**Dynamics of Acrylamide Hydrogels, Polymers, and Monomer in Water
Measured with Optical Heterodyne Detected Optical Kerr Effect Spectroscopy**

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A. Evaluation of OHD-OKE signal strength through calculation of polarizability anisotropy

The signal strength of optical Kerr effect spectroscopy will be proportional to the polarizability anisotropy, which is given by, $\left[\left(\alpha_{xx} - \alpha_{yy} \right)^2 + \left(\alpha_{yy} - \alpha_{zz} \right)^2 + \left(\alpha_{zz} - \alpha_{xx} \right)^2 \right]$, where the α_{ii}'s are the elements of the diagonalized polarizability tensor. The polarizability anisotropies were calculated for water, acrylamide, and small oligomer of acrylamide. A DFT method was used for the calculation, specifically wb97xd/6-311++g(d,p), which was performed using Gaussian09 (Rev. B.01).[1] The default SCRF implicit water model was selected in Gaussian. Acrylamide and water had polarizability anisotropy of 42.1 $Å^3$ and 0.0835 $Å^3$, respectively. This implies that acrylamide has signal strength that is 504 times larger than water. Calculation of the acrylamide dimer yielded a polarizability anisotropy of 3.58 $Å^3$ per acrylamide moiety, which makes its signal strength 43 times larger than water.
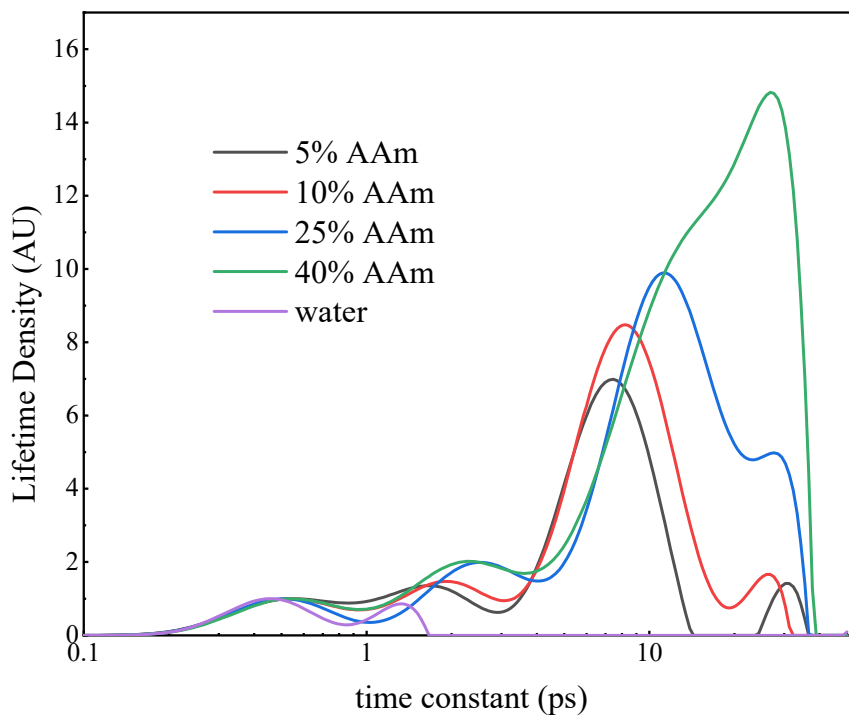
B. Lifetime density analysis of AAm

Figure S1. Lifetime density analysis of AAm and water. The lifetime density is weighted by the time constants and therefore reports on the correlation function. The number of peaks reflect the number of time components with the width representing uncertainty. It can be seen that AAm and water have four and two time components, respectively. The fast time components is nearly the same for all samples.

C. Time constants from acrylamide subtracted and relative water populations
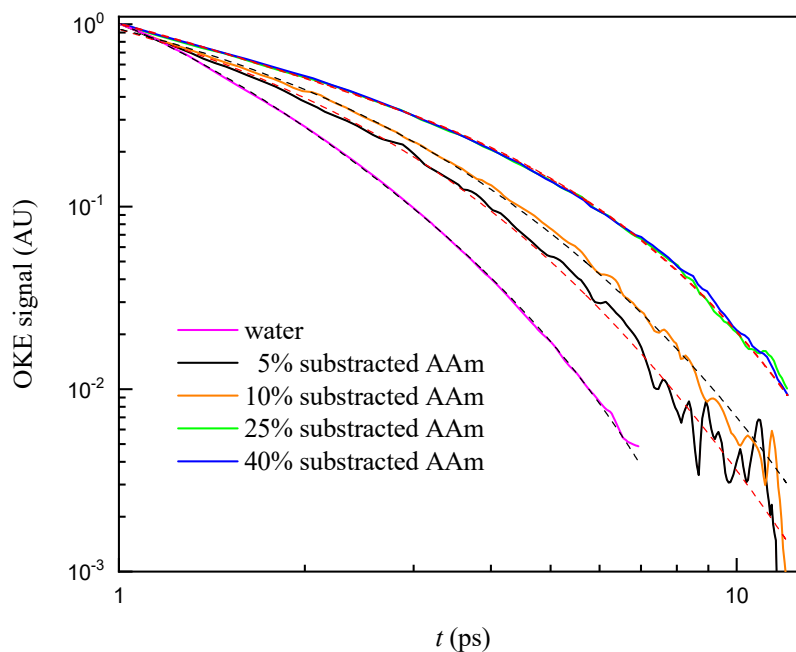

Figure S2. OHD-OKE spectra of water (purple) and 5% (black), 10% (orange), 25% (green), and 40% (blue) AAm with water's signal subtracted out. Spectra were normalized at 1 ps.

Table S1. Parameters from water subtracted AAm in Fig. S2.

Conc. (w/v)	τ_1 (ps)[+]	τ_2 (ps)[+]	τ_3 (ps)[#]	C_1 norm	C_2 norm	C_3 norm
5%	0.52	1.29	2.6	0.664	0.293	0.043
10%	0.52	1.29	2.6	0.654	0.253	0.092
25%	0.52	1.29	2.6	0.71	0	0.29
40%	0.52	1.29	2.6	0.72	0	0.28

[+]fixed parameters for water not associated with the acrylamide.
[#]fixed parameters for water associated with the acrylamide.

Data of AAm with water's signal subtracted outare given in Figure S2 This data was fitted to a triexponentials function.

$$r'(t) = C_1 \exp\left(-\frac{t}{t_1}\right) + C_2 \exp\left(-\frac{t}{t_2}\right) + C_3 \exp\left(-\frac{t}{t_3}\right)$$

In order to correctly evaluate the relative populations based on their distinctive time scales, the amplitudes of the polarizability-polarizability correlation function are need. This can be found by simply weighing amplitudes of $r'(t)$ by their associated time constant yielding $r(t)$.

$$r(t) = C_1 t_1 \exp\left(-\frac{t}{t_1}\right) + C_2 t_2 \exp\left(-\frac{t}{t_2}\right) + C_3 t_3 \exp\left(-\frac{t}{t_3}\right)$$

The ratios of second and third processes are of interest, which represent bulk and surface water, respectively. Using the known number of waters per acrylamide, the number of surface waters can be easily found.

Table S2. Results from the calculation of number of surface waters based on parameters in Table S1.

Conc. (w/v)	$C_2 t_2$	$C_3 t_3$	Ratio $C_2 t_2 / C_3 t_3$	Waters per Acrylamide	Surface Waters
5%	0.378	0.112	3.38	79	18
10%	0.326	0.239	1.36	36	15
25%	0	0.754	0	12	12
40%	0	0.728	0	6	6

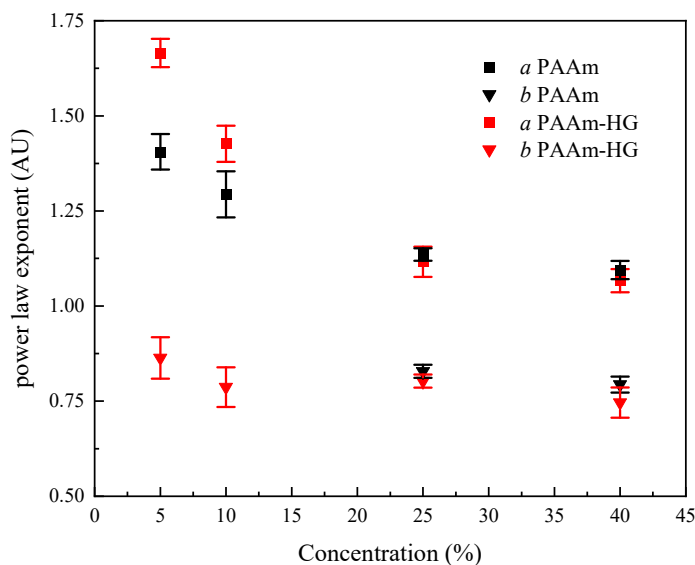## D. Comparisons of AAm, PAAm, and PAAm-HG.

Figure S3. The power law exponentials of PAAm and PAAm-HG as function of concentration. 5% and 10% PAAm are fit to Eq. 7. All other samples were fit to Eq 1. The 25% and 40% PAAm and PAAm-HG have nearly identical dynamics.
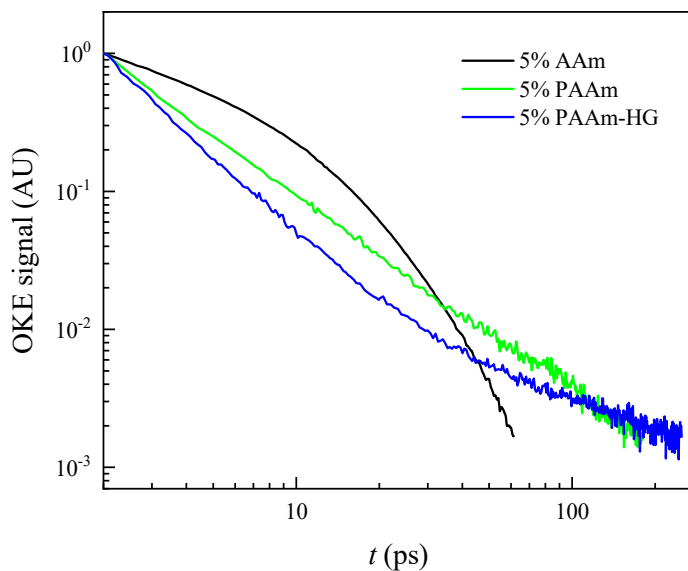

Figure S4. Comparison between AAm (black), PAAm (green), and PAAm-HG (blue) at 5% in water. Spectra were normalized at 2 ps. There is a clear difference between PAAm and PAAm-HG
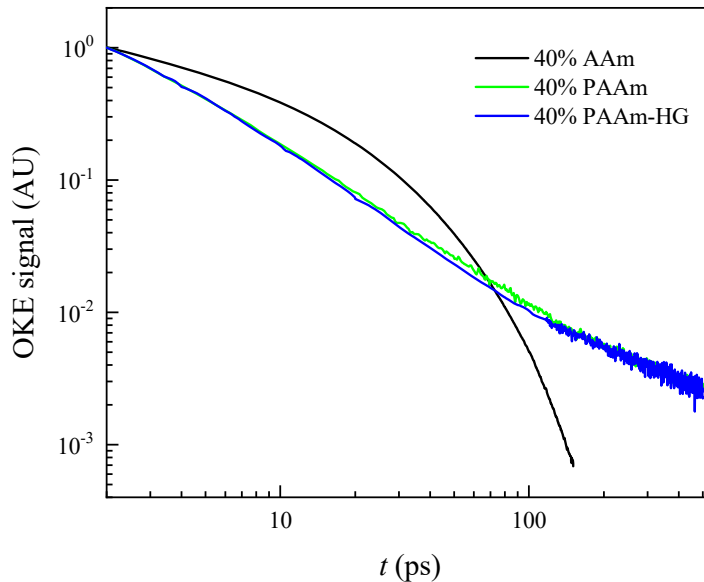
Figure S5. Comparison between AAm (black), PAAm (green), and PAAm-HG (blue) at 40% in water. Spectra were normalized at 2 ps. PAAm and PAAm-HG exhibited very similar dynamics.

Reference

1. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.