Supplementary Information to: ^{2}H and ^{17}O NMR Studies of Solvent Dynamics Related to the Cononsolvency of Poly(N-Isopropyl Acrylamide) in Ethanol-Water Mixtures

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In the main text, we study ethanol-water mixtures with and without poly(N-isopropyl acrylamide) (pNIPAM) based on ^{2}H and ^{17}O NMR relaxation times T_1 and T_2. Here, we show examples of data and fits from which these parameters were obtained. Moreover, we scrutinize the reproducibility of the results.

T_1 relaxation times were measured using the inversion-recovery pulse sequence. Exemplary ^{2}H and ^{17}O buildup curves $M(t)$ resulting from these measurements for samples with and without pNIPAM are shown in Figures S1–S6. For a first analysis, these data were fitted with a stretched exponential buildup:

$$M(t) = \Delta M\{1 - A\exp\left[-(t/T_1)^{\beta}\right]\} + M_0. \tag{1}$$

This analysis yielded stretching parameters $\beta \approx 1.0$ for all measured data sets. Therefore, for the final analysis, we fixed the stretching parameter at $\beta = 1$, i.e., we assumed single exponential spin-lattice relaxation. In Figures S1–S6, we see that this approach yields a very good interpolation of the ^{2}H and ^{17}O experimental data.

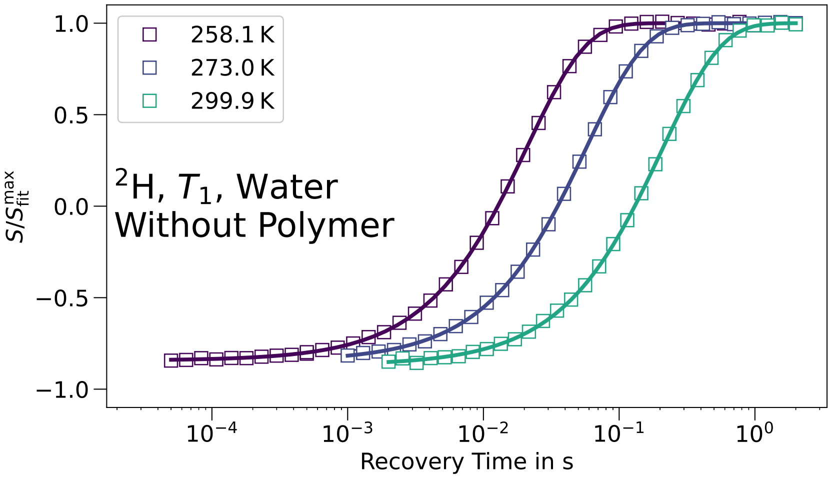

Figure S1: ^{2}H magnetization buildup (symbols) and fits (lines, $\beta = 1$) for a polymer-free mixture of 30 vol% CH_3CH_2OH and 70 vol% D_2O as obtained from inversion-recovery experiments at the indicated temperatures. Note that, for this sample, H/D exchange leads to statistical distribution of the deuterons among the hydroxy groups of ethanol and water.

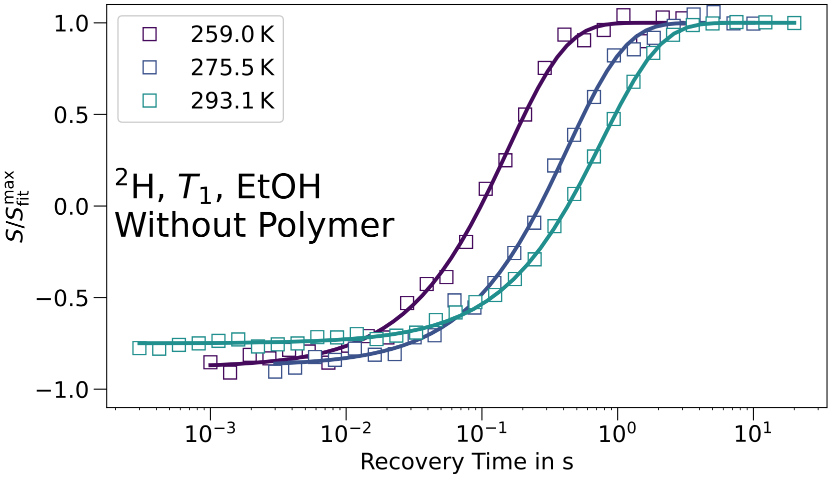

Figure S2: ^{2}H magnetization buildup (symbols) and fits (lines, $\beta = 1$) for a polymer-free mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ as obtained from inversion-recovery experiments at the indicated temperatures.

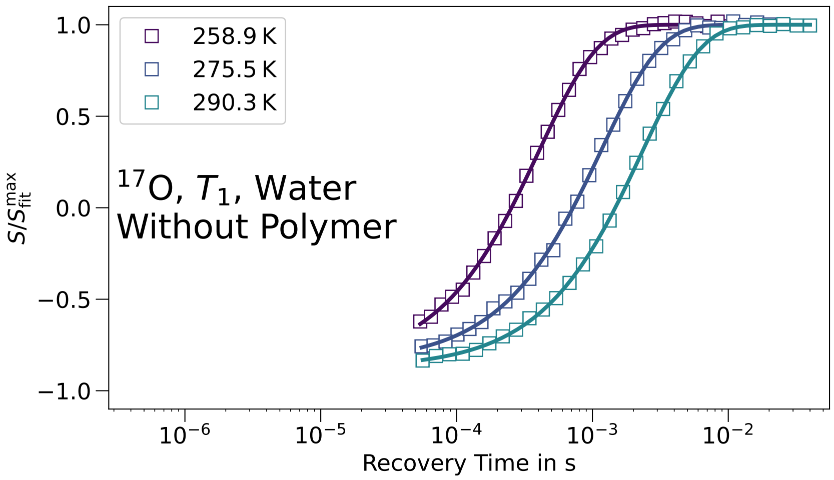

Figure S3: ^{17}O magnetization buildup (symbols) and fits (lines, $\beta = 1$) for a polymer-free mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ as obtained from inversion-recovery experiments at the indicated temperatures. The short-time plateau cannot be fully observed because recovery times shorter than the pulse length are not accessible.

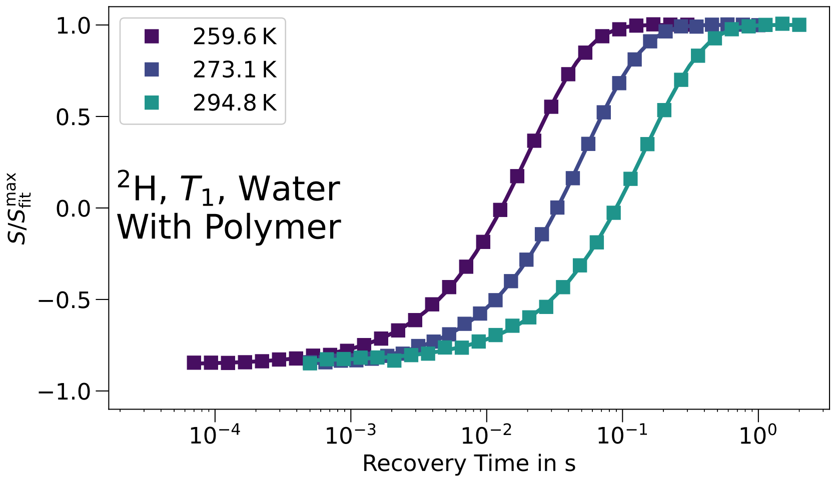

Figure S4: ^{2}H magnetization buildup (symbols) and fits (lines, $\beta = 1$) for a mixture of 30 vol% CH_3CH_2OH and 70 vol% D_2O containing 4 wt% pNIPAM as obtained from inversion-recovery experiments at the indicated temperatures. Note that, for this sample, H/D exchange leads to a redistribution of the deuterons among the components.

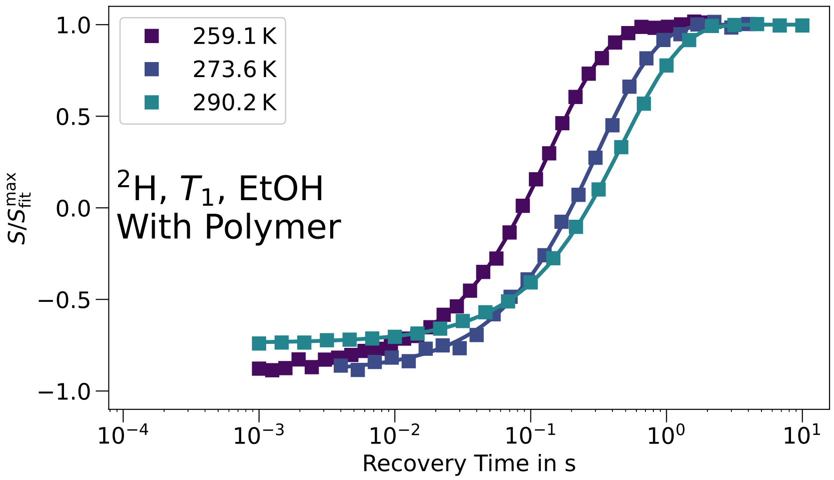

Figure S5: ^{2}H magnetization buildup (symbols) and fits (lines, $\beta = 1$) for a mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ containing 4 wt% pNIPAM as obtained from inversion-recovery experiments at the indicated temperatures.

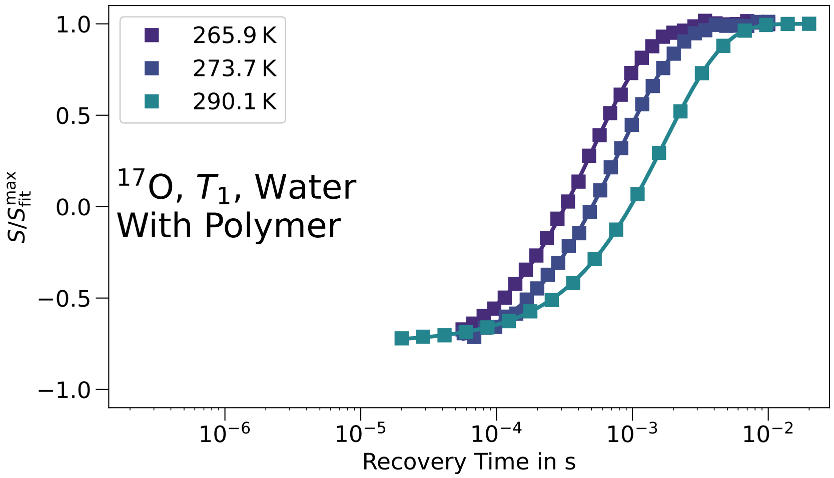

Figure S6: ^{17}O magnetization buildup (symbols) and fits (lines, $\beta = 1$) for a mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ containing 4 wt% pNIPAM as obtained from inversion-recovery experiments at the indicated temperatures.

T_2 relaxation times were obtained from CPMG experiments. Exemplary ^{2}H and ^{17}O data are presented in Figures S7–S9. For analysis, these data were fitted with a single exponential decay:

$$M(t) = \Delta M \exp\left(-\frac{t}{T_2}\right). \tag{2}$$

In Figures S7–S9, we see that this approach enabled a very good interpolation of the experimental data for ethanol-water mixtures containing 4 wt% pNIPAM.

As mentioned in the main text, we took precautions to avoid an uncontrolled heating of the sample during the CPMG multi-pulse sequence. For this purpose, the magnetization decay was probed in subsequent CPMG experiments with different half-interpulse-distance (HPD) between the expected center of the echo and the center of either of the adjacent refocusing pulses. Comparing the CPMG decays for various HDP values, we found that the obtained T_2 time hardly depended on the exact HPD value, as long as it was ensured that most of the magnetization decay was covered. Moreover, this comparison allowed us to show that our results are not affected by echo attenuation due to molecular diffusion across field inhomogeneities. In Figures S7–S9, the data sets for the HDP value, which was chosen for the final analysis, are highlighted with larger symbols and the fits of these data sets with Eq. (2) are shown as lines.

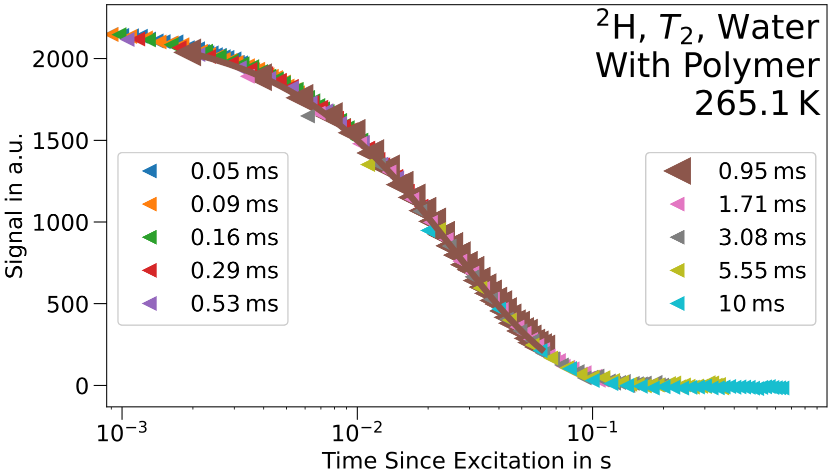

Figure S7: ^{2}H magnetization decays (symbols) for a mixture of 30 vol% CH_3CH_2OH and 70 vol% D_2O containing 4 wt% pNIPAM as obtained from CPMG experiments for the indicated HPD values at 265 K. The data set used for the final analysis is highlighted with larger symbols and its fit is included as line. Note that, for this sample, H/D exchange leads to a redistribution of the deuterons among the components.

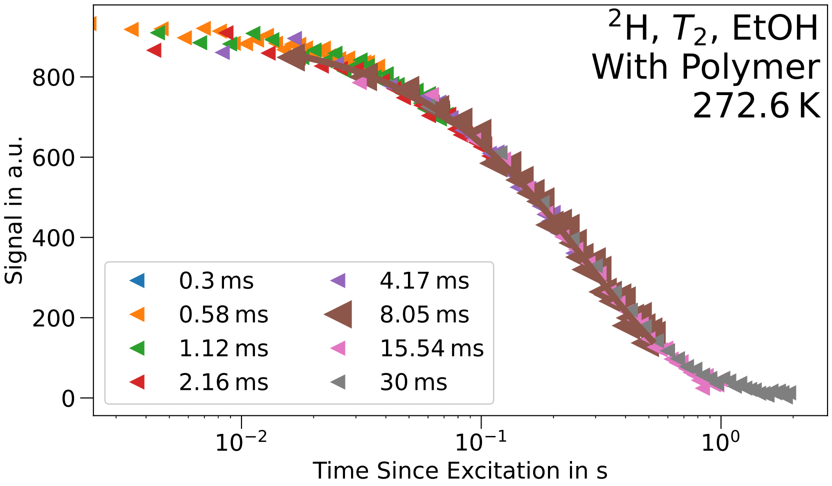

Figure S8: ^{2}H magnetization decays (symbols) for a mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ containing 4 wt% pNIPAM as obtained from CPMG experiments for the indicated HPD values at 273 K. The data set used for the final analysis is highlighted with larger symbols and its fit is included as line.

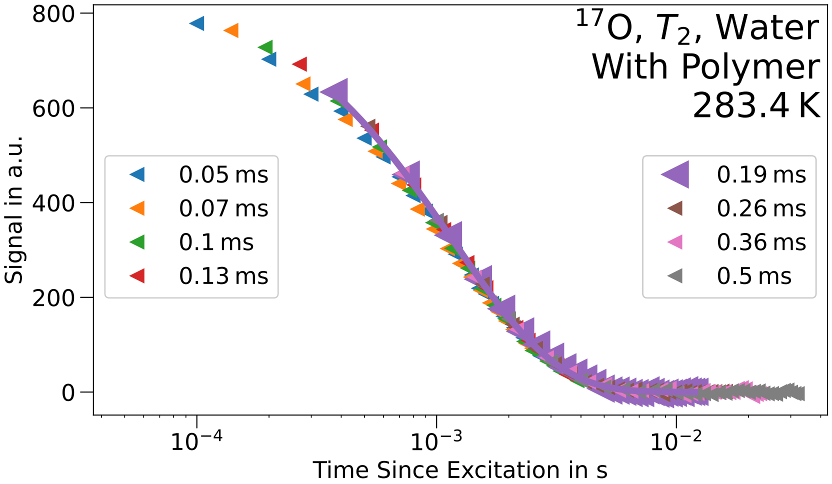

Figure S9: ^{17}O magnetization decays (symbols) for a mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ containing 4 wt% pNIPAM as obtained from CPMG experiments for the indicated HPD values at 283 K. The data set used for the final analysis is highlighted with larger symbols and its fit is included as line.

The reproducibility of the results was tested by repeating the measurements on some of the samples. In Figures S10 and S11, we present results from two ^{2}H and ^{17}O NMR measurement series for a mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ containing 4 wt% pNIPAM. For both nuclei, we see that differences between the data from the original measurements (orange), which are shown in the main text, and the data from the repeat measurements (green) are negligible. Because fit errors are even smaller, we expect that the fixed-field T_1 and T_2 values in the main text have uncertainties smaller than the symbol sizes below the LCST.

Above the LCST, the samples may be in a metastable state [1]. Hence, the findings may depend on the thermal history, e.g., on the time the sample has been kept above its LCST. An advantage of our approach is that, due to the chosen isotope labelling, data on ethanol and water dynamics can be measured in direct succession at a given temperature. Thus, the system can be reasonably assumed to have gone through the same temperature protocol and to be in a practically identical state during the ^{2}H and ^{17}O measurements, thereby enabling a straightforward comparison between the solvent components. Explicitly, when comparing ^{2}H and ^{17}O relaxation times for a given sample in the main text, we expect that the uncertainties are smaller than the symbol size even above the LCST. The uncertainties may be somewhat larger when comparing results for different samples above the LCST but we paid attention to keep possible discrepancies at a minimum by using, although not identical,

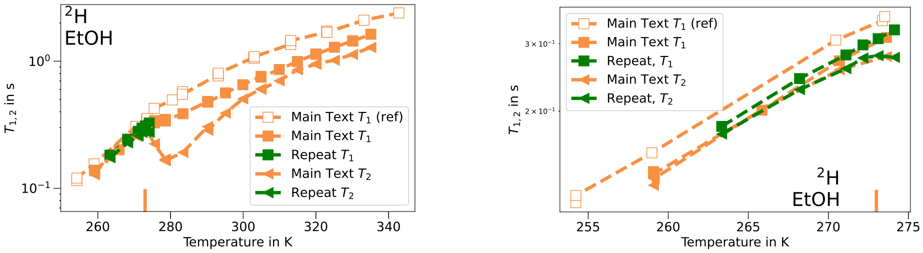

Figure S10: ^{2}H T_1 and T_2 relaxation times for a mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ containing 4 wt% pNIPAM (solid symbols), as obtained from two independent measurement series (orange/green). For reference, results for the polymer-free solution are included (open symbols). The left and right panels show identical sets of data on different axes sections, explicitly, the left panel shows all data and the right one is a zoom.

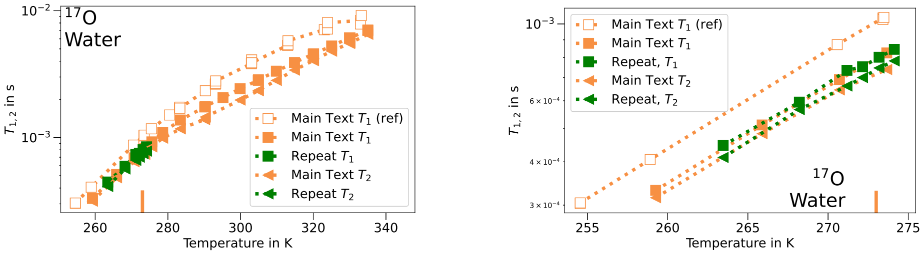

Figure S11: ^{17}O T_1 and T_2 relaxation times for a mixture of 30 vol% CH_3CD_2OH and 70 vol% $H_2{}^{17}O$ containing 4 wt% pNIPAM (solid symbols), as obtained from two independent measurement series (orange/green). For reference, results for the polymer-free solution are included (open symbols). The left and right panels show identical sets of data on different axes sections, explicitly, the left panel shows all data and the right one is a zoom.

at least comparable temperature protocols.

References

[1] Larisa Starovoytova and Jiří Spěváček. “Effect of time on the hydration and temperature-induced phase separation in aqueous polymer solutions. 1H NMR study”. In: *Polymer* 47 (2006). DOI: `10.1016/j.polymer.2006.08.002`.