate
355 models for both hydrogels. For that purpose, we start from the fact that above the transition
356 temperature SANS curves demonstrate the existence of a two-phase system with a
357 characteristic wavelength (correlation peak) and a sharp interface as deduced from the
358 asymptotic regime. Moreover, we assume here that GPD-N forms a more regular and stable
359 structure with PNIPA-rich domains dispersed into the PDMA network. This assumption,
360 which is consistent with SANS data reported for analogous graft copolymers,²¹ comes from
361 the relatively narrow mid-width of the correlation peak observed in **Figure 3** as well as the
362 presence of weak additional oscillations at 0.0226 and 0.0341 Å⁻¹. For GPD-N, we assume
363 that a fraction of PNIPA side-chains (f_{PNIPA}) self-assemble at a given temperature, above the
364 transition, into polydisperse spherical domains (with R_2 , σ , N_{agg} and ϕ_{PNIPA} : the core radius,
365 the standard deviation of the Gaussian size distribution, **the number of PNIPA chains inside**
366 **the micelle** and the volume fraction of PNIPA inside the core) which behave with a repulsive
367 hard sphere potential of radius R_{HS} . In this micellar model (core-shell with hard sphere
368 repulsions), R_{HS} is higher than R_2 in order to take into account the surrounding PDMA chains
369 (see inset in **Figure 5a**). For the microphase separation of GPN-D, the continuous phase being
370 topologically defined by the PNIPA network, we assume the formation of a bicontinuous
371 structure between PNIPA-rich domains and PDMA/water phase and apply the Teubner-Strey
372 model. This phenomenological model was originally introduced to represent the micellar
373 structure of ternary systems: water/oil/surfactant mixtures.²⁵ Since then, it is widely used to
374 describe random bicontinuous structures in microemulsions. This model assumes a pair
375 correlation function of the form:

$$376 \quad \gamma(r) = \frac{d}{2\pi r} \exp\left(-\frac{r}{\xi}\right) \sin\left(\frac{2\pi r}{d}\right) \quad \{\text{eq.1}\}$$

377 with ξ a correlation length (length beyond which correlations die out) and d the typical length
 378 scale of the structure (see inset in **Figure 5b**), characteristic of a domain size or periodicity
 379 and roughly equal to $d_c=2\pi/q_{\text{peak}}$. The analytical description of these two models is given in
 380 supporting information.

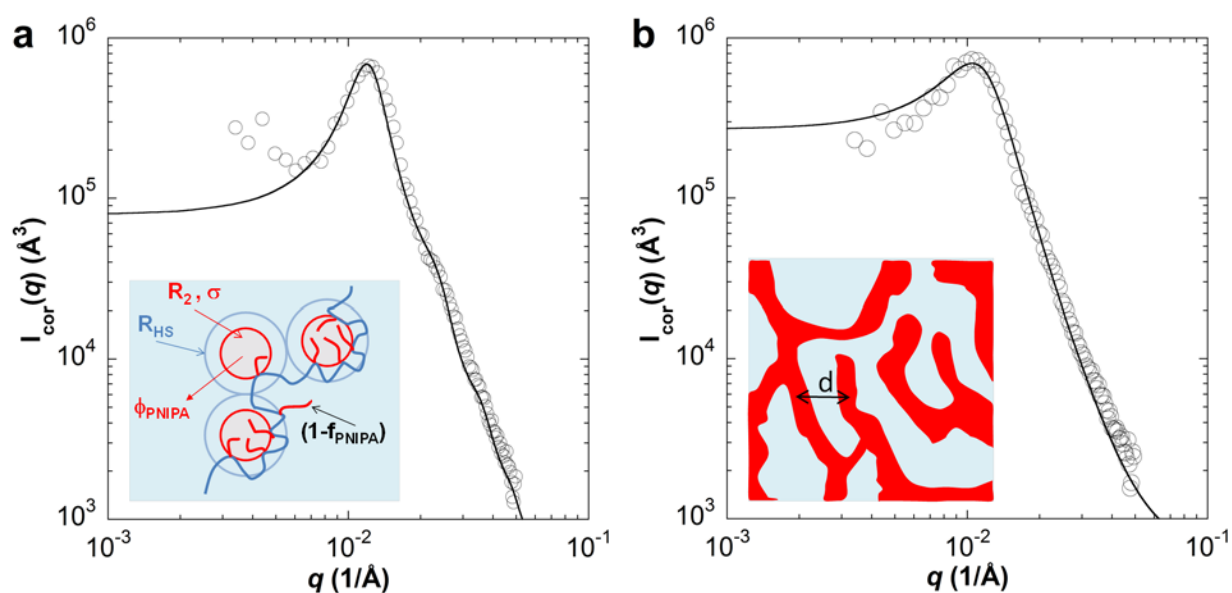


Figure 5. Normalized scattered intensity profiles of **a)** GPD-N and **b)** GPN-D at 50 °C. Solid lines represent fits according to the two applied models. The insets correspond to the models: Micellar model for GPD-N with R_2 , the radius of the micellar core, σ the standard deviation of the Gaussian size distribution, N_{agg} the number of PNIPA chains inside the micelle core, R_{HS} the hard sphere radius, ϕ_{PNIPA} , the volume fraction of PNIPA inside the core, and $(1-f_{\text{PNIPA}})$, the fraction of non aggregated PNIPA chains. Teubner-Strey model (TS) based on a bicontinuous system with average periodicity d .

381
 382 An example of model fitting is shown in **Figure 5** in the case of scattering data obtained at
 383 high temperature (50 °C) and the fitting parameters determined at all temperatures above the
 384 phase transition are reported in **Tables 2** and **3**.

385

386 In the case of GPD-N, the micellar model fits reasonably well the experimental data without
 387 any adjusting parameter in the whole q -range, except the small upturn observed at low q value
 388 in relation with interactions at larger scales. According to this model, PNIPA side-chains are
 389 assumed to self-associate into polydisperse spherical domains surrounded by a PDMA shell
 390 which characteristic size remains almost constant above T_c ($R_2 = 160 \text{ \AA}$ and $R_{HS} = 260 \text{ \AA}$), as
 391 well as its polydispersity that can be defined by $\sigma/R_2 = 0.28$. In the same temperature range,
 392 the main variations come from the increasing number of PNIPA side chains embedded into
 393 these domains ($f_{PNIPA} = 0.3$ to 0.75) and from their increasing concentration inside the
 394 micellar core ($\phi_{PNIPA} = 0.5$ to 0.77). At $50 \text{ }^\circ\text{C}$, 75 % of PNIPA chains are involved in the
 395 formation of micro-domains and their volume fraction inside the core is about 77 %. In these
 396 conditions, the level of the phase separation defined by $f_{PNIPA} \cdot \phi_{PNIPA}$ is about 0.6 and close to
 397 the values already reported for analogous graft copolymers.²¹

Table 2. Fitting parameters obtained for GPD-N at different temperatures using the core-shell model with hard sphere repulsions.

Temperature ($^\circ\text{C}$)	R_2 (\AA)	σ (\AA)	R_{HS} (\AA)	f_{PNIPA}	ϕ_{PNIPA}	ϕ_{HS}	N_{agg}
31.3	---	---	---	0.3*	0.5*	0.21*	158*
32.7	160	45	260	0.5	0.57	0.31	180
34.2	160	45	260	0.6	0.6	0.36	190
38.7	160	45	260	0.7	0.68	0.37	215
42.5	160	45	260	0.75	0.72	0.37	227
50.1	160	45	260	0.75	0.77	0.35	243

**Approximate values*

398

399 In the case of GPN-D, the Teubner-Strey model fits also quite well the experimental data over
 400 the whole q -range for all temperatures above $31 \text{ }^\circ\text{C}$. As the temperature increases, we observe
 401 that the periodicity, d , continuously increases above $34 \text{ }^\circ\text{C}$ while the correlation length, ξ ,

402 does not evidence clear variation in this range, mainly because of a larger standard deviation
403 for this parameter (**Table 3**).

Table 3. Fitting parameters obtained for GPN-D at different temperatures using the Teubner-Strey model.

Temperature (°C)	d (Å)	ξ (Å)	$\xi_{S/V}$ (Å)
31.3	440	248	202
32.7	446	278	237
34.2	452	279	245
38.7	490	277	253
42.5	521	264	262
50.1	565	261	268

404

405 According to Teubner and Strey, the correlation lengths can also be calculated from the total
406 interfacial area (S_2) as:²⁶ $\xi_{S/V} = a\phi_1\phi_2(S_2/V)$ with ϕ_2 and $\phi_1 = 1 - \phi_2$, the volume fraction of
407 each phase (here 2 refers to the PNIPA-rich phase); S/V , the total specific area of the internal
408 interface (see the details in supporting information) and a , a numerical value taken equal to
409 7.16 used for a large variety of bicontinuous emulsions.²⁶ As shown in **Table 3**, these
410 calculated values ($\xi_{S/V}$) are similar in magnitude from those extracted from the TS model but
411 they display a regular **increase** with increasing temperature, underlining the increasing size of
412 PNIPA domains in GPN-D gels contrary to GPD-N where their size remain constant .

413 Such a drastic change of the gel structure induced by the phase-separation of PNIPA is
414 expected to drive concurrently large modifications of the macroscopic properties. The absence
415 of volume transition when heating the gels from their preparation state fully satisfied the
416 isochoric conditions and a first investigation of the linear viscoelastic properties was carried
417 out by dynamic rheology. The results reported in **Figure 6** with both gel samples, demonstrate
418 that the collapse of PNIPA segments that occurs at the molecular level is capable of inducing
419 large modifications of the elastic properties, even in the absence of volume transition. When

420 PNIPA chains are under the coil state, for $T \ll T_c$, the shear elastic moduli are slightly the
 421 same for both topologies as expected from their similar syntheses, grafted architectures and
 422 solvent affinity. Interestingly, for $T \gg T_c$, although the micro-phase separated structure varies
 423 with the gel topology, GPN-D and GPD-N continue to display very similar viscoelastic
 424 responses with temperature. At 60 °C, viscoelastic behaviors (G' and G'') are almost similar
 425 for the two hydrogels with a relatively low contribution of viscoelastic losses ($G''/G' \cong 0.1$).

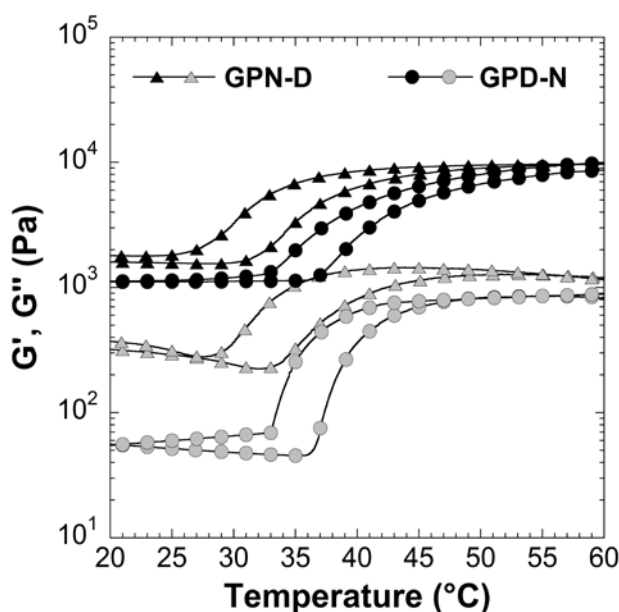


Figure 6. Temperature dependence of viscoelastic properties at 1 Hz of GPD-N (circles) and GPN-D (triangles) hydrogels at preparation state with a heating/cooling rate of 0.5 °C/min. Black symbols stand for G' and grey symbols for G'' .

426 Note that the variation of the viscoelastic properties is totally reversible and the same values
 427 of G' , around 1 and 10 kPa, are obtained at low and high temperatures respectively even after
 428 several heating/cooling cycles. This result is in good agreement with the fact that the gel does
 429 not change its volume during the phase transition as water would be irreversibly expelled
 430 from the rheometer during heating in the opposite case. On the other hand, depending of the
 431 heating/cooling rate, a strong symmetric hysteresis can be observed between heating and

432 cooling cycles. This hysteresis can be highly reduced from almost $\Delta T=30$ to $5\text{ }^{\circ}\text{C}$ by simply
433 decreasing the scanning rate respectively from 10 to $0.5\text{ }^{\circ}\text{C}/\text{min}$ (see **Figure S2** in Supporting
434 information). Thermal hysteresis has been widely reported in the literature from DSC
435 experiments performed on PNIPA gels.²⁷ It is generally observed that the rate of cooling
436 strongly impacts the transition temperature due to the slow relaxation of the frozen network.
437 On the other hand the rate of heating is expected to have little influence on the onset of the
438 phase separation since the segregation between PNIPA-rich and water-rich regions is very
439 prompt compared to the characteristic times involved in the reorganization of the polymer-
440 rich and solvent-rich interfaces featured by a diffusion coefficient typical of the glassy state.²⁷
441 Here, as shown in **Figure S2**, the hysteresis signature is very symmetric on both sides of the
442 transition temperature determined by DSC. The main reason for this artifact can be related to
443 the relatively high gap used with the plate/plate geometry (2 mm for gels instead of $56\text{ }\mu\text{m}$ for
444 solutions with cone/plate geometry) that does not allow reaching instantaneous thermal
445 equilibrium in the whole discoid sample.

446
447 **Large strain behavior: structure and mechanical properties.**

448
449 SANS is widely used to analyze the structure of polymer networks under deformation as
450 thermal fluctuations of polymer chains and more especially frozen inhomogeneities give rise
451 to very informative anisotropic patterns.^{25, 28-31} Working with hydrogels, deformation can be
452 induced by swelling experiments which emphasize their structural inhomogeneities or more
453 simply by mechanical stretching. Here, the complex spatial distribution of strains and stresses
454 in deformed hydrogels is a crucial issue for understanding the reinforcement mechanisms.^{23, 32}
455 As the dynamics of PNIPA-rich domains greatly slow down at high temperature forming
456 some quenched heterogeneities, these scatterers can be used as probes to follow their average
457 displacement under mechanical deformation and to investigate the local nanostructure of
458 thermo-responsive hydrogels. For that purpose, a series of SANS experiments have been

459 carried out on GPN-D and GPD-N hydrogels, under incremental elongation ratio, from $\lambda = 1$
460 to 3-5 at 60 °C, i.e. well above the phase transition temperature. The 2D SANS spectra are
461 reported in **Figures 7a** and **7d**, for GPD-N and GPN-D respectively, and for comparison, their
462 corresponding monotonic tensile behavior after thermal equilibrium at 20 and 60 °C are
463 shown in **Figure 7b**. At 20 °C, below the phase transition, both topologies demonstrate the
464 classical response of a polymer network that is dominated by entropic elasticity, with an
465 initial tensile modulus around 4 kPa in agreement with dynamic experiments. On the other
466 hand, at 60 °C, well above the transition temperature, the stress-strain mechanical response
467 highlights the formation of PNIPA-rich domains that strongly enhances the stiffness of the
468 mechanical response (i.e. the initial modulus is increased by one order of magnitude),
469 independently of the gels topologies. Interestingly, both stiffness and elongation at break are
470 simultaneously enhanced. Thus work of extension, defined by the area under the tensile curve
471 increased from 11 to 149 kJ.m⁻³ and 30 to 288 kJ.m⁻³, respectively for GPD-N and GPN-D.
472 From these results, thermo-toughening is clearly demonstrated and the GPN-D topology
473 appears to be more efficient. Note that as previously observed with the dynamic analysis
474 performed within the linear regime, the large strain behaviors of both topologies are
475 surprisingly perfectly superimposed.

476 From a structural point of view (**Figures 7a** and **7d**), both unstrained samples ($\lambda = 1$), GPN-D
477 and GPD-N, display at 60 °C an isotropic pattern with a circular diffraction ring
478 corresponding to the correlation peak of the structure factor discussed in the previous section
479 (**Figure 3**). At intermediate deformation ($\lambda = 1.75$), the pattern of GPD-N changes to a rather
480 uniform elliptically shaped correlation band qualitatively showing that PNIPA microdomains
481 move apart in the stretching direction while they get closer in the perpendicular direction due
482 to the transverse compression.

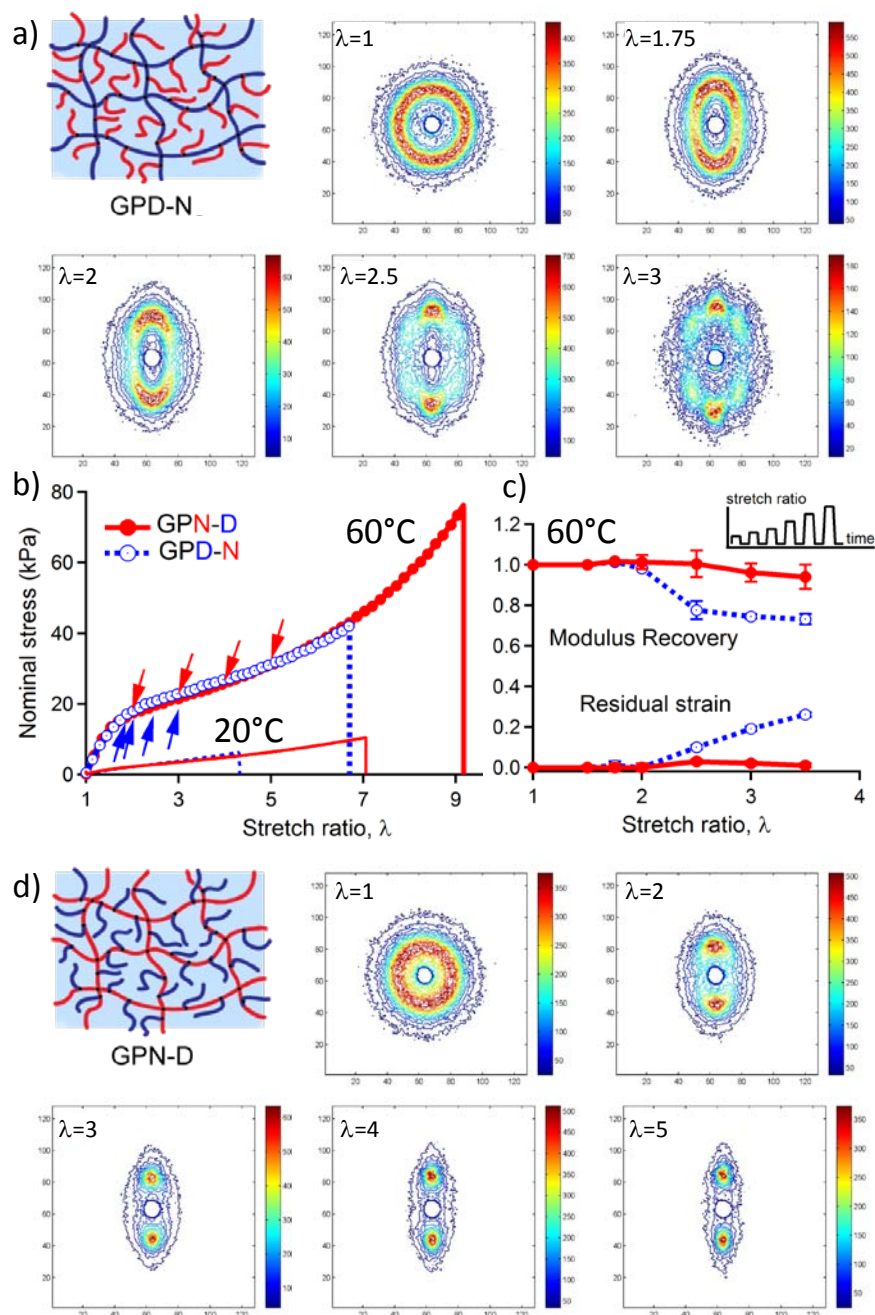


Figure 7. Structure and properties of GPD-N and GPN-D under deformation. **a)** and **d)**

Primary structure of GPD-N and GPN-D, respectively, along with their iso-intensity SANS patterns obtained after a step-by-step loading at 60 °C. The direction of the uni-axial deformation is along the horizontal axis. **b)** Uni-axial tensile stress-strain curves of GPN-D (red continuous line) and GPD-N (blue dashed line) hydrogels at 20 and 60 °C.

The arrows refer to the elongation ratio studied by SANS. **c)** Modulus recovery and

residual strain at 60 °C for GPN-D (red **continuous line**) and GPD-N (blue **dashed line**)
after a series of loading/unloading steps up to different maximal stretch ratio.

484

485 At higher deformation the 2D spectrum turns to a non-uniform azimuthal intensity
486 distribution, effectively showing up diffraction arcs and then spots for $\lambda \geq 2$ in the
487 perpendicular direction. At a macroscopic scale (**Figure 7c**) this threshold value of applied
488 stretch ratio corresponds to the initiation of irreversible processes, suggesting damage
489 phenomenon within the network. Indeed, for $\lambda > 2$ the mechanical behavior of GPD-N exhibits
490 a loss in modulus recovery with residual strain, at least within the time of experiment. At very
491 high deformation ($\lambda = 2.5-3$), four additional spots are clearly observed for azimuthal angles μ
492 around 60, 120, 240 and 300°; μ being defined as $\mu=0^\circ$ in the stretching direction. These four
493 new spots highlight some reorganization within the microstructure which can have different
494 origins. For instance, this has been observed with micellar gels of triblock copolymers by
495 Reynders and co-workers.³³ Depending on the block composition and solvent concentration,
496 they show that under stretching the initial hexagonal arrangement of polystyrene (PS) micellar
497 cores undergo either affine deformation or improved angular as well as spatial order,
498 indicating the formation of well defined layers of regularly spaced PS domains in the
499 perpendicular direction of stretching. Diffraction patterns combining these two extreme cases
500 have been obtained with different micellar systems. It is worth noting that the development of
501 a similar 4 spot-patterns has been reported under stretching with a lot of hybrid materials like
502 silica particles in dry polyacrylate latex films,³⁴ polyisoprene/silica³⁵ and nanocomposite or
503 nano-hybrid hydrogels.^{22, 32, 36} This morphological modification observed under stretching
504 originates from the transverse compression that pushes the particles towards each other and
505 from the localized shear displacements of these particles avoiding each other when they are in
506 close contact. The main difference with hydrogels reinforced with inorganic nanoparticles is

507 that in our system the microdomains are deformable under stretching. In this case, another
508 possible scenario would be that at low relative deformation (below $\lambda=2$) the spherical
509 microdomains are distorted into prolate ellipsoid with their major axis along the equatorial
510 direction. In this case the PNIPA-rich domains become closer in the perpendicular direction
511 and farther along the deformation axis. At higher level of deformation, above some critical
512 stress, the prolate microdomain becomes unstable and undergoes disruption processes. In this
513 case, the formation of additional scatterers would be responsible for the emergence of new
514 diffraction spots.

515 By comparison, the isotropic circular pattern of GPN-D rapidly turns into an elliptically
516 shaped correlation band with a non-uniform azimuthal intensity distribution with two
517 diffraction spots above $\lambda =2$ in the perpendicular direction. Note that in this case, the behavior
518 is highly recoverable, up to $\lambda=4$: the GPN-D topology is capable to maintain 94 % of its
519 initial modulus and residual strain is negligible after 3 minutes at rest. At higher deformation
520 ($\lambda=3-5$), the anisotropy becomes even more important with the same spots always centered at
521 about the same position. Qualitatively, this means that the inter-domains distance in GPN-D is
522 more or less preserved in the perpendicular direction during the process of domain
523 deformation upon stretching. Taking into account the values of q_{peak} determined in the
524 parallel- and perpendicular-directions at each deformation, the ratio $R = q_{\text{peak},\lambda=1}/q_{\text{peak},\lambda}$ allows
525 to correlate the local displacement with the macroscopic deformation of the gel ($\lambda =L/L_0$). As
526 shown in **Figure 8**, the local deformation in GPD-N is rather affine with the macroscopic
527 deformation in both parallel (//) and perpendicular (\perp) directions, at least up to $\lambda =2$ along the
528 deformation axis and up to $\lambda =3$, the largest deformation applied to this sample, in the
529 perpendicular direction.

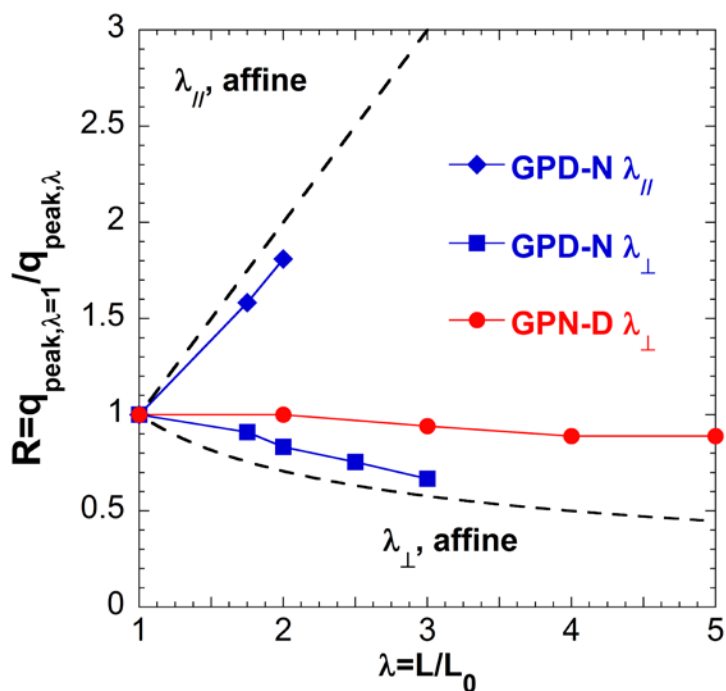


Figure 8.

Comparison between the macroscopic affine deformation of hydrogel samples, along parallel- ($//$) and perpendicular-axis (\perp), and the local deformation probed through the scattering peak ratio: $R = q_{\text{peak},\lambda=1} / q_{\text{peak},\lambda}$

530 By contrast, the behavior of GPN-D is not affine at all as the correlation peak rapidly
 531 disappears in the parallel direction for $\lambda < 2$, as the inter-domain distance increases much more
 532 rapidly along the x-axis, while it remains almost constant in the transverse direction. Note that
 533 these very different behaviors between the two networks an important clue supporting the
 534 idea that the two hydrogels self-associate differently, even if they have the same average
 535 composition and share some close properties at low deformation.

536 In order to get additional information in the low intensity region, and more especially in the
 537 high q -range, the SANS data obtained with two neutron configurations were radially averaged
 538 along a given direction within a rectangular sector of axis parallel ($//$) or perpendicular (\perp),
 539 respectively, to the deformation axis. The corresponding intensities $I_{//}(q)$ and $I_{\perp}(q)$ are plotted
 540 respectively in **Figure 9** and **Figure S5**.

541 In the case of GPN-D (**Figures 9a** and **S5a**), the whole scattering spectra determined in the
 542 perpendicular direction remains almost unaffected by the deformation. The main difference
 543 arises at low q values where we simply observe a small decrease of the osmotic

544 compressibility that can be correlated to increasing repulsions between microdomains
 545 becoming closer. At large q values, the same interfaces are probed whatever the deformation
 546 is. The situation is very different in the stretching direction ($//$) as the Porod plots show that
 547 the q^{-4} dependence is shifted towards low q values with increasing deformation and that
 548 additional $q^{-\alpha}$ dependences appear at large q values with α ranging between 2 and 1;
 549 exponents corresponding to Gaussian or extended chains (see **Figure S6**). As this
 550 phenomenon occurs in the softening zone of the mechanical properties (i.e., above $\lambda=2$) it
 551 could be attributed to the stretching and unfolding of PNIPA chains within the polymer-rich
 552 phase as recently evoked by Sato et al. for hydrogels containing phase-separated polymer
 553 domains.¹⁷ A similar scenario with domain distortion and splitting, initially proposed for
 554 GPD-N, can also be considered for GPN-D but as PNIPA chains now form the cross-linked
 555 backbone of the network, the deformation of bicontinuous microdomains should proceed
 556 differently.

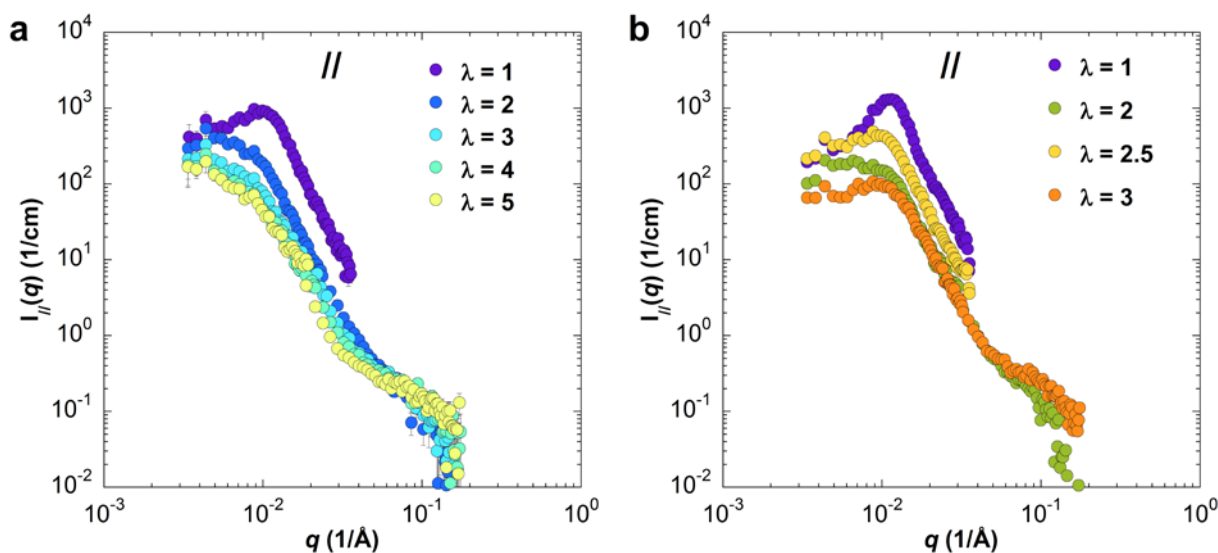


Figure 9. Scattered intensity profiles at 60 °C of hydrogels under uni-axial deformation. **a)** GPN-D (from $\lambda = 1$ to $\lambda = 5$) and **b)** GPD-N (from $\lambda = 1$ to $\lambda = 3$). The data were obtained from 2D-SANS after sector averaging in the parallel ($//$) direction of the deformation axis.

557

558 To support this discussion we can start from the theoretical works of Polotsky et al.³⁷ which
559 describe the mechanical unfolding of a homopolymer globule. According to their self-
560 consistent-field approach, the transition from the initial globular state to an extended
561 conformation, above a critical deformation rate, is accompanied by an abrupt unfolding of the
562 depleted globular head and a corresponding jump-wise drop in the intra-chain tension. It is
563 worth noting that a similar macroscopic behavior has also been predicted a long time ago by
564 Dušek and Patterson with stretched hydrogels in poor-solvent conditions.³⁸ If we transpose
565 this concept of conformational transition to GPN-D, we can assume 1) that under weak
566 deformation the microdomains will be gently elongated in the direction of stretching and
567 compressed in the transverse direction and 2) that rapidly, above a given deformation
568 threshold, domains will disrupt and “split” into dense regions connected by extended chains.
569 This unfolding process with the formation of domains with stretched PNIPA chains can be
570 supported by the asymptotic behavior observed in the parallel-direction as shown in **Figure**
571 **9a** and **Figure S6**. By comparison with the predictions of Polotsky et al.³⁷ the unfolding
572 transition of PNIPA does not give rise to an abrupt drop of the internal stress of the network
573 but the softening observed beyond $\lambda = 2$ in **Figure 7b** could be a signature of such process.

574 In the case of GPD-N (**Figure 9b** and **S5b**), the asymptotic behavior at large q has been
575 studied only for two stretch ratios and it is more difficult to conclude with this system.
576 Nevertheless we can see at $\lambda = 3$ some Porod’s law with $\alpha \cong 2$ in agreement with a similar
577 process of chain extension upon stretching.

578

579 *Impact of network topology on fracture behavior.*

580 With the micro-phase separation of PNIPA segments into polymer-rich domains, both
581 hydrogels demonstrate qualitatively a large improvement of fracture resistance upon heating

582 beyond T_c (see **Figure 7b**). By introducing an initial edge notch on the gel, a clear distinction
583 between toughening mechanisms at play in GPD-N and GPN-D topologies can be drawn. As
584 shown in **Figure 10a**, the fracture resistance is greatly improved at 60 °C for both
585 microphase-separated gels, but the thermo-toughening mechanisms operates differently for
586 the two opposite gel topologies; the GPN-D structure with PNIPA forming the cross-linked
587 network being more efficient and exhibiting a systematic crack bifurcation although the crack
588 proceeds straightly in GPD-N. In the collapsed network GPN-D topology, the fibrillar
589 collapsed PNIPA-rich domains (i.e. bearing the chemical cross-links), as schematically shown
590 in **Figure 10b**, orient in the stretching direction especially in the vicinity of the crack tip
591 where strain amplification is high. The structure is then similar to a laminate material where
592 tough PNIPA-rich fibres are alternating with the PDMA swollen phase. As SANS
593 experiments show that the average distance between PNIPA domains remains mostly
594 unchanged in the transverse direction, this suggests that PNIPA-rich domains become thicker
595 upon stretching. In these conditions, the crack will propagate more easily through the PDMA
596 phase (i.e. in the direction of stretching) and then a crack deviation perpendicularly to the
597 initial notch direction is induced. This mode of crack propagation involving deflection of the
598 crack propagation direction is usually described as 'knotty tearing' and classically expected in
599 natural rubbers,³⁹ but not in gels so far. By analogy with the natural rubber strain-
600 crystallization, crack bifurcation in GPN-D gels may be directly related to the collapsed
601 network topology. As reported previously,²⁰ there is a strong impact of the primary structure
602 of GPN-D networks as the average molar mass of PNIPA sequences between PDMA side-
603 chains, as well as the weight fraction of both polymers, control the characteristic length-scale
604 of the phase separated morphology as the crack bifurcation process.

605 By comparison, the micellar morphology obtained with GPD-N (see **Figure 10b**) improves
606 the overall mechanical properties by the introduction of physical cross-links at high

607 temperature but in this case crack proceeds straightly within the gel. The crack propagation
 608 mechanisms of GPN-D and GPD-N are illustrated in **Figure S7** (see Supporting information)
 609 with pictures taken at various strain levels.

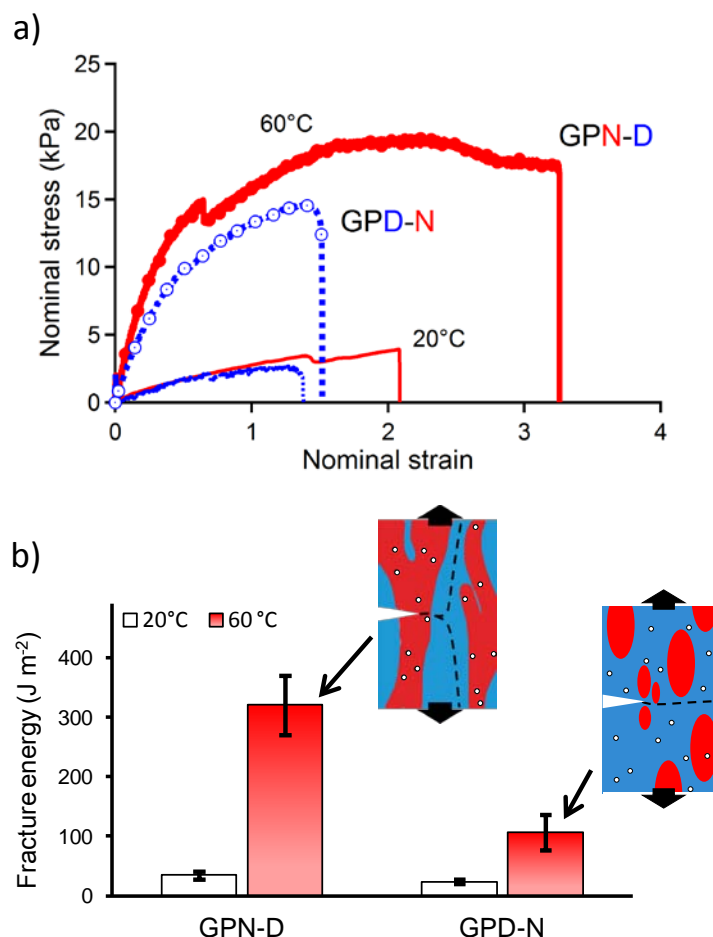


Figure 10. a) Fracture behavior of GPN-D (red **continuous line**) and GPD-N (blue **dashed line**) notched specimens at 20 and 60 °C and b) Fracture energies obtained at 20 and 60 °C.

The scheme is a view of the reinforcing mechanisms at microscale. Dotted lines refer to damage mechanisms and define weak interfaces.

610
 611 **Other route, other history.**

612 In previous experiments, 2D SANS were performed under deformation at 60 °C, starting from
 613 an undeformed microphase separated sample. Interestingly, complementary information can

614 be obtained by changing the route, i.e. starting at 20 °C with a deformed sample (here $\lambda=2$)
 615 and then increasing the temperature to initiate the PNIPA phase separation in the deformed
 616 state. The 2D SANS spectra obtained from these two routes are compared in **Figures 11a** and
 617 **11b**. In the case of GPD-N, deformed below the phase transition, and heated up after
 618 deformation, the SANS pattern is almost isotropic with only a very weak prolate distortion of
 619 5 % in the perpendicular direction (**Figure 11a**). This result highlights that even in a stretched
 620 PDMA network, the PNIPA side chains self-associate with their surrounding neighbors
 621 forming isotropically distributed domains in good agreement with the micellar model and
 622 rather independently of the PDMA network stretching.

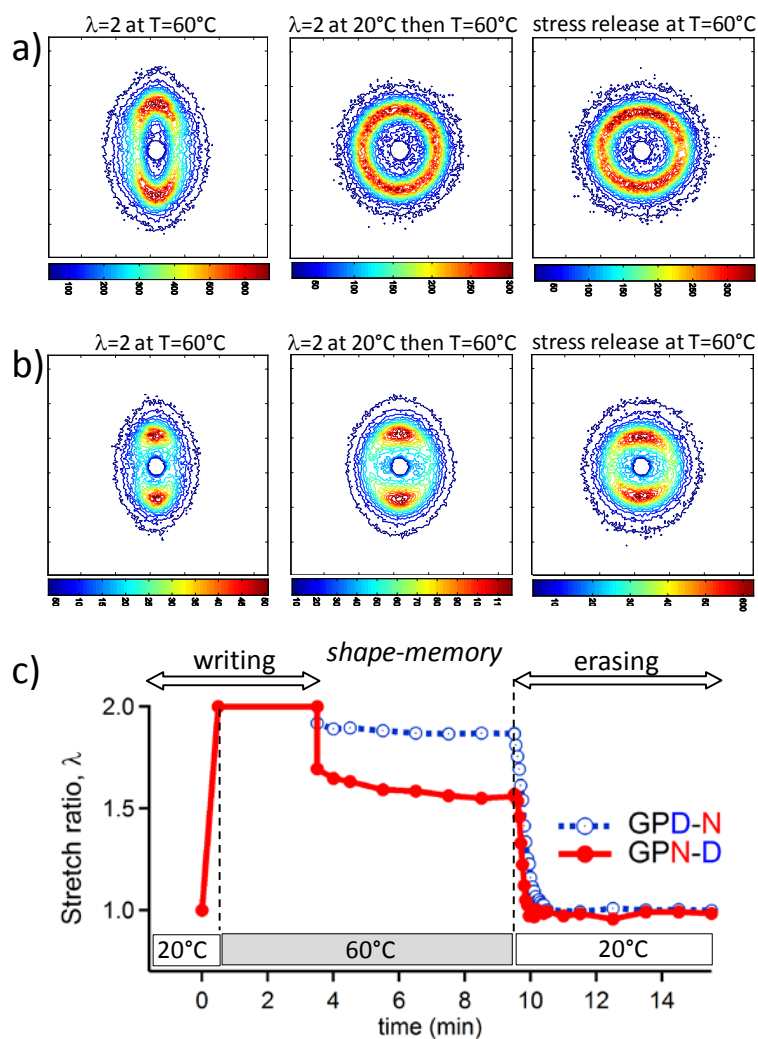


Figure 11. Shape memory behaviors of gels. Two-dimensional SANS images of a step-by-

step loading/heating process of **a)** GPD-N and **b)** GPN-D. The gels are heated at 60 °C prior to be deformed at $\lambda=2$ (left). The gels, initially deformed at $\lambda=2$ at 20 °C, are then heated at 60 °C (center). Then the stress of gels in the center is released at 60 °C (right): note that in these conditions the gels keep a residual strain to avoid buckling of the sample. The direction of the uni-axial deformation is along the horizontal axis. **c)** Shape recovery curves GPD-N (red **continuous line**) and GPN-D (blue **dashed line**) with time. First, the gels were stretched to $\lambda=2$ at 20 °C prior to be heated in oil at 60 °C to perform the "writing" procedure. After keeping $\lambda=2$ for 3 min at 60 °C, stress was released and the residual stretched ratio was measured over time. Finally, the gels were cooled at 20 °C to fulfill the "erasing" process.

623

624 The formation of concentrated aggregates, exhibiting slow dynamics as described previously,
625 is also responsible for the shape memory effect as illustrated in **Figure 11c**. After "writing" a
626 stretch level of $\lambda=2$ at 60 °C during 3 min, stress was removed with only a weak retraction of
627 the structure. The stretch ratio is maintained overtime without significant relaxation
628 processes. This result suggests that internal stresses due to the extension of the PDMA
629 network are compensated by the formation of collapsed PNIPA microdomains that play the
630 role of thermo-triggered cross-links. The dynamics of these physical cross-links is very slow
631 down, otherwise the relaxation would have been much more important.

632 In the case of GPN-D, the difference between the two routes appears less pronounced as now
633 the PNIPA backbone is topologically defined as the load bearing phase (**Figure 11b**). At 60
634 °C and $\lambda=2$, the two patterns are anisotropic. At macroscopic scale, as illustrated in **Figure**
635 **11c**, after removing the stress, the gel maintains its stretch level with a partial strain recovery
636 (around 30%) and also slight relaxation processes..

637 This set of structural and mechanical analyzes clearly demonstrates that different
638 morphologies with different mechanical properties can be obtained with the same topology
639 according to the route of self-assembling. If the structure of PNIPA-rich domains is clearly

640 the central feature of the thermo-toughening mechanism, the dynamic properties of segregated
641 PNIPA chains is an important characteristic to consider. According to the results obtained in
642 this work it appears that phase separated PNIPA domains cannot be considered as frozen with
643 the meaning of glassy (arrested phase) as they are able to respond elastically but the dynamics
644 of exchange is intrinsically very slow and is responsible for the apparent stability of PNIPA-
645 rich domains.

646

647 **CONCLUSION**

648 The original aim of this work was to investigate the effect of topology on thermo-toughening.
649 Our original gel designs combine hydrophilic and LCST polymer chains within the same
650 hydrogel in order to get thermo-responsive mechanical properties whilst avoiding the issue of
651 the volume phase transition. This challenge was achieved successfully by playing with the
652 network architecture and testing opposite topologies. Indeed, we show that graft hydrogels
653 designed with the same PDMA/PNIPA composition (50/50), are able to develop responsive
654 and reversible toughness with large enhancement of these properties by working under
655 isochoric conditions. Nevertheless, the primary architecture is crucial, depending whether or
656 not the responsive polymer belongs to the backbone.

657 When hydrogels are designed with a thermo-responsive PNIPA backbone, the phase transition
658 occurs promptly above the critical temperature but PDMA side-chains allow to stabilize the
659 phase separation at a microscopic level and to maintain a relative high level of swelling.
660 Indeed, from DSC and SANS studies, GPN-D has been shown to respond with temperature
661 with the formation of a bicontinuous structure which length scale grows with increasing
662 temperature while remaining at a microscopic level. This gel shows remarkable responsive
663 toughness with temperature and SANS clearly highlights that the distortion of the local

664 structure is non-affine with the network deformation. The responsive toughening of
665 mechanical properties above the transition temperature can be attributed to the formation of a
666 continuous rich-PNIPA phase that greatly enhances the energy dissipation within the hydrogel
667 with in particular some original mechanism of crack bifurcation. This thermo-responsive
668 enhancement of the mechanical properties can be compared with recent results reported by
669 Gong et al.¹⁷ in the case of polyacrylamide gels where toughening was induced by phase
670 separation in water/organic solvent mixtures. Taking into account the literature background
671 related to the stretching of single globular chain or polymer network in bad solvent, we
672 propose that under stretching the PNIPA domains start to deform and give rise to yielding
673 with chain extension and unfolding. On the contrary, when hydrogels are designed with
674 PNIPA side-chains, these latter self-assemble above the transition temperature forming a
675 micellar network with a fairly high polymer concentration inside the core (~ 75%). The
676 transition temperature is a little bit higher for these systems because they are attached to the
677 PDMA backbone with no direct neighbors. The very low dissociation rate of PNIPA chains
678 from aggregates at high temperature is responsible for their frozen-like morphologies. This
679 aspect was highlighted macroscopically with shape memory experiments, and locally as well
680 with SANS patterns obtained by following different routes. Even if the covalent cross-links
681 which belong to the PDMA frame are located outside the PNIPA cores, the rheology and
682 tensile tests suggest a strong coupling between covalent and physical cross-links as the elastic
683 modulus is very close for both GPD-N and GPN-D. Nevertheless, fracture experiments
684 performed on notched samples have shown that the micellar organization of PNIPA domains
685 in GPD-N is less effective to reduce the fracture propagation. The micellar morphology of
686 GPD-N displays common features with hybrid hydrogels which are prepared by dispersing
687 silica nanoparticles in a PDMA network for similar polymer composition.²³ Indeed, in this
688 case, the reinforcement arises from a strong coupling between the covalent PDMA network

689 and the specific interactions taking place between silica surfaces and PDMA chains. One of
690 the main differences is that nanoparticles are non-deformable, while in GPD-N gels, PNIPA
691 spherical domains can be distorted in the direction of deformation and split for large
692 deformation.

693 The main conclusion of this work is that the LCST-type phase transition can be readily used
694 as a trigger to strongly and reversibly enhance the mechanical properties of hydrogels; their
695 swelling ability being retained at high temperature by the hydrophilic counterpart. The phase
696 separated structure is strongly correlated to the initial network architecture and the
697 introduction of PNIPA within the backbone provides the best coupling between physical and
698 covalent cross-links. Not only the structure but also the scale of the phase separation is a
699 critical parameter to control the mechanical properties. These considerations pave the way for
700 new ideas concerning the structure/properties relationships in responsive toughening of
701 hydrogels with applications in biomedicine and other industrial fields.

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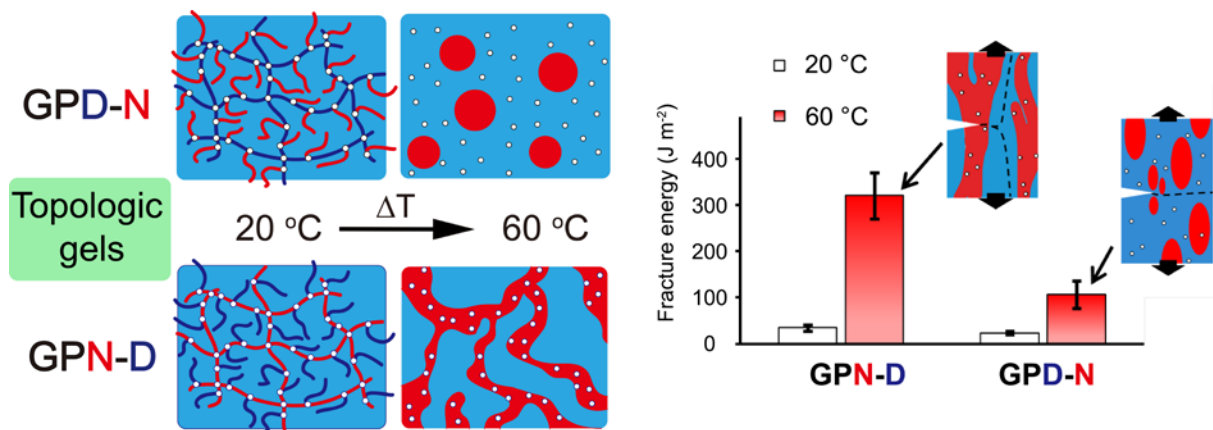
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818 Thermo-responsive Toughening in LCST-type Hydrogels with Opposite Topology: From
819 Structure to Fracture Properties.

820 Hui Guo, Cécile Mussault, Annie Brûlet, Alba Marcellan,* Dominique Hourdet,* and Nicolas

821 Sanson*

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Thermo-Toughening of Hydrogels under Isochoric Condition

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