Supplementary Material
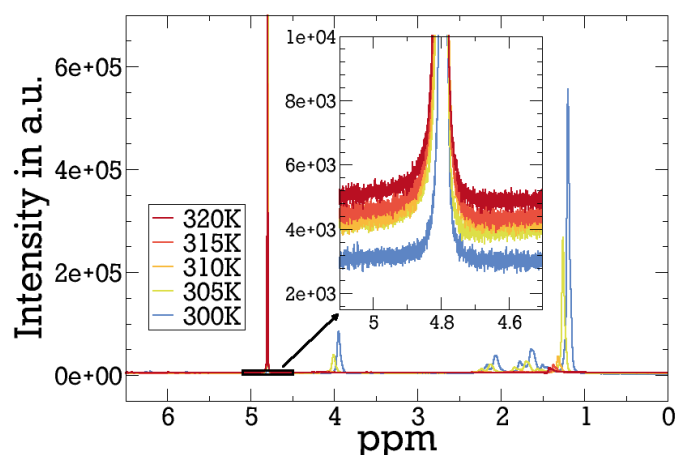

Figure S1: High resolution ^{1}H NMR spectra of the D_2O-pNIPAM mixture at temperatures below and above the LCST. The five main peaks are assigned as in the existing literature, e.g. (Zeng et al., 1997), to HDO residues in D_2O (4.8 ppm), while the others at 3.9 ppm, 2.1 ppm, 1.6 ppm and 1.2 ppm are assigned to the polymer protons, i. e. (in the same order) the CH of the side chain, the CH of the backbone, the CH_2 and the CH_3. The inset shows a magnified view of the solvent peak. Despite the excellent resolution and sensitivity, no contribution of an additional water species with a shift of 0.1 ppm (Hofmann et al., 2013; Wang et al., 2009) is visible, which supports our assumption of fast exchange between free and bound water.
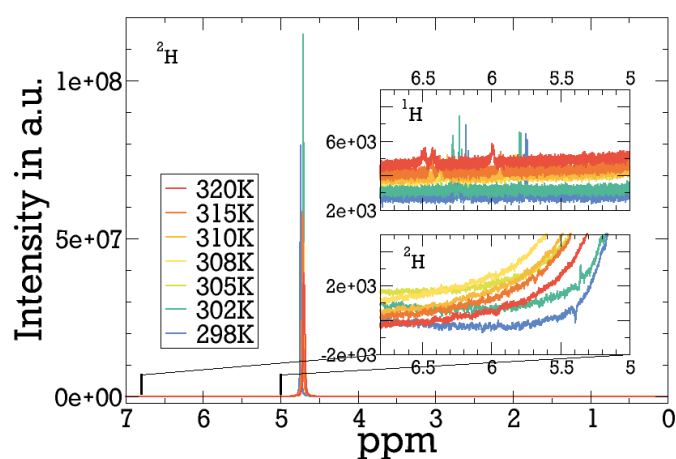

Figure S2: High resolution ^{1}H and ^{2}H NMR spectra of the D_2O-pNIPAM mixture at temperatures below and above the LCST. The insets show a magnified view of the region where a contribution from the amide protons/deuterons might be expected.

We used the Bruker 1 GHz-AEON spectrometer of the Northern Bavarian NMR Centre to record high resolution ^{1}H and ^{2}H NMR spectra, some of which are shown in Figure S1 and Figure S2. For both nuclei, the observation of a single solvent peak above the LCST hints at fast exchange between free and bound water molecules, as discussed in the main text. In the ^{1}H NMR spectra, the overall polymer contribution to the signal is strongly reduced as the LCST is crossed, which is attributed to a sudden decrease in polymer mobility (Zeng et al., 1997; Spěváček, 2009).

The amide proton of the polymer was assigned to a peak near $3\,\mathrm{ppm}$ in CDCl$_3$ (Zeng et al., 1997). No signal can be detected in this range, implying exchange with the excess D$_2$O deuterons. Other references (National Institute of Advanced Industrial Science and Technology (AIST), 1999) placed the NH signal at $6.2\,\mathrm{ppm}$. There, a weak contribution can be seen in the upper inset of Figure S2 showing ^{1}H spectra. However, considering the extreme magnification, it is unclear if it actually belongs to residual protons at the amide groups of the polymer or to other unidentified sources.

To further check our assumption of fast exchange between the bound and free water fractions, we analyze the time dependence of the magnetization recovery in T_1 measurements. In Figure S3, we show exemplary fits of T_1 data with a stretched exponential function, see Eq. (10) of the main text, where the stretching parameter β is treated as a free parameter ($0 \leq \beta \leq 1$). The fits describe the data very well both below and above the LCST. With one exception, $\beta \geq 0.99$ is found at all temperatures, indicating that $\beta = 1$ is obeyed within the experimental uncertainty. This finding confirms that exchange between dynamically distinguishable water molecules, in particular, between free and bound water is fast on the time scale of spin-lattice relation, $T_1 = 0.1\text{--}1\,\mathrm{s}$.
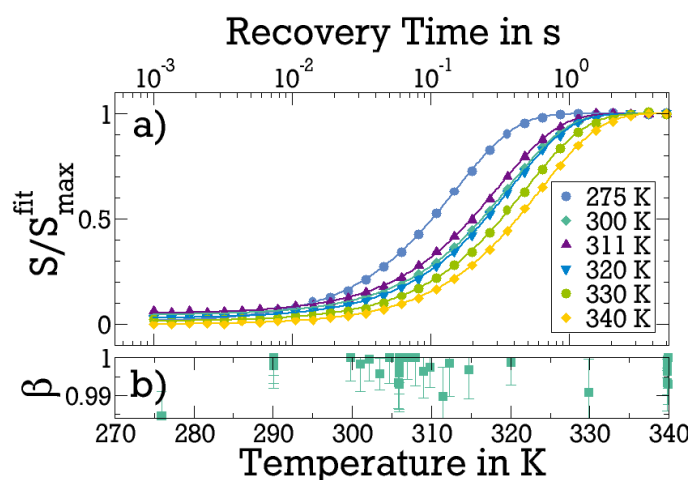

Figure S3: (a) Normalized buildup of ^{2}H magnetization from saturation-recovery experiments at $\omega_{\mathrm{L}}/(2\pi) = 24.9\,\mathrm{MHz}$ and various temperatures together with fits with a stretched exponential function. (b) Resulting stretching parameter β in a very narrow range.

In the main text, we discuss the sudden decrease in T_1 and T_2 during pNIPAM's coil-to-globule transition as the result of changed rotational dynamics of water. Initially, one might consider that the observations instead result from altered motion of the pNIPAM side chain, as probed by deuterons, which arrived at the amide groups of the polymer by chemical exchange with heavy water. Evidence to the contrary is presented in Figure S4, where similar behaviour is observed for (non-exchanging) [17]O in a pNIPAM solution with
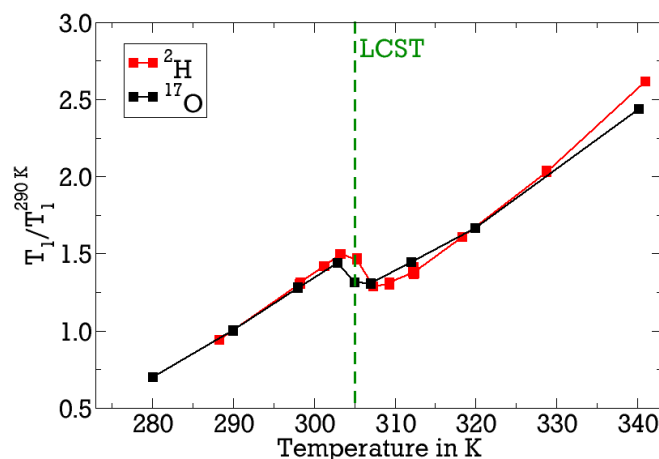
Figure S4: Temperature-dependent ^{17}O T_1 relaxation times for a solution of pNIPAM in isotope labelled H$_2$^{17}O water in comparison to ^{2}H T_1 in a pNIPAM-D$_2$O mixture, both normalised on their respective (interpolated) value at $290\,\mathrm{K}$. The ^{2}H data are those presented in Figure 1 of the main text. The vertical dashed line marks the LCST.

^{17}O-enriched water. Both datasets shown in Figure S4 were normalized to the respective T_1 values at $290\,\mathrm{K}$ to facilitate a direct comparison of the effects associated with the pNIPAM coil-to-globule transition.

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