

Supporting Information

Structure and dynamics of a temperature sensitive hydrogel

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S11. Mechanical properties of TriPIC polymer solution

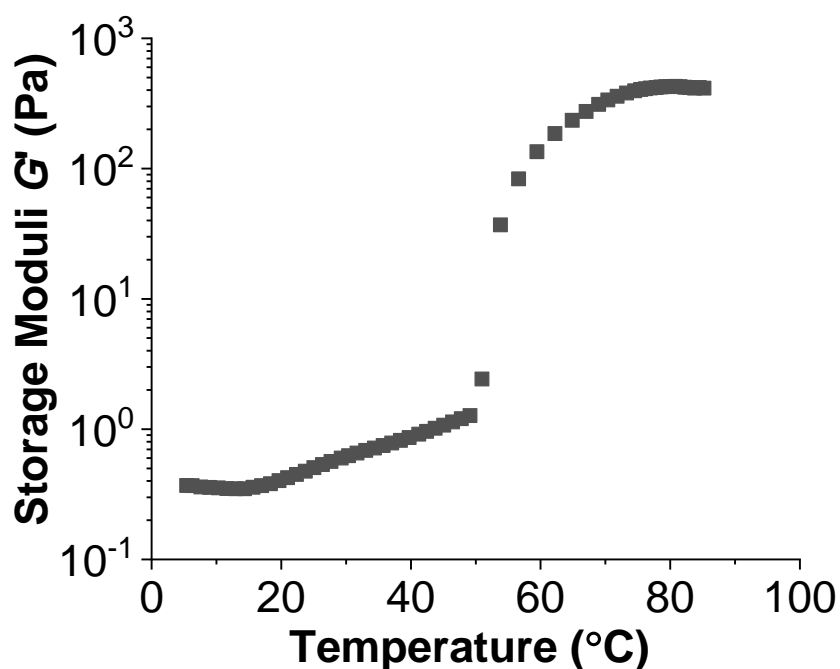


Figure S1. Storage modulus as a function of temperature for the TriPIC polymer sample. The sample ($c = 4.0 \text{ g L}^{-1}$) was loaded at $T = 5 \text{ }^\circ\text{C}$ and heated to $T = 95 \text{ }^\circ\text{C}$ at a rate of $2 \text{ }^\circ\text{C min}^{-1}$, during which the storage modulus G' was measured in oscillation with amplitude $\gamma = 0.04$ and frequency $\omega = 1.0 \text{ Hz}$. The gelation temperature value was determined by the onset of the increase of the storage modulus G' .

The mechanical properties of the TriPIC polymer solution were determined according to reference¹. Figure S1 shows the storage modulus as a function of temperature, and its sharp increase indicates a transformation from the liquid to the gel state.

S12. Solvent accessibility at different temperatures

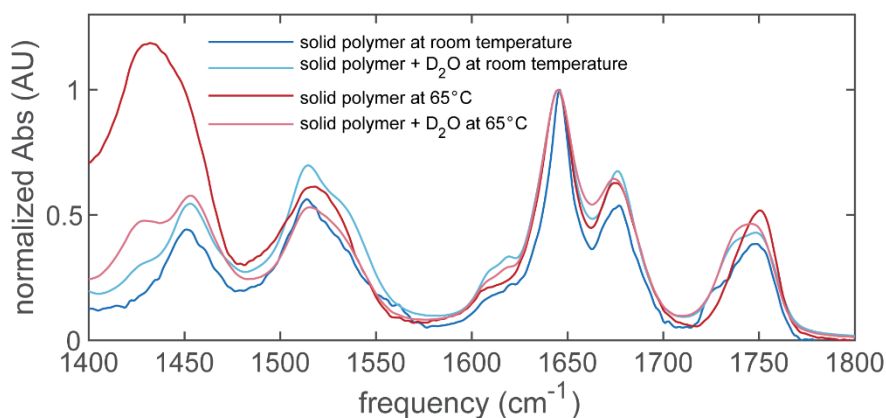


Figure S12. ATR spectra at room temperature of solid TriPIC polymer (dark blue) and solid TriPIC polymer with a drop of D₂O (light blue), and ATR spectra at 65°C of solid TriPIC polymer (red) and solid TriPIC polymer with a drop of D₂O (pink).

To investigate whether the solvent accessibility of the TriPIC polymer is temperature-dependent, we performed H/D exchange experiments at a temperature above gelation temperature ($T_{\text{gel}} = 50^\circ\text{C}$), at 65°C. Figure S12 shows the results of this experiment. In this case, we start the experiment with a solid TriPIC polymer sample. The solid sample will be completely protonated since the molecule was synthesized under protonated conditions. In both spectra of the solid sample, at room temperature and at 65°C, we observe the amide II band and no amide II' band. After a drop of D₂O has been added to the solid sample, the spectrum shows a shoulder at 1428 cm⁻¹ (the amide II' band) both at room temperature and at 65°C. In addition, the amide II band remains present, meaning that at both temperatures, the amide closest to the helical backbone (amide A) is solvent inaccessible.

S13. Temperature dependent pump-probe measurements of isotopically diluted water

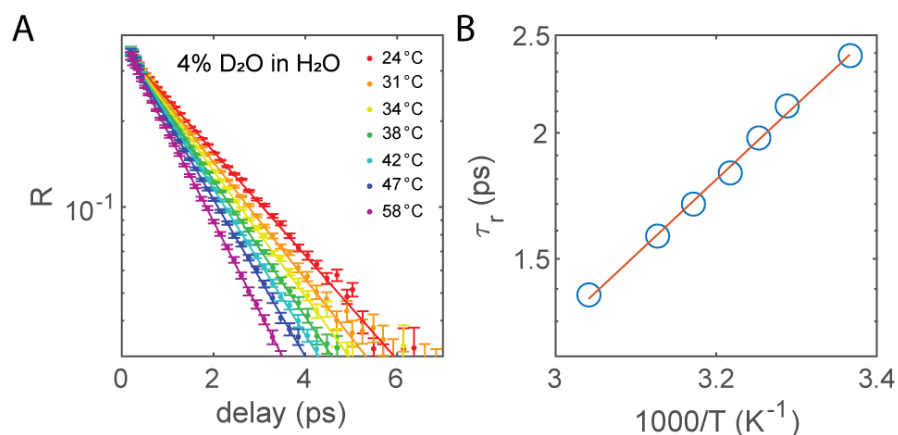


Figure S13. (A) Anisotropy decay of the OD stretch vibration as a function of delay time for a solution of 4% D₂O in H₂O, at different temperatures. The solid lines are fits to an exponential function. (B) Reorientation time τ_r as a function of inverse temperature, obtained from the fit to the anisotropy decay. The solid line represents an Arrhenius-type fit.

We fit the anisotropy decays of the TriPIC solutions at different temperatures with an exponential decay with an offset. The reorientation time τ_r is determined from independent measurements of isotopically diluted water at different temperatures, and the reorientation time obtained is fixed in the anisotropy decay fit of the TriPIC solutions.

Figure S13A shows the anisotropy decay of isotopically diluted water as a function of delay time, for different temperatures. Since the anisotropy of isotopically diluted water does not contain a slow component, we fit the anisotropy using an exponential decay. The obtained reorientation time is shown in figure S13B, where it is plotted on a logarithmic scale as a function of the inverse temperature. The reorientation time decreases with increasing temperature, and this relation can be described with an Arrhenius-type fit using the following the equation:

$$1/\tau_r = Ae^{-E_{act}/RT}$$

Where A is the pre-exponential factor, E_{act} is the activation energy (in J/mol), and R is the gas constant. For isotopically diluted water we find the activation energy to be 14 ± 1 kJ/mol, in agreement with previous findings.²⁻⁴ For the fit of the anisotropic decay of the TriPIC solutions, we use the reorientation time determined by the Arrhenius-type fit for isotopically diluted water, while keeping the offset as a free fitting parameter.

References

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