Supporting Information for

Bulking Up: The Impact of Polymer Sterics on Emulsion Stability

Ashley N. Mapile, Lawrence F. Scatena*

Department of Chemistry and Biochemistry,
University of Oregon, Eugene, OR 97403

Table of Contents

VSFSS Schematic **2**
Figure S1
Varying Molecular Weight C=O Data **2-3**
Figure S2
Figure S3
PMAA Characterization **4**
Figure S4
Table S1
Figure S5
Temperature-Dependent PDI **5**
Figure S6
Fitting Parameters **6-9**
Table S2-S5

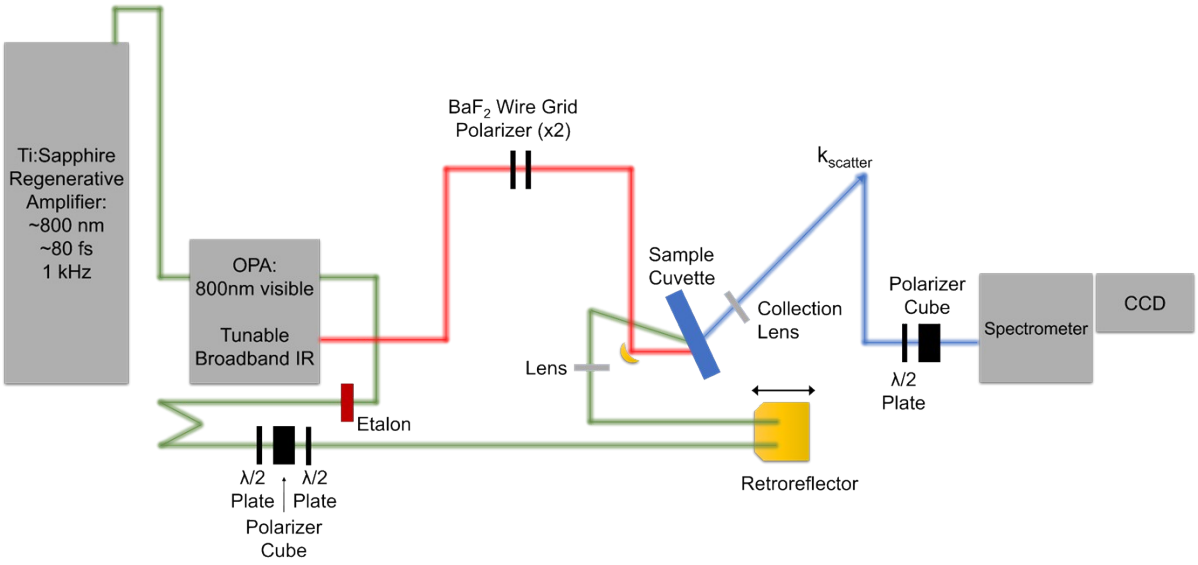

Figure S1. Schematic of the vibrational sum frequency scattering spectroscopy (VSFSS) experimental setup used in this work.

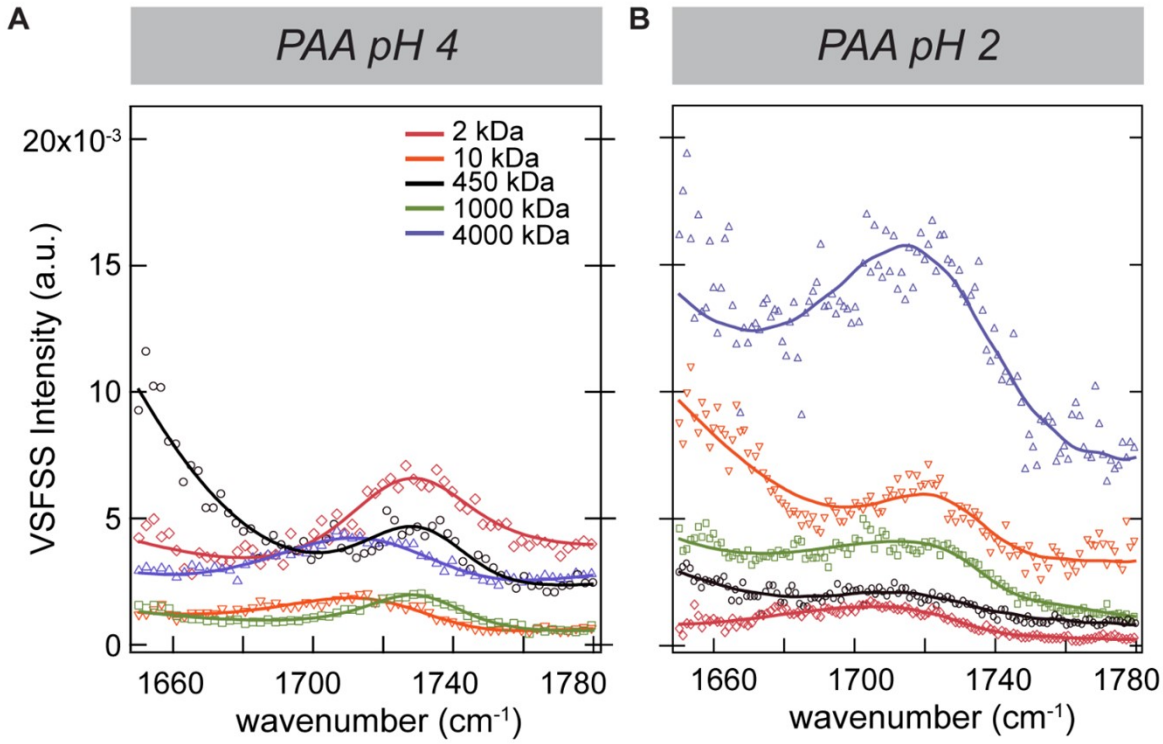

Figure S2. VSFSS measurements (*ssp* polarization) of D-hexadecane emulsions in D_2O stabilized with 500 ppm PAA of varying molecular weight at pH 4 (A) and pH 2 (B) in the C=O stretching region. Solid lines represent fits of the data.

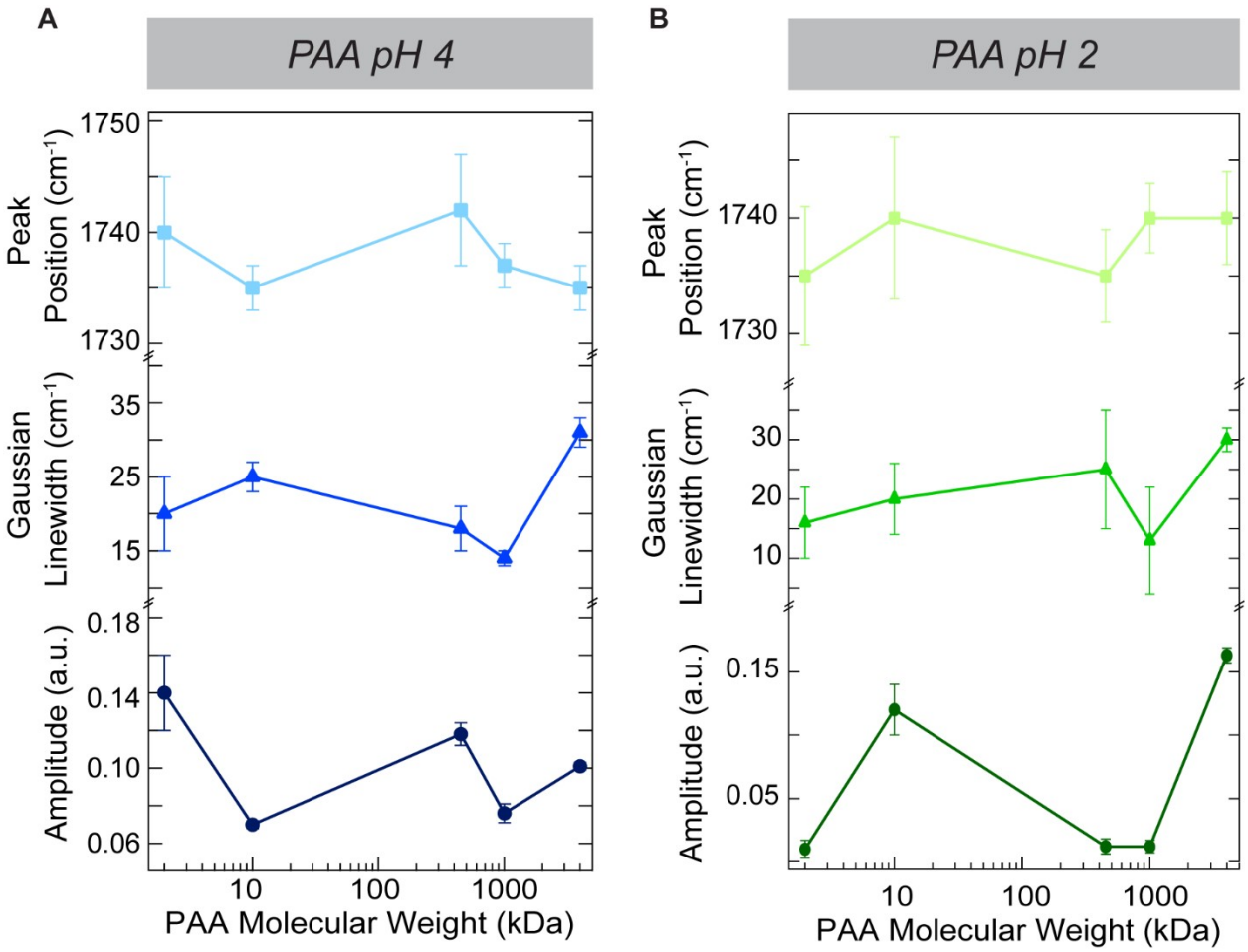

Figure S3. Fit parameter trends for VSFSS measurements of PAA of varying molecular weight at pH 4 (A) and pH 2 (B) in the C=O stretching region, corresponding to Figure 5.

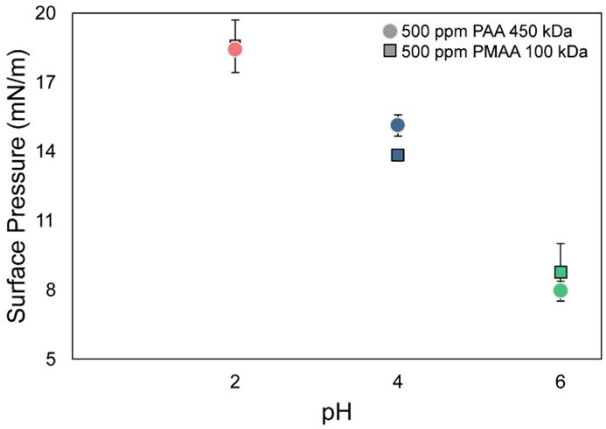

Figure S4. Equilibrium surface pressure of 500 ppm poly(acrylic acid) (circles) and 500 ppm poly(methacrylic acid) (squares) measured by pendant drop surface tensiometery at the hexadecane and water interface in varying pH conditions.

Table S1. Characteristics (diameter, polydispersity index, and zeta potential) of nanoemulsions formed with 500 ppm and 2687 ppm poly(methacrylic acid) (PMAA) at varying pH conditions.

[PMAA] (ppm)	*pH*	*Diameter (nm)*	*Polydispersity Index*	*Zeta Potential (mV)*
500	2	491.5	0.196	-4.21
	4	505.9	0.265	-8.47
	6	720.0	0.433	-23.4
2687	2	383.0	0.200	-1.71
	4	280.6	0.232	-5.33
	6	572.8	0.674	-44.0

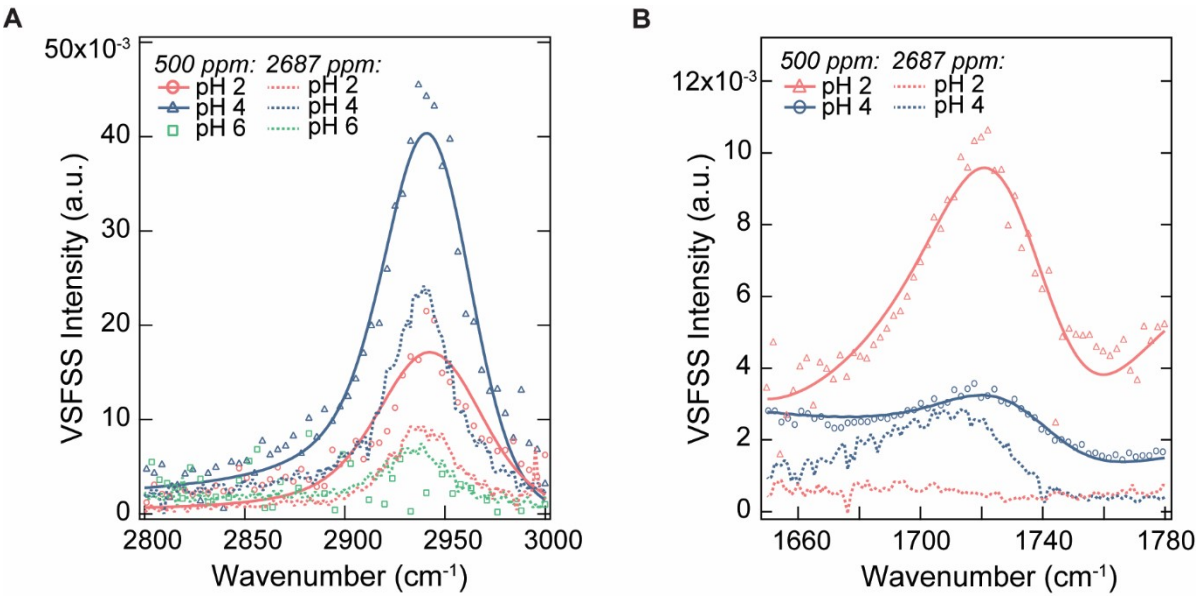

Figure S5. VSFSS measurements (ssp polarization) of D-hexadecane emulsions in D2O stabilized with PMAA in the (A) C-H and (B) C=O stretching regions in varying pH conditions. Lines represent fits of the data, corresponding to Figure 7 in the main text.

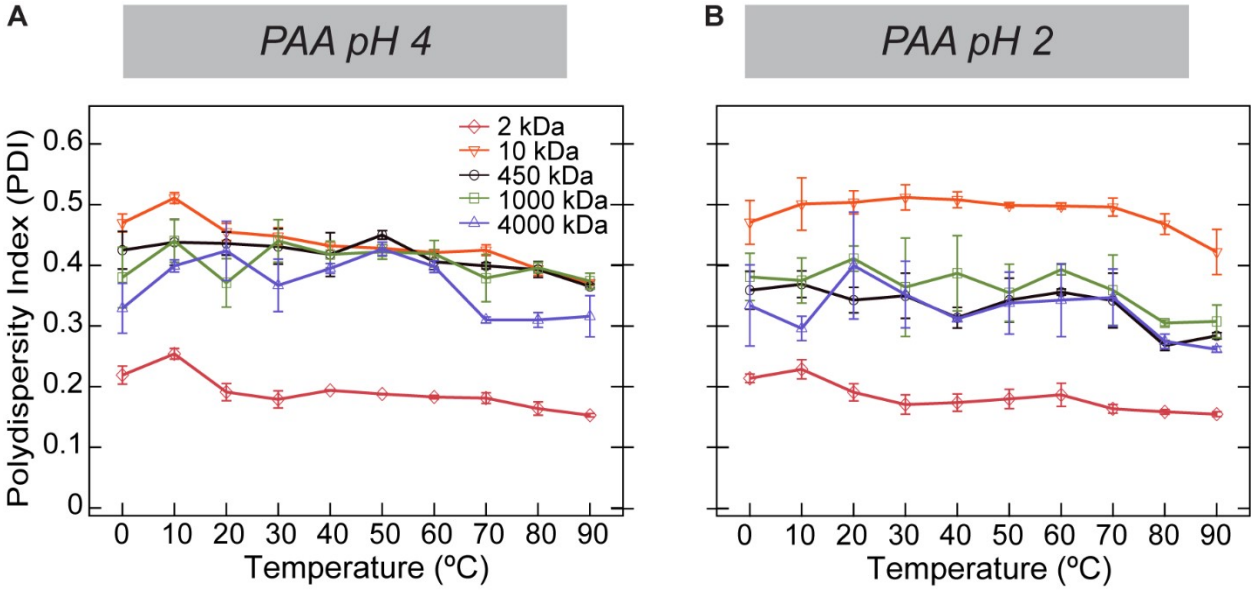

Figure S6. Polydispersity index (PDI) of nanoemulsions coated with 500 ppm PAA of varying molecular weight as a function of temperature at (A) pH 4 and (B) pH 2.

Table S2. Fitting parameters for C-H spectra of *d*-hexadecane emulsions in D_2O coated with 500 ppm PAA with varying molecular weight, corresponding to Figure 2A and Figure 3A.

Alkane C-H Stretches, *ssp* polarization						
PAA, pH 4						
Peak Assignment	**Parameters**	**2 kDa**	**10 kDa**	**450 kDa**	**1000 kDa**	**4000 kDa**
Methine Stretch	Amplitude	0.045 ± 0.001	0.0486 ± 0.0009	0.074 ± 0.002	0.073 ± 0.001	0.0544 ± 0.0009
	Phase	0	0	0	0	0
	Lorentzian linewidth	2	2	2	2	2
	Peak position	2868.2 ± 0.6	2873.3 ± 0.5	2871 ± 1	2865.3 ± 0.5	2870.7 ± 0.5
	Gaussian linewidth	62 ± 2	57.8 ± 0.8	42 ± 2	58.0 ± 0.8	60.0 ± 0.8
Methylene Symmetric Stretch	Amplitude	0.101 ± 0.001	0.105 ± 0.001	0.190 ± 0.003	0.156 ± 0.002	0.117 ± 0.001
	Phase	0	0	0	0	0
	Lorentzian linewidth	2	2	2	2	2
	Peak position	2931.1 ± 0.4	2930.9 ± 0.3	2931.5 ± 0.4	2928.0 ± 0.2	2930.6 ± 0.2
	Gaussian linewidth	15.8 ± 0.3	16.7 ± 0.2	17.1 ± 0.3	15.8 ± 0.2	15.7 ± 0.2
Non-resonant	Amplitude	0.003 ± 0.001	0.0031 ± 0.0007	0.010 ± 0.002	0.003 ± 0.001	0.0009 ± 0.0008
	Phase	0	0	0	0	0
pH 2						
Peak Assignment	**Parameters**	**2 kDa**	**10 kDa**	**450 kDa**	**1000 kDa**	**4000 kDa**
Methine Stretch	Amplitude	0.049 ± 0.003	0.04 ± 0.02	0.073 ± 0.002	0.194 ± 0.004	0.139 ± 0.003
	Phase	0	0	0	0	0
	Lorentzian linewidth	2	2	2	2	2
	Peak position	2871 ± 1	2871 ± 3	2872 ± 2	2872 ± 2	2871 ± 1
	Gaussian linewidth	134 ± 3	78 ± 5	60 ± 3	82 ± 4	111 ± 2
Methylene Symmetric Stretch	Amplitude	0.171 ± 0.004	0.17 ± 0.01	0.181 ± 0.004	0.460 ± 0.006	0.285 ± 0.005
	Phase	0	0	0	0	0
	Lorentzian linewidth	2	2	2	2	2
	Peak position	2932.7 ± 0.5	2933 ± 3	2932.0 ± 0.4	2929.3 ± 0.3	2931.9 ± 0.4
	Gaussian linewidth	14.3 ± 0.5	12 ± 1	15.4 ± 0.3	14.6 ± 0.2	14.9 ± 0.4
Non-resonant	Amplitude	0.003 ± 0.003	0.02 ± 0.01	0.012 ± 0.002	0.005 ± 0.004	0.004 ± 0.004
	Phase	0	0	0	0	0

Table S3. Fitting parameters for C=O spectra of *d*-hexadecane emulsions in D_2O coated with 500 ppm PAA with varying molecular weight, corresponding to Figure 5.

C=O Stretches, *ssp* polarization						
PAA, pH 4						
Peak Assignment	**Parameters**	**2 kDa**	**10 kDa**	**450 kDa**	**1000 kDa**	**4000 kDa**
Background Peak 1	Amplitude	0.08 ± 0.01	0.046 ± 0.002	0.170 ± 0.007	0.17 ± 0.07	0.18 ± 0.08
	Phase	3.14	3.14	3.14	3.14	3.14
	Lorentzian linewidth	10	10	10	10	10
	Peak position	1555 ± 42	1593 ± 7	1603 ± 6	1527 ± 16	1479 ± 34
	Gaussian linewidth	90 ± 43	31 ± 6	46 ± 7	32 ± 6	65 ± 7
C=O Stretch	Amplitude	0.14 ± 0.02	0.070 ± 0.002	0.118 ± 0.006	0.076 ± 0.005	0.101 ± 0.002
	Phase	0	0	0	0	0
	Lorentzian linewidth	5	5	5	5	5
	Peak position	1740 ± 5	1735 ± 2	1742 ± 5	1737 ± 2	1735 ± 2
	Gaussian linewidth	20 ± 5	25 ± 2	18 ± 3	14 ± 1	31 ± 2
Background Peak 2	Amplitude	0.091 ± 0.005	0.0318 ± 0.0009	0.065 ± 0.008	0.12 ± 0.02	0.09 ± 0.01
	Phase	3.14	3.14	3.14	3.14	3.14
	Lorentzian linewidth	10	10	10	10	10
	Peak Position	1862 ± 25	1956 ± 39	1830 ± 40	2134 ± 95	1935 ± 50
	Gaussian linewidth	113 ± 32	427 ± 67	88 ± 40	255 ± 64	179 ± 37
Non-resonant	Amplitude	0.03 ± 0.01	0.019 ± 0.002	0.007 ± 0.006	0.05 ± 0.01	0.03 ± 0.02
	Phase	0	0	0	0	0

Table S3. *Continued from previous page*

PAA, pH 2						
Peak Assignment	**Parameters**	**2 kDa**	**10 kDa**	**450 kDa**	**1000 kDa**	**4000 kDa**
Background Peak 1	Amplitude	0.028 ± 0.003	0.13 ± 0.01	0.029 ± 0.007	0.03 ± 0.01	0.19 ± 0.01
	Phase	3.14	3.14	3.14	3.14	3.14
	Lorentzian linewidth	10	10	10	10	0
	Peak position	1694 ± 10	1583 ± 14	1721 ± 6	1705 ± 10	1577 ± 11
	Gaussian linewidth	50 ± 11	63 ± 17	44 ± 4	47 ± 17	25 ± 8
C=O Stretch	Amplitude	0.010 ± 0.007	0.12 ± 0.02	0.012 ± 0.006	0.012 ± 0.005	0.163 ± 0.006
	Phase	0	0	0	0	0
	Lorentzian linewidth	5	5	5	5	5
	Peak position	1735 ± 6	1740 ± 7	1735 ± 4	1740 ± 3	1740 ± 4
	Gaussian linewidth	16 ± 6	20 ± 6	25 ± 10	13 ± 9	30 ± 2
Background Peak 2	Amplitude	0.7 ± 0.2	0.4 ± 0.1	1.04 ± 0.07	1.1 ± 0.6	0.67 ± 0.05
	Phase	3.14	3.14	3.14	3.14	3.14
	Lorentzian linewidth	10	10	10	10	10
	Peak Position	2539 ± 257	2205 ± 189	2506 ± 65	2539 ± 550	2305 ± 45
	Gaussian linewidth	365 ± 117	270 ± 111	360 ± 31	378 ± 269	309 ± 28
Non-resonant	Amplitude	0.23 ± 0.06	0.12 ± 0.05	0.34 ± 0.02	0.4 ± 0.2	0.25 ± 0.02
	Phase	0	0	0	0	0

Table S4. Fitting parameters for C-H spectra of *d*-hexadecane emulsions in D_2O coated with 500 ppm PMAA, corresponding to Figure S5A.

Alkane C-H Stretches, *ssp* polarization			
PMAA, 500 ppm			
Peak Assignment	**Parameters**	**pH 2**	**pH 4**
Polymer Endcap Methyl Stretch	Amplitude	0.054 ± 0.002	0.067 ± 0.004
	Phase	0	0
	Lorentzian linewidth	2	2
	Peak position	2887.0 ± 0.8	2890 ± 5
	Gaussian linewidth	121 ± 2	80 ± 8
Methyl Symmetric Stretch	Amplitude	0.097 ± 0.003	0.172 ± 0.005
	Phase	0	0
	Lorentzian linewidth	2	2
	Peak position	2939.8 ± 0.7	2937.1 ± 0.9
	Gaussian linewidth	22.1 ± 0.8	22.0 ± 0.6
Non-resonant	Amplitude	0.002 ± 0.002	0.003 ± 0.003
	Phase	0	0

Table S5. Fitting parameters for C=O spectra of *d*-hexadecane emulsions in D_2O coated with 500 ppm PMAA, corresponding to Figure S5B.

C=O stretches, *ssp* polarization			
PMAA, 500 ppm			
Peak Assignment	**Parameters**	**pH 2**	**pH 4**
Background Peak	Amplitude	0.16 ± 0.01	0.047 ± 0.001
	Phase	0	0
	Lorentzian linewidth	5	5
	Peak position	1536 ± 13	1470 ± 7
	Gaussian linewidth	87 ± 9	242 ± 8
C=O Stretch	Amplitude	0.051 ± 0.002	0.0205 ± 0.0006
	Phase	0	0
	Lorentzian linewidth	5	5
	Peak position	1735.6 ± 0.6	1736.4 ± 0.6
	Gaussian linewidth	22 ± 1	21 ± 1
Non-resonant Contribution	Amplitude	0.121 ± 0.004	0.0699 ± 0.0006
	Phase	0	0