Supporting Information

Water Dynamics in Aqueous Poly-*N*-Isopropylacrylamide Below and Through the Lower Critical Solution Temperature Phase Transition

Sean A. Roget, Kimberly A. Carter-Fenk, and Michael D. Fayer*

Department of Chemistry, Stanford University, Stanford, CA 94305, United States
*Email: fayer@stanford.edu; Phone: (650) 723-4446

A. Representative polarized pump-probe signals

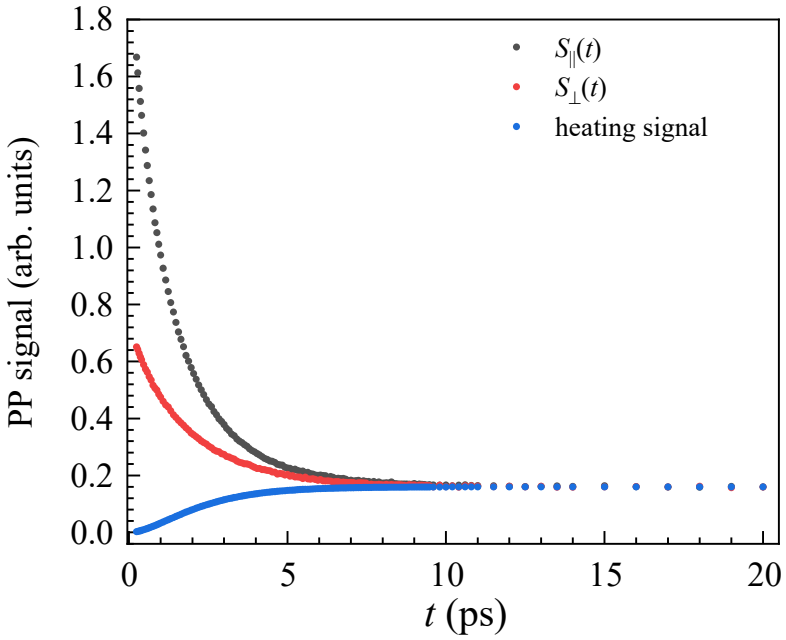

Figure S1. Polarized pump-probe decays (parallel – black; perpendicular – red) of the OD stretch of HOD in PNIPAM at 23 °C. Calculated heating signal determined from a well-described procedure (blue).[1-2] Heating signal is subtracted from parallel and perpendicular signals before calculating the anisotropy.

B. Linear spectra of acrylamide solution and polyacrylamide

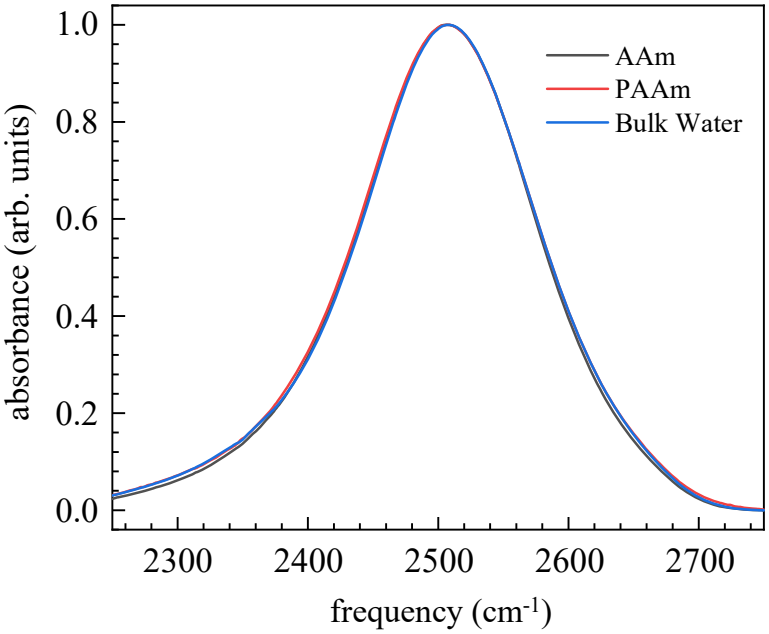

Figure S2. Normalized and background-subtracted linear absorption spectra of the OD stretch of dilute HOD in bulk water, and solutions of AAm and PAAm at 36-1 molar ratio (water to monomer unit).

C. Temperature-dependent orientational dynamics in bulk water

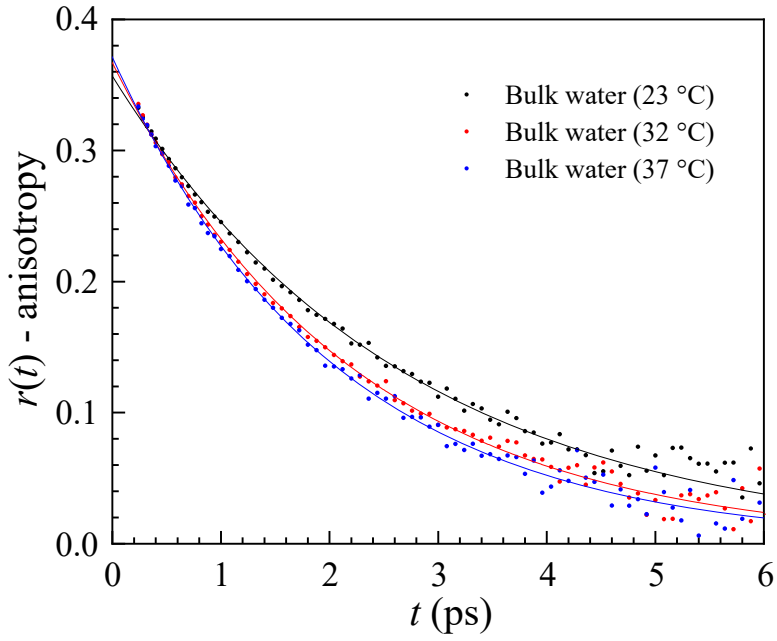

Figure S3. Anisotropy decays and their corresponding single exponential fits (purple lines) of the OD stretch of HOD in bulk water at 23 °C, 32 °C, and 37 °C.

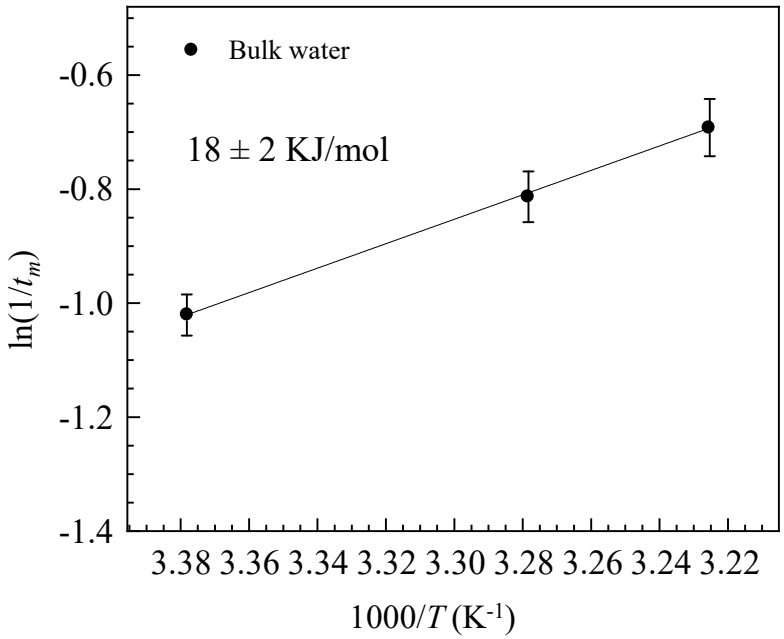

Figure S4. Arrhenius plot of free diffusion time constant of HOD in bulk water. Error bars are propagated error of the time constants. Linear fits (weighted by error) are used to determine the activation energy.

Table S1. Single exponential fit parameters of the anisotropy of the OD stretch of HOD in bulk water near the center frequency at various temperatures.

Sample	a_1	t_1 (ps)
Bulk water (23 °C)	0.36 ± 0.01	2.6 ± 0.1
Bulk water (32 °C)	0.37 ± 0.01	2.2 ± 0.1
Bulk water (37 °C)	0.37 ± 0.01	2.0 ± 0.1

D. Orientational dynamics in AAm, PAAm, NIPAM and PNIPAM fit to biexponential decays

Table S2. Biexponential fit parameters of the anisotropy of the OD stretch of HOD in AAm, PAAm, NIPAM, and PNIPAM at 36 waters per monomer near the center frequency at various temperatures.

Sample	a_1	t_1 (ps)	a_2	t_2 (ps)
AAm/PAAm (23 °C) (simultaneous fit)	0.06 ± 0.02	0.8 ± 0.2	0.31 ± 0.02	3.5 ± 0.2
AAm/PAAm (32 °C) (simultaneous fit)	0.06 ± 0.02	0.8 ± 0.2	0.32 ± 0.02	2.8 ± 0.2
AAm/PAAm (37 °C) (simultaneous fit)	0.05 ± 0.02	0.8 ± 0.2	0.33 ± 0.02	2.5 ± 0.2
NIPAM/PNIPAM (23 °C) (simultaneous fit)	0.14 ± 0.02	1.4 ± 0.2	0.22 ± 0.03	10 ± 1
NIPAM/PNIPAM (30 °C) (simultaneous fit)	0.15 ± 0.02	1.3 ± 0.2	0.22 ± 0.03	7 ± 1
NIPAM (32 °C)	0.17 ± 0.02	1.5 ± 0.2	0.20 ± 0.02	6.7 ± 0.8
NIPAM (34 °C)	0.15 ± 0.02	1.4 ± 0.2	0.23 ± 0.02	5.6 ± 0.5
NIPAM (37 °C)	0.17 ± 0.02	1.4 ± 0.2	0.21 ± 0.02	5.4 ± 0.4
PNIPAM (34 °C)	0.31 ± 0.01	1.8 ± 0.1	0.07 ± 0.01	-

References

1. Steinel, T.; Asbury, J. B.; Zheng, J. R.; Fayer, M. D., Watching hydrogen bonds break: A transient absorption study of water. *J. Phys. Chem. A* **2004,** *108*, 10957-10964.

2. Rezus, Y. L. A.; Bakker, H. J., On the orientational relaxation of HDO in liquid water. *J. Chem. Phys.* **2005,** *123*, 114502.