Supplementary Information

Sum Frequency Generation Vibrational Spectroscopy of the Methacrylate-based Functional Monomers at the Hydrophilic Solid-Liquid Interface

Narendra M. Adhikari, Uvinduni I. Premadasa, and Katherine A. Cimatu

Department of Chemistry and Biochemistry, Ohio University Athens, 45701 OH USA

SFG Spectrum of a clean quartz window



Figure S1. A representative SSP spectrum of a clean quartz window collected at 2900 cm⁻¹ IR center.



Figure S2. PSS and SPS polarization spectra in the C-H stretching region from the hydrophilic quartz-monomer interface. (a) 2-Hydroxyethyl methacrylate (HEMA) (b), 2-Methoxyethyl methacrylate (MEMA), (c) 2-Isopropoxyethyl methacrylate (IEMA), (d) 2-Tertbutoxyethyl methacrylate (TEMA) and (e) 2-Phenoxyethyl methacrylate (PhEMA).





Figure S3. SFG spectra for HEMA monomer at hydrophilic quartz interface in O-H stretching region.



Figure S4. SFG spectrum of (a) 7% acetic acid and (b) IEMA both at SSP polarization combination in the C=O region (acquired for 9 minutes) with IR beam centered at 1750 cm⁻¹.



Figure S5. SSP spectra of the MEMA monomer obtained in the same day from three different regions: C=O, CH, and OH regions at the hydrophilic quartz-monomer interface.



Figure S6. The SSP spectra of the MEMA monomer characterized at two different interfaces: air-monomer and hydrophilic quartz-monomer interfaces.

Spectral Fitting

Spectral fitting was done using Mathematica software. The detail of the fitting is available in our earlier publications.^{1, 2} The spectra are fitted using the formula for SFG intensity as given in equation S1:

$$I_{SFG} = n_1 + e^{-\frac{(\omega - \omega_{IR})^2}{(2\delta\omega)^2}} \left| ne^{-ip} + \sum \frac{A_q}{\omega_{IR} - \omega_q - i\Gamma_q} \right|^2$$
(S1)

Where n_1 is a non-resonant contribution, $\delta \omega$ is the spectral width of the broadband pulse, n is baseline correction factor, p is the phase factor. A_q is the amplitude, ω_q is the vibrational frequency, and Γ_q is peak width or damping constant of vibrational mode q.

					HEMA					
	Peak		SSP		РРР			PSS		
		Estimate	Standard Error	95% CL	Estimate	Standard Error	95% CL	Estimate	Standard Error	95% CL
1	ω (cm- 1)	2800	3	5	2787	1	1	2775	2	5
	A	13	2	4	46	1	3	9	2	5
	Г	50	4	9	40	1	2	50	7	1E+0 1
2	ເ (cm⁻¹)	2854	3E-01	1	2855	4E-01	4E-01	2851	1	3
	A	28	1	3	37	2	4	10	2	4
	Г	18	1	1	25	1	2	25	2	5
3	ເ (cm⁻¹)	2880	2E-01	0	2896	3E-01	3E-01	2889	1	3
	A	26	2	4	38	3	5	10	3	6
	Г	15	1	1	19	1	1	25	4	8
4	ຝ (cm⁻¹)	2920	1	2	2927	6E-01	6E-01	2916	1	2
	A	17	4	8	3E+01	3E+01	6E+01	1	1	2
	Г	19	2	4	23	1	2	11	4	7
5	ຝ (cm⁻¹)	2945	3E-01	1	2964	1E-01	1E-01	2966	1	2
	A	37	2	4	37	1	1	3	3E-01	1
	Г	16	1	1	10	1E-01	2E-01	10	1	2
	n	7E-01	1E-01	2E-01	4E-01	4E-02	8E-02	5E-01	1E-01	1E- 01
	р	4	2E-01	3E-01	4	1E-01	2E-01	11	3E-02	5E- 02
	n1	6E-13	8E-02	2E-01	1E-11	2E-02	3E-02	1E-02	5E-02	1E- 01
	R^2	R^2 0.9917			0.9406		0.9831			

Table S1. Fitting parameters for SSP and PPP spectra in C-H stretching region of 2-Hydroxyethyl methacrylate (HEMA)

					MEMA					
	Peak		SSP		РРР			PSS		
		Estimate	Standard Error	95% CL	Estimate	Standard Error	95% CL	Estimate	Standard Error	95% CL
1	ω (cm- 1)	2722	3	6	2778	5E+04	1E+05	2778	1E+01	5
	A	1	3E-01	6E-01	4E-06	2E-02	5E-02	0	7	5
	Г	9	3	6	1E-01	1E+03	3E+03	0	2E+01	1E+0 1
2	ເ (cm⁻¹)	2853	0.9	2	2857	4E-01	8E-01	2857	4	3
	A	25	2	5	32	1	2	32	4	4
	Г	20	2	3	25	1	1	25	9	5
3	ເ (cm⁻¹)	2880	5E-01	1	2894	3E-01	3E-01	2894	2	3
	A	15	3	6	23	2	4	23	2	6
	Г	13	1	3	16	1	2	16	6	8
4	ຝ (cm⁻¹)	2920	1	3	2925	3E-01	3E-01	2925	6	2
	Α	19	6	1E+01	5	3	7	5E+01	6	2
	Г	21	3	6	22	1	2	22	1E+01	7
5	ເ (cm⁻¹)	2950	6E-01	1	2964	2E-01	2E-01	2964	1	2
	A	27	3	5	55	1	2	55	1	1
	Г	16	1	2	13	2E-01	5E-01	13	1	2
	n	2E-01	1E-01	2E-01	1	2E-02	3E-02	1E-01	0	1E- 01
	р	4	1	2	3	1E-01	3E-01	0	2	5E- 02
	n1	0	2E-02	3E-02	2E-04	1E-02	2E-02	1E-02	1E-02	1E- 01
	R^2		0.9833			0.9655		0.9611		

Table S2. Fitting parameters for SSP and PPP spectra in C-H stretching region of 2-Methoxyethyl methacrylate (MEMA)

	IEMA									
	Peak		SSP		РРР			PSS		
		Estimate	Standard	95%	Estimate	Standard	95%	Estimate	Standar	95%
			Error	CL		Error	CL		d Error	CL
1	ω	2800	5	1E+01	2768	1	1	2762	5	1E+01
	(cm-1)									
	A	9	3	5	100	3	7	29	2E+01	3E+01
	Г	45	7	1E+01	62	1	1	50	5	1E+01
2	ເ (cm⁻¹)	2853	5E-01	1	2855	5E-01	5E-01	2850	3	7
	А	27	2	5	26	2	5	5	3	5
	Г	21	1	2	25	1	2	25	8	2E+01
3	ເ (cm⁻¹)	2880	3E-01	1	2895	4E-01	4E-01	2898	1	2
	А	19	2	4	18	2	3	3E-01	3E-01	1
	Г	13	1	1	16	1	2	2	2	3
4	ය (cm⁻¹)	2919	1	1	2930	4E-01	4E-01	2926	18	4E+01
	A	14	3	7	20	2	4	2	3	6
	Г	19	2	4	17	1	2	25	4E+01	8E+01
5	ເ (cm⁻¹)	2950	5E-01	1	2964	2E-01	2E-01	2964	3	7
	А	27	1	2	26	1	1	3	1	3
	Г	15	1	1	10	3E-01	5E-01	11	5	1E+01
	n	5E-01	1E-01	2E-01	4E-01	8E-02	2E-01	5E-01	1E-02	3E-02
	р	4	2E-01	4E-01	5	0	0	1	1	1
	n1	6E-03	7E-02	1E-01	5E-12	3E-02	5E-02	9E-02	1E-02	1E-02
	R^2		0.9820			0.9705			0.9490	

 Table S3. Fitting parameters for SSP and PPP spectra in C-H stretching region of 2-Isopropoxyethyl methacrylate (IEMA)

	TEMA									
	Peak		SSP	РРР				PSS		
		Estimate	Standard Error	95% CL	Estimate	Standar d Error	95% CL	Estimate	Standard Error	95% CL
1	ධ (cm⁻¹)	2800	2	4	2794	1	1	2800	3E+01	6E+01
	А	25	3	5	50	2	4	1	5	1E+01
	Г	50	4	8	48	1	3	27	7E+01	1E+02
2	ຝ (cm⁻¹)	2854	3E-01	1	2856	4E-01	4E-01	2859	6	1E+01
	А	24	1	2	34	2	5	22	3E+01	6E+01
	Г	16	0	1	25	1	2	25	1E+01	2E+01
3	ධ (cm⁻¹)	2880	2E-01	0	2895	2E-01	2E-01	2889	7	1E+01
	А	25	2	3	42	2	5	19	3E+01	6E+01
	Г	14	0	1	22	1	1	25	1E+01	3E+01
4	ິ (ເm⁻¹)	2920	0	1	2930	6E-01	6E-01	2923	8E+06	2E+06
	А	7	2	4	2E+01	2	5	0.00	3	7
	Г	14	2	4	22	2	4	19	1E+07	3E+07
5	ධ (cm⁻¹)	2950	4E-01	1	2965	2E-01	2E-01	2968	5	1E+01
	А	38	1	2	24	1	1	8	5	9
	Г	18	0	1	11	2E-01	5E-01	25	7	1E+01
	n	3E-01	0	0	1	6E-02	1E-01	1	1E-01	1E-01
	р	3	3E-01	6E-01	4	0	1E-01	2	3E-02	6E-02
	n1	9E-02	8E-03	2E-02	0	7E-02	1E-01	0	7E-02	1E-01
	R^2	0.9932				0.9803			0.9347	

Table S4. Fitting parameters for SSP and PPP spectra in C-H stretching region of 2-Tertbutoxyethyl methacrylate (TEMA).

					PhEMA						
	Peak		SSP			РРР			PSS		
		Estimate	Standard Error	95% CL	Estimate	Standar d Error	95% CL	Estimate	Standar d Error	95% CL	
1	ር (cm- 1)	2776	4	8	2800	2	2	2769	1E+01	2E+0 1	
	A	18	5	1E+01	54	4	9	5	8	1E+0 1	
	Г	50	7	1E+01	49	2	5	50	4E+01	8E+0 1	
2	₩ (cm ⁻¹)	2854	1	1	2855	1	1	2859	2E+01	4E+0 1	
	A	29	4	7	35	6	1E+01	5	2E+01	4E+0 1	
	Г	21	1	2	25	2	4	25	2E+01	4E+0 1	
3	ω (cm⁻¹)	2880	4E-01	1	2892	1E-01	1E-01	2889	2E+01	4E-01	
	A	8	1	3	40	6	11	4	1E+02	7E+0 1	
	Г	11	1	2	23	2	4	2E+01	1E+01	2E+0 2	
4	ω (cm⁻¹)	2917	1	1	2930	6E-01	6E-01	2916	17	34	
	A	14	4	8	4E+01	5	1E+01	5	2E+01	3E+0 1	
	Г	18	2	4	25	2	4	22	2E+01	4E+0 1	
5	ω (cm⁻¹)	2949	1	2	2964	3E-01	3E-01	2974	4	9	
	А	16	1	3	21	1	2	2	1	2	
	Г	16	1	3	11	4E-01	1	12	6	1E+0 1	
	n	6E-01	2E-01	4E-01	7E-01	1E-01	2E-01	6E-01	3E-01	5E-01	
	р	4	2E-01	4E-01	4	1E-01	2E-01	4	2E-01	4E-01	
	n1	0	2E-01	3E-01	0	1E-01	2E-01	0	2E-01	5E-01	
	R^2		0.9947			0.9904			0.9535		

Table S5. Fitting parameters for SSP and PPP spectra in C-H stretching region of 2-Phenoxyethyl methacrylate (PhEMA)

 Table S6. Fitting parameters for SSP spectrum in C=O stretching region of 2-Hydroxyethyl methacrylate (HEMA).

HEMA							
		Estimate	Standard				
			Error				
	ω (cm⁻¹)	1734	1				
peak 1	А	1.29	2E-02				
	Г	19	4E-01				

n	2E-02	7E-04
р	88.91	3E-02
n1	2E-03	8E-06
R^2	0.94	466

Table S7. Fitting parameters for SSP spectrum in C=O stretching region of 2-Methoxyethyl methacrylate (MEMA).

MEMA							
		Estimate	Standard				
			Error				
	ω (cm ⁻¹)	1729	2E-01				
peak 1	А	3.27	2E-02				
	Г	17	3E-01				
	n	4E-02	1E-03				
	р	114	1E-02				
	n1	2E-04	7				
	R^2	0.9	572				

Table S8. Fitting parameters for SSP spectrum in C=O stretching region of 2-Isopropoxyethyl methacrylate (IEMA)

IEMA							
		Estimate	Standard				
			Error				
	ω (cm⁻¹)	1729	4E-06				
peak 1	А	1.98	5E-07				
	Г	15	4E-06				
	n	3E-02	1E-08				
	р	100	4E-07				
	n1	1E-03	2E-10				
	R^2	0.9	685				

Table S9. Fitting parameters for SSP spectrum in C=O stretching region of 2-Tertbutoxyethyl methacrylate (TEMA).

TEMA						
		Estimate	Standard			
			Error			
	ω (cm ⁻¹)	1734	2E-01			
peak 1	А	1.65	2E-02			
	Г	18	3E-01			
	n	2E-02	8E-04			
	р	101	6E-02			
	n1	1E-03	1E-05			

R^2	0.9517
-----	--------

	PhEMA						
			Standard				
			Error				
	ω (cm⁻¹)	1722	3E-01				
peak 1	А	1.65	8E-02				
	Г	19	4E-01				
	n	3E-02	7E-04				
	р	101	1E-01				
	n1	1E-03	2E-05				
	R^2	0.9	790				

Table S10. Fitting parameters for SSP spectrum in C=O stretching region of 2-Phenoxyethyl methacrylate (PhEMA)

References

- 1. S. C. Chan, J. H. Jang and K. L. A. Cimatu, *The Journal of Physical Chemistry C*, 2016.
- 2. K. A. Cimatu, S. C. Chan, J. H. Jang and K. Hafer, *The Journal of Physical Chemistry C*, 2015, **119**, 25327-25339.