Supporting Information

Gel preparation

18.75 mL of a 1 M aqueous solution of NIPA (Wako Pure Chemicals) and 1.225 mL of a 0.1 M solution of N,N-methylenebis- (acrylamide) (BA, Aldrich) were mixed with 4.9 mL of water and 0.25 µL of N,N,N,N-tetramethylethylenediamine (TEMED, Aldrich). Finally, 125 µL of ammonium persulfate (APS) was added to the mixture, and polymerization took place at 20 °C for 24 hours. This yielded gels having a molar ratio of [NIPA]/[BA] equal to 150. For the uptake measurements, gel films of thickness 2 mm were prepared. Samples were then dialyzed in water to remove unreacted chemicals. The films were cut into disks (diameter 7 mm). Phenol of high purity (99.5%) (Merck) was used to prepare the 50 mM aqueous solution. For the phenol stock solution deuterated water was used to suppress the intensity of sharp resonances originating of exchangeable protons. The LCST temperature of pNIPA in D_2O is the same as in H_2O (K. Kosik, PhD Thesis, Budapest 2007). Fully swollen gel disks were equilibrated at 25 °C (i.e., above the transition temperature, as shown in Figure S1) for 30 days before the measurements.

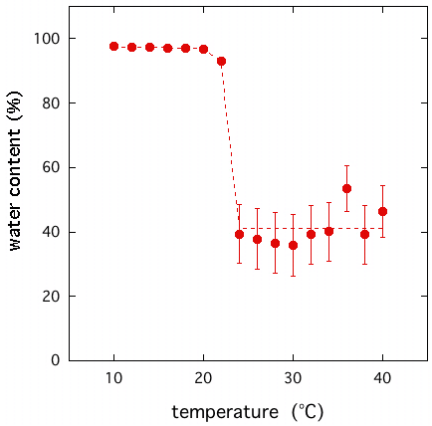

Figure S1. Water content of PNIPA gel in equilibrium with 50 mM aqueous phenol solution at various temperatures (filled symbols). Dotted line is to guide the eye.

In the swollen state the gel displays syneresis when a uniaxial stress is applied (Figure S2). In the deswollen state at moderate rotor speeds and for observation times not exceeding 24 hours, no syneresis is observed.

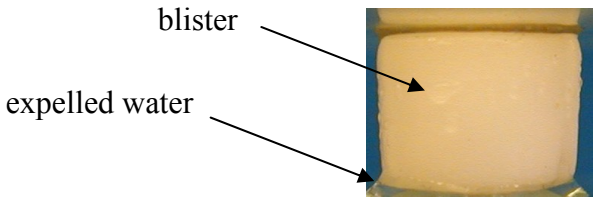

Figure S2 Pressure induced syneresis of fully swollen PNIPA gel in 50 mM phenol aqueous solution at 20°C (Ref. 7 in the paper). The unperturbed height of the gel is 1 cm.

NMR experiments

The pNIPA sample was equilibrated in 50 mmol phenol/D_2O solution at 25°C before the NMR measurements. All the NMR spectra were recorded on a Varian NMR System operating at ^1H frequency of 600 MHz with a Chemagnetics 3.2 mm narrow bore triple resonance T3 probe in double resonance mode. The sample was centred in the rotor by means of teflon spacers to improve the B_1 homogeneity. The length of the sample was approximately 3 mm. The spinning frequency of the rotor was 10 kHz for all experiments. The time needed for swelling equilibrium, determined by weighing, is about a week.[7] After 7 days of equilibration, upon inserting the samples into the rotor and spinning at 10 kHz, the tuning and matching conditions altered dramatically after several minutes. After 30 days of equilibration, however, the tuning and matching under rotation in the magnet remained stable for at least 24 hours. The $\pi/2$ pulse length was 2.5 μs (calibrated with glycine) and 4s repetition delay was used for all experiments. The 2 dimensional ^1H-^1H spin-diffusion spectra were recorded with 8 transients and 256 increments in the t1 dimension. The States-TPPI method was used to achieve sign discrimination in the F1 dimension. PMLG-5 sequences were used in the indirect dimension and wPMLG-5 sequences in the direct dimension. The experimental scaling factor was 0.41. The on-resonance position of the RF field lay outside the spectra (-5 kHz from the centre of the proton spectra).

Rate matrix analysis

For the analysis the following assumptions were made:

- Since the system is a hydrogel, its structure is amorphous, only the phenol - side chain distance is constant.
- Methyl and phenol rotation is much faster than the timescale of the applied NMR experiment. The methyl and phenyl groups were replaced with point-like entities with 3 times and 5 times ½ spin (similar to REF5).
- The exchange process depends on inverse sixth-order of the distance.
- Contribution of the main chain to the correlation spectra was neglected.
- In calculations on the Fig S3 exposed distances (a, b, c, d) were changed. The initial values were taken from DFT calculations (phenol molecule attached to the repeating unit with H-bond).

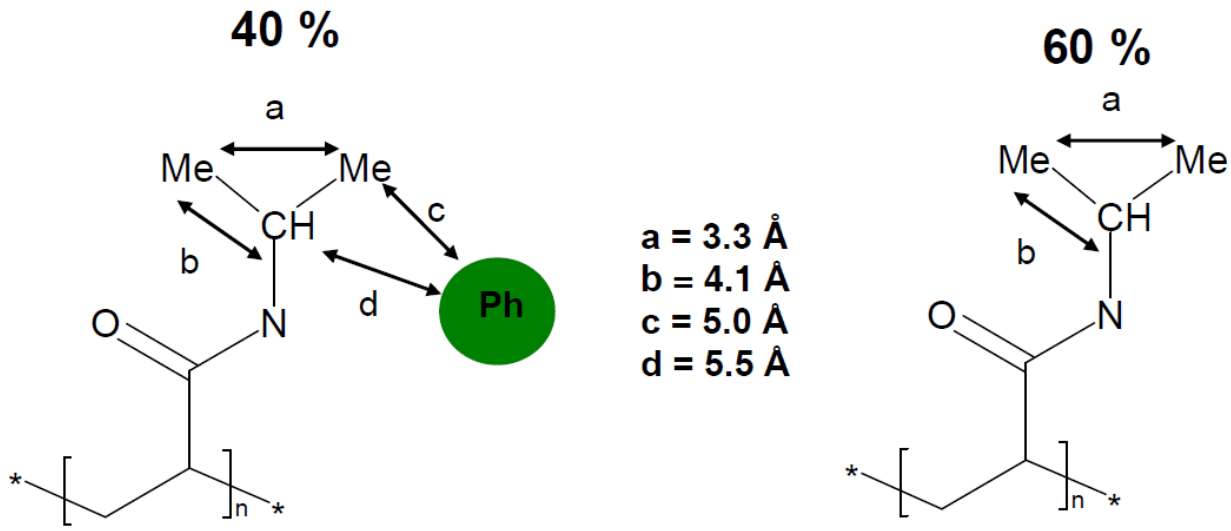

Figure S3 Model for rate matrix analisys

If any distance were altered with 1 Å, then at least on 2-3 graph the difference between measured and calculated values was a factor of 2.