SUPPORTING INFORMATION

Conformational Changes of the Methacrylate-Based Monomers at the Air-Liquid Interface Due to Bulky Substituents

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MATERIALS AND METHODS

Synthesis of 2-isopropoxyethyl methacrylate (IEMA), and 2-tertbutoxyethyl methacrylate (TEMA)

IEMA. To a solution of 2-isopropoxy ethanol (37.2 g, 0.36 mol) in pyridine (102 mL) and dichloromethane (68 mL), methacryloyl chloride (41.9 g, 0.40 mol) and dichloromethane (21 mL) were added. The reaction was carried out below 5°C in an ice bath, and once all the reagents are added, the mixture was continuously stirred at room temperature overnight. The reaction mixture was washed with 5% sodium bicarbonate solution (1.05 L) and deionized water (0.45 L). The mixture was dried with calcium sulfate and filtered after washing. 1% (w/v) monomethyl hydroquinone (MEHQ) was added to the solution before purification. The Vigreux distillation of the product produced a clear liquid (86 mL, 82.6 g, 62% yield, and 97% purity). ^{1}H NMR δ 1.17

(-C(CH_3)$_2$, d, 6H, J=6.2 Hz), δ 1.95 (alpha CH_3, s, 3H), δ 3.62 (-CH-O, m, 1H J= 6.0, 6.1, 6.1, 6.1 Hz), δ 3.66 (-O-CH_2, t, 2H, J= 5.1, 4.9 Hz), δ 4.26 (-O-CH_2CH_2, t, 2H, J= 5.0, 5.0 Hz), δ 5.56 (-C=CH, s, 1H),δ 6.12 (-C=CH, s, 1H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 167.2 (C=O), δ 136.1 (C=), δ 125.5 (=CH_2), δ 71.9 (CH), δ 65.8(CH_2), δ 64.1 (CH_2), δ 21.9 (2 CH_3), δ 18. 2 (CH_3); MS (ESI FT-MS) m/z 173.11732 (calcd for $[C_9H_{16}O_3 + H]^+$, 173.11778).^{1}H and ^{13}C NMR spectra of IEMA monomer are available in Figure S1 in SI.

TEMA. This monomer was prepared similarly to IEMA**.** To a solution of 2-tertbutoxy ethanol (58.0 g, 0.49 mol) in pyridine (108 mL) and dichloromethane (162 mL), methacryloyl chloride (57.6 g, 0.55 mol) and dichloromethane (30 mL) were added. The reaction was carried out below 5°C in an ice bath, and once all the reagents are added, the mixture was continuously stirred at room temperature overnight. The reaction mixture was washed with 5% sodium bicarbonate solution (1.05 L) and deionized water (0.45 L). The mixture was dried with calcium sulfate and filtered after washing.1% (w/v) monomethyl hydroquinone (MEHQ) was added to the solution before purification The Vigreux distillation of the product produced a clear liquid (99 mL, 91.8 g, 50% yield, and 98% purity). ^{1}H NMR δ 1.17 (-C(CH_3)$_3$, s, 9H), δ 1.92 (alpha CH_3, s, 3H), δ 3.58 (-O-CH_2, t, 2H, J= 5.2, 5.2 Hz), δ 4.21 (-OCH_2CH_2, t, 2H, J= 5.2, 5.2 Hz), δ 5.53 (-C=CH, s, 1H), δ 6.09 (-C=CH, s, 1H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 167.2 (C=O), δ 136.2 (C=), δ 125.3 (=CH_2), δ 73.1 (C), δ 64.4 (CH_2), δ 59.8 (CH_2), δ 27.3 (3 CH_3), δ 18.2 (CH_3); MS (ESI FT-MS) m/z 187.13290 (calcd for $[C_{10}H_{18}O_3 + H]^+$, 187.13342). ^{1}H and ^{13}C NMR spectra of TEMA monomer are available in Figure S2 in SI.

^{1}H and ^{13}C NMR of monomers.

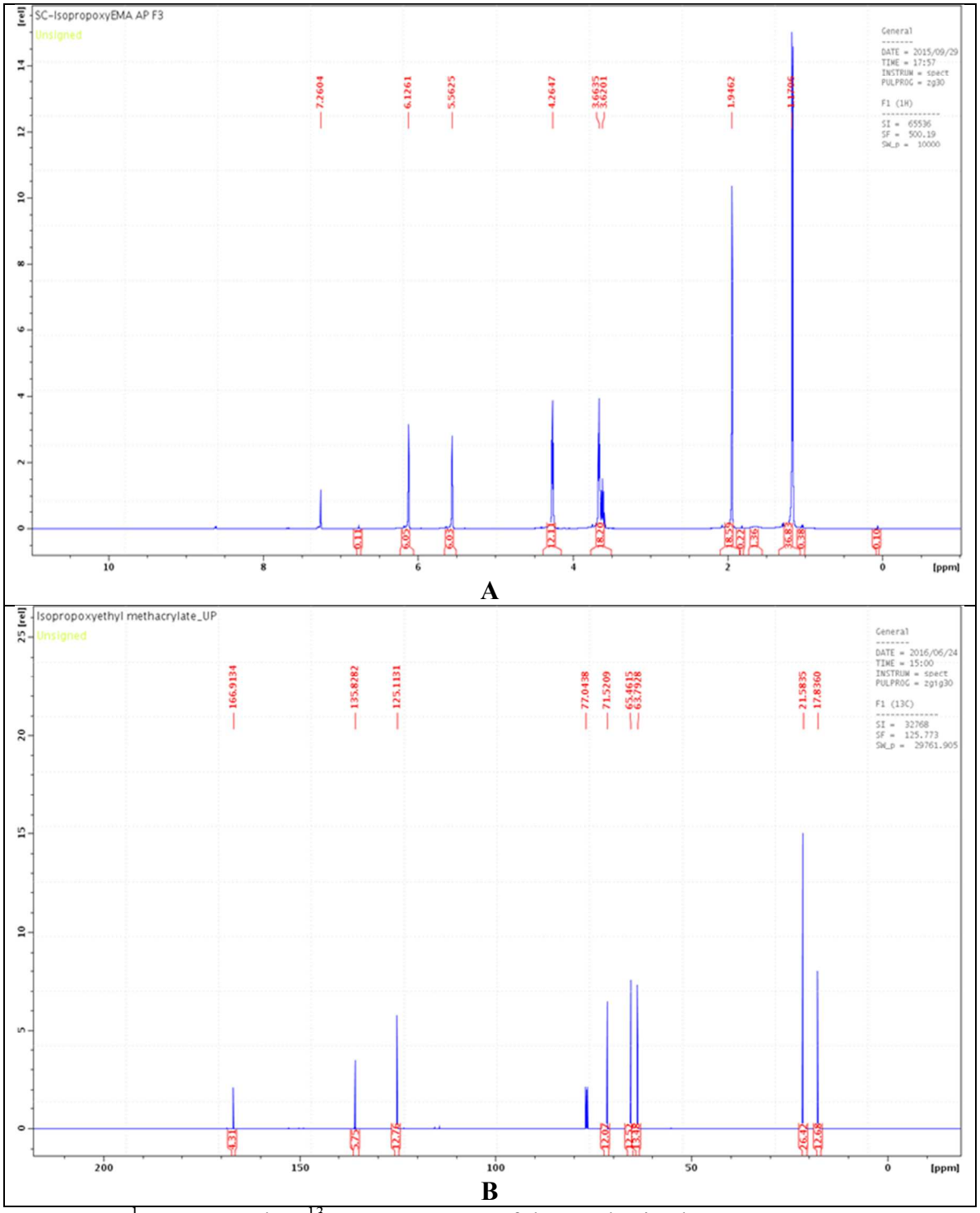

Figure S1. A. ^{1}H NMR and B. ^{13}C NMR spectra of the synthesized IEMA monomer

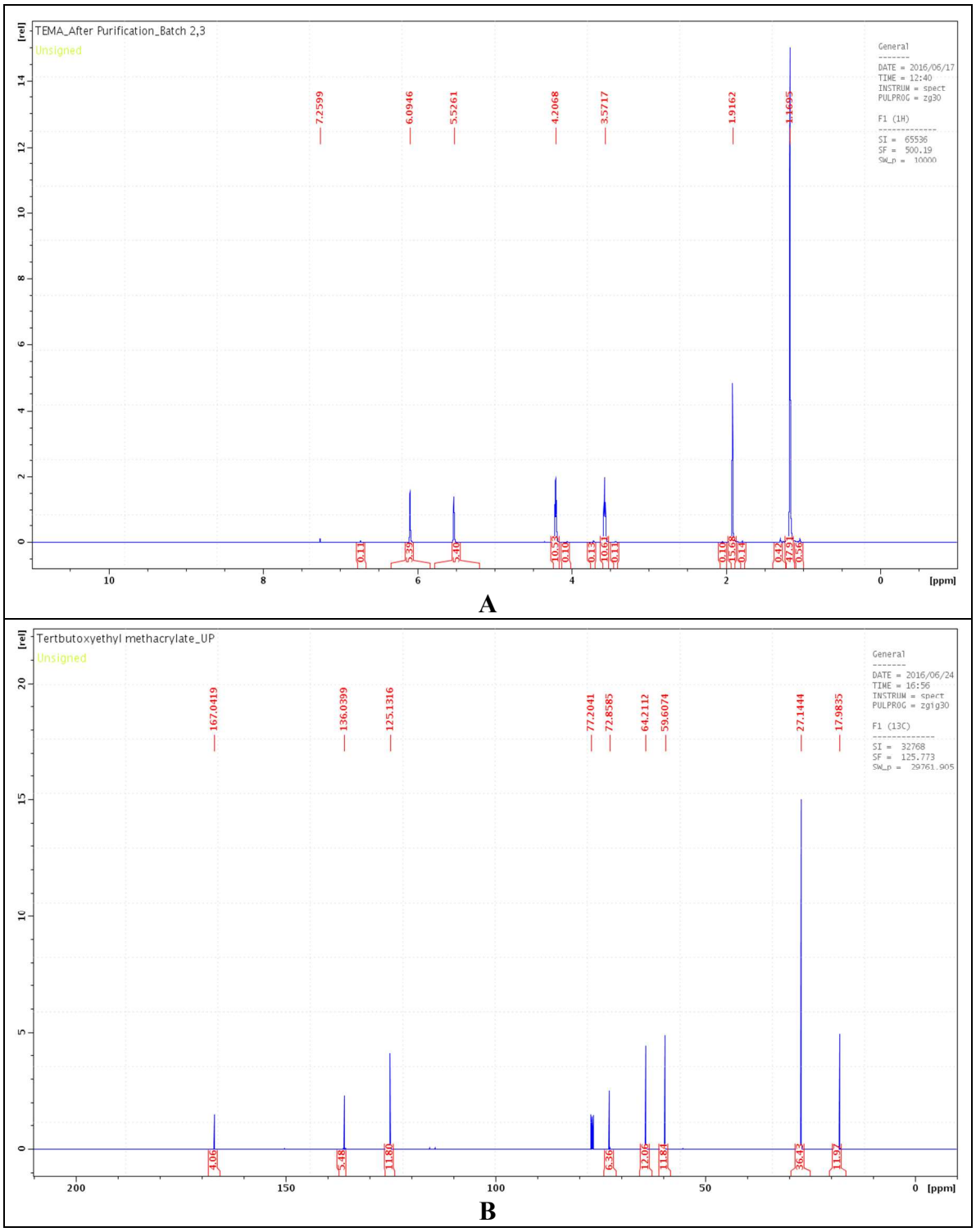

Figure S2. A. ^{1}H and B. ^{13}C NMR spectra of the synthesized TEMA monomer.

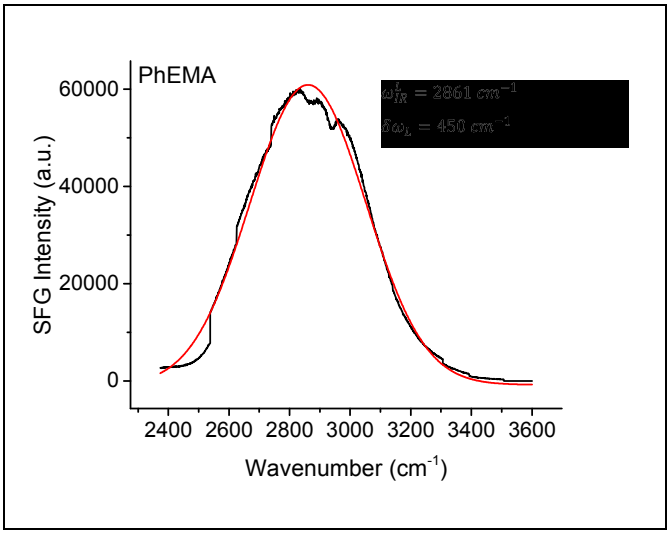

Figure S3. A representative gold spectrum obtained from the sum of four gold spectra obtained at the for IR centers of 2800cm^{-1}, 2900 cm^{-1}, 3000 cm^{-1}, and 3100 cm^{-1}. The spectrum was fitted using the Gaussian equation to determine the ω_{IR}^{L} and $\delta\omega_L$. These two parameters are used in the SFG curve-fitting equation (Equation 2 in the manuscript). The values obtained were used to fit the PhEMA monomer SSP and PPP spectra.

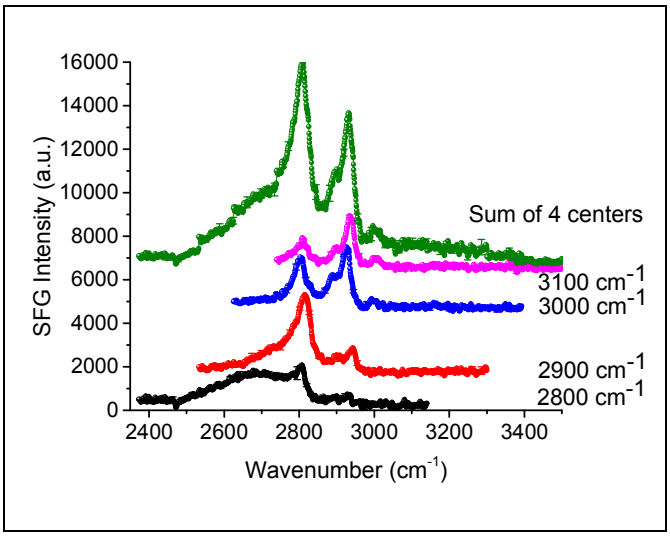

Figure S4. Example SFG SSP spectrum collected at different centers from 2800 cm^{-1} (black), 2900 cm^{-1} (red), 3000 cm^{-1} (blue), and 3100 cm^{-1} (magenta). The green SFG spectrum is the sum of the spectra from the four centers, which constitute the distribution of several peaks.

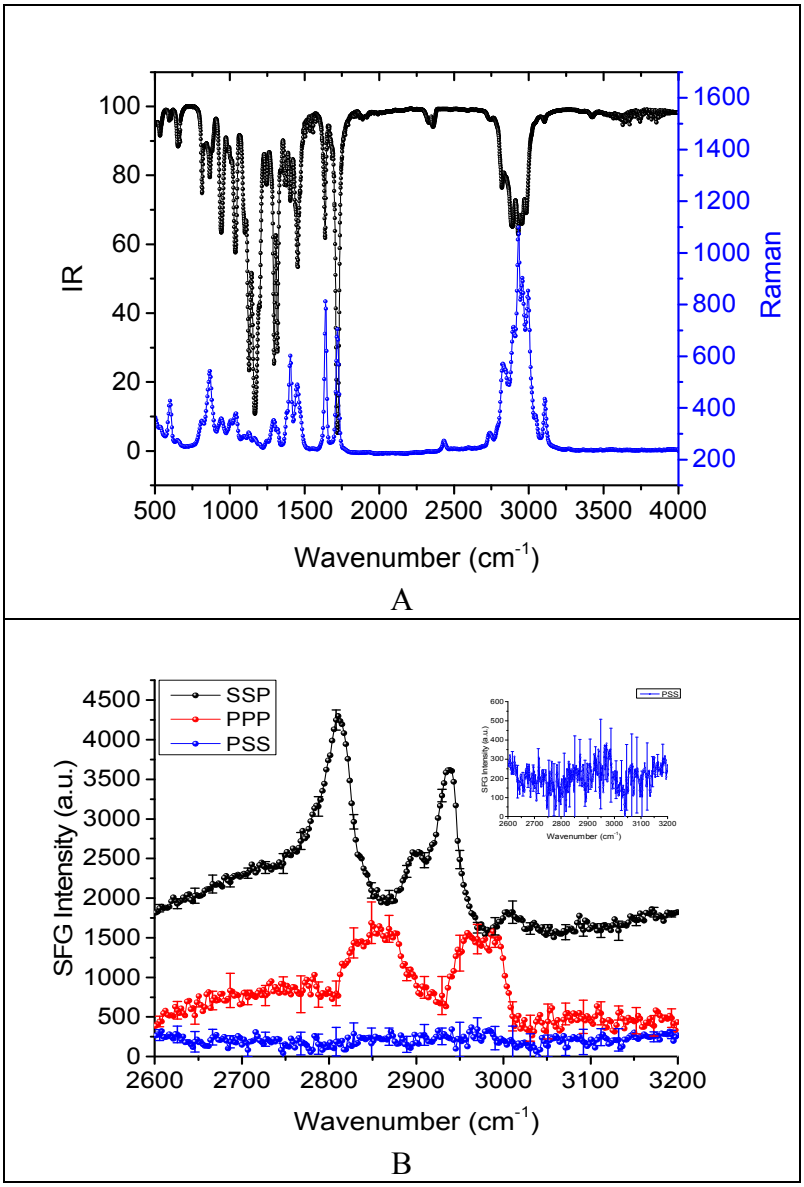

Figure S5. A. IR and Raman spectra of the 2-methoxyethyl methacrylate (MEMA) monomer are presented from 500-4000 cm^{-1}. B. SFG spectra of MEMA monomer at SSP PPP and PSS polarization combinations plotted with vertcicle offset for clarity with SFG spectrum of PSS polarization shown as the inset . The vibrational peak assignments are available in Table S1.

Table S1. List the peak positions of 2-methoxyethyl methacrylate (MEMA) including their suggested peak vibrational assignments.

Vibrational Assignment	MEMA				
	IR	Raman	SSP	PPP	PSS
1) Unassigned[1]	2732	2732	2751	2751	
2) O-CH_3 symmetric stretch[2-5]	2820	2826	2819	2819	
3) CH_2 symmetric stretch (SSP)[2, 5-8] / Fermi related methylene vibrational mode (PPP)[9-10]	2842	2846	2861	2861	2846
4) CH_3 symmetric stretch[7-9, 11]	2890	2897	2905	2905	
5) CH_3 symmetric stretch (FR) [9, 12-13]	2930	2931	2937		2934
6) CH_3 asymmetric stretch (in-plane)	2956	2958		2959	2968
7) O- CH_3 asymmetric stretch[7, 9, 14-17] / CH_3 asymmetric stretch (out-of-plane)	2983	2994		2985	
8) Alkene- methylene CH stretch[18]	3020	2999	3011		
10) Presence of hydroxyl peaks of adsorbed water[16, 19-21]	3104, 3150	3108, 3153	3149	3149	3065

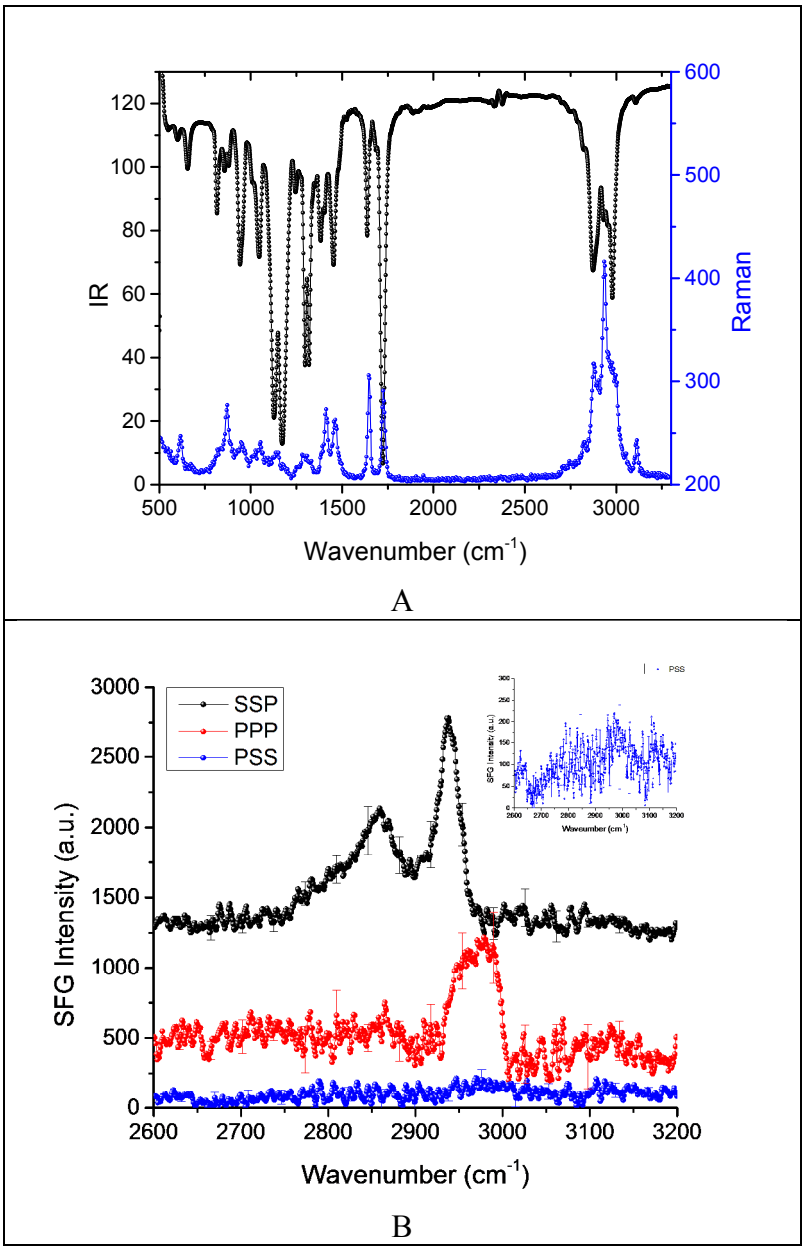

Figure S6. A. IR and Raman spectra of the 2-ethoxyethyl methacrylate (EEMA) monomer are presented from 500-4000 cm^{-1}. B. SFG spectra of EEMA monomer at SSP PPP and PSS polarization combinations plotted with vertcicle offset for clarity with SFG spectrum of PSS polarization shown as the inset. The vibrational peak assignments are available in Table S2.

Table S2. List the peak positions of 2-ethoxyethyl methacrylate (EEMA) including their suggested peak vibrational assignments.

Vibrational Assignment	EEMA				
	IR	**Raman**	**SSP**	**PPP**	**PSS**
1) Unassigned[1]	2747	2741	2756		
3) CH_2 symmetric stretch(SSP)[2, 5-8]/ Fermi related methylene vibrational mode (PPP)[9-10]	2869	2875	2868	2868	2856
4) CH_3 symmetric stretch[7-9, 11]	2897	2904	2903	2903	
5) CH_3 symmetric stretch (FR) [9, 12-13]	2932	2934	2939		
6) CH_3 asymmetric stretch (in-plane) [14, 22]	2953	2955		2968	
7) CH_3 asymmetric stretch (out-of-plane)[7, 9, 14-17]	2979	2979		2990	2976
8) Alkene- methylene CH stretch[18]	3019	3001	3016		
10) Presence of hydroxyl peaks of adsorbed water[16, 19-21]	3104	3114		3098	3120

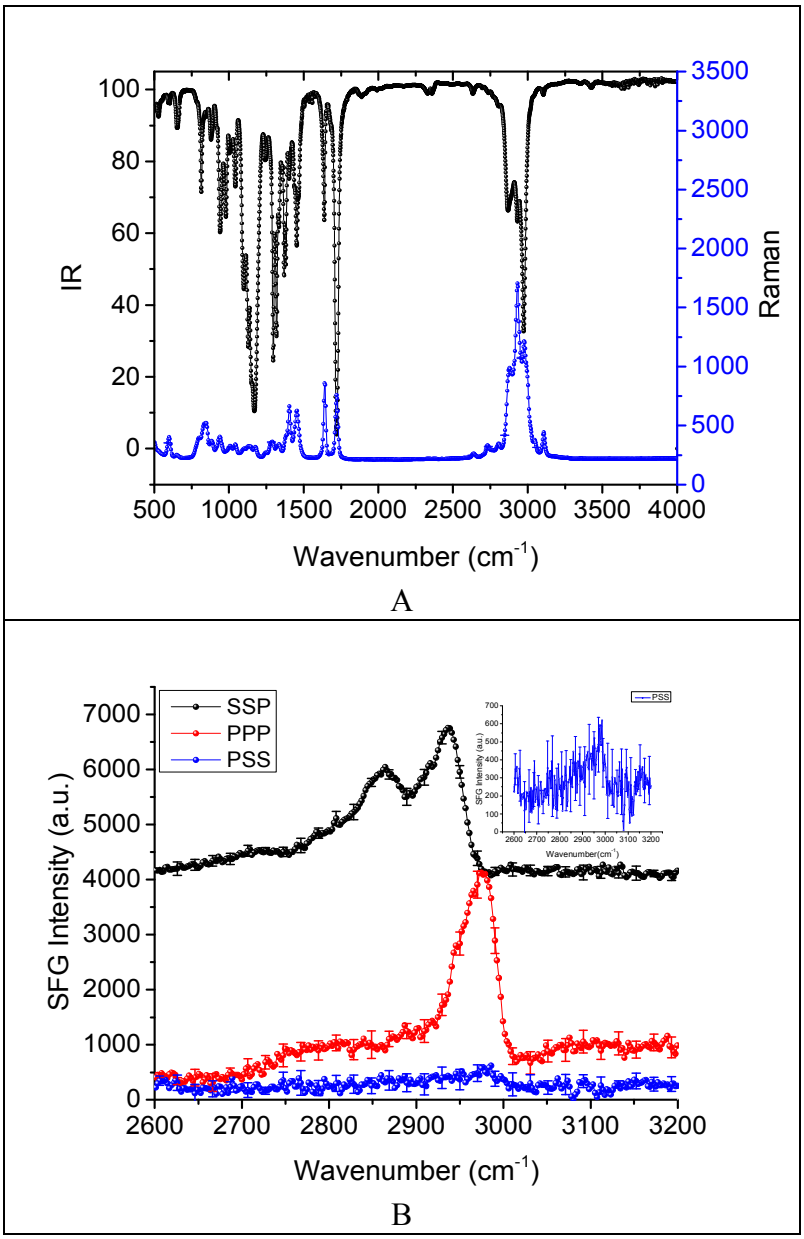

Figure S7. A. IR and Raman spectra of the 2-isoproxyethyl methacrylate (IEMA) monomer are presented from 500-4000 cm^{-1}. B. SFG spectra of IEMA monomer at SSP PPP and PSS polarization combinations plotted with vertcicle offset for clarity with SFG spectrum of PSS polarization shown as the inset. The vibrational peak assignments are available in Table S3.

Table S3. List the peak positions of 2-isopropoxyethyl methacrylate (IEMA) including their suggested peak vibrational assignments.

Vibrational Assignment	IEMA				
	IR	**Raman**	**SSP**	**PPP**	**PSS**
1) Unassigned[1]	2738	2739	2737		
3) CH_2 symmetric stretch (SSP) [2-3, 7-9] /Fermi related methylene vibrational mode (PPP)[9-10]	2868	2877	2869	2869	2870
4) CH_3 symmetric stretch[8-9, 12-13]	2900	2890	2910	2910	
5) CH_3 symmetric stretch (FR) [9, 12-13]	2930	2930	2938	2938	2929
7) CH_3 asymmetric stretch[7, 15]	2973	2977		2980	2975
8) Alkene-methylene CH stretch[18]	3021	3024	3017		
10) Presence of hydroxyl peaks of adsorbed water[16, 19-21]	3107	3106		3089	3064

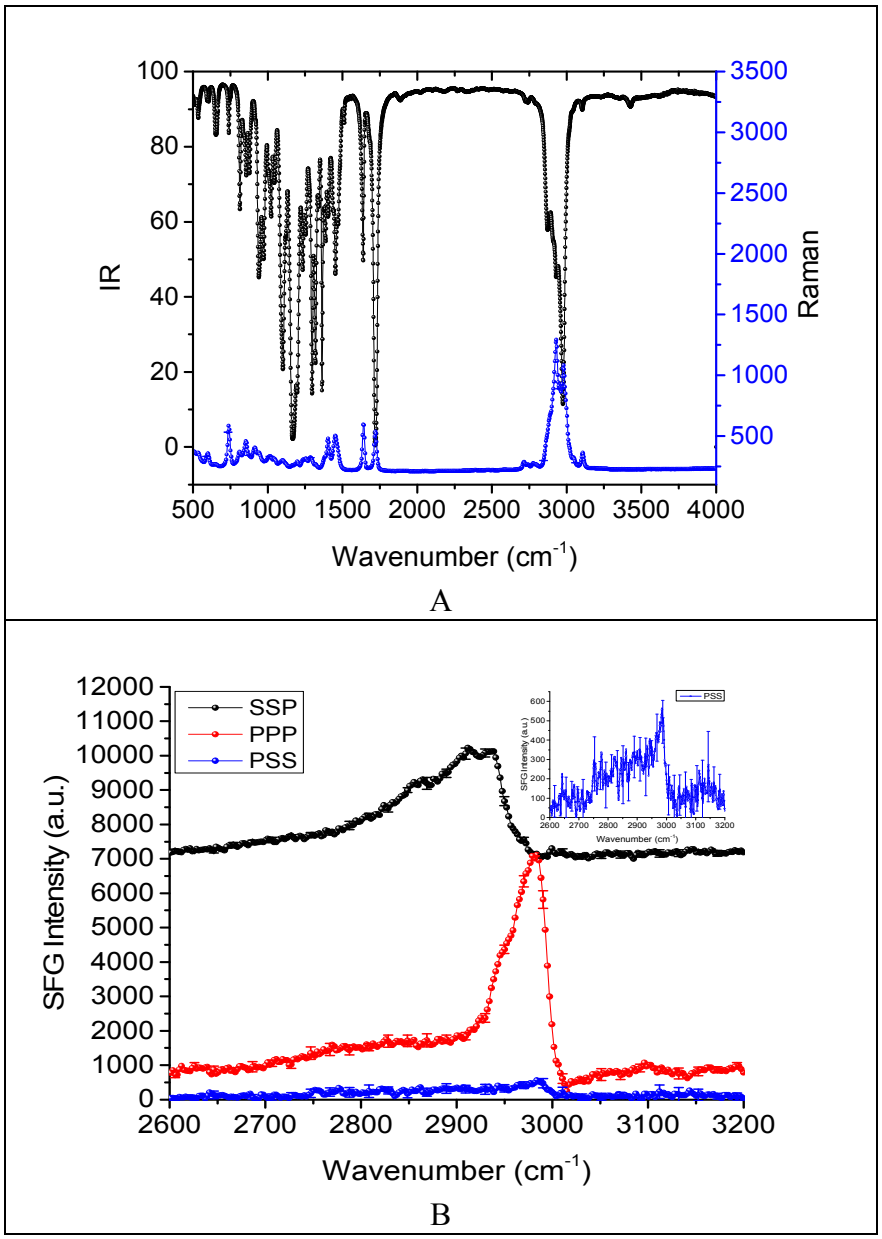

Figure S8. A. IR and Raman spectra of the 2-tertbutoxyethyl methacrylate (TEMA) monomer are presented from 500-4000 cm^{-1}. B. SFG spectra of TEMA monomer at SSP PPP and PSS polarization combinations plotted with vertcicle offset for clarity with SFG spectrum of PSS polarization shown as the inset. The vibrational peak assignments are available in Table S4.

Table S4. List the peak positions of 2-terbutoxyethyl methacrylate (TEMA) including their suggested peak vibrational assignments.

Vibrational Assignment	TEMA				
	IR	**Raman**	**SSP**	**PPP**	**PSS**
1) Unassigned[1]	2738	2743	2739		
3) CH_2 symmetric stretch (SSP)[2-3,7-9] /Fermi related methylene vibrational mode (PPP)[9-10]	2872	2873	2872	2872	
4) CH_3 symmetric stretch[8-9, 12-13]	2908	2899	2912	2912	
5) CH_3 symmetric stretch (FR) [9, 12-13]	2929	2931	2935	2935	2934
7) CH_3 asymmetric stretch[7, 15]	2974	2979		2982	2984
8) Alkene-Methylene CH stretch[18]	3021	3028	3016		
10) Presence of hydroxyl peaks of adsorbed water[21, 25-27]	3103	3108		3106	3057

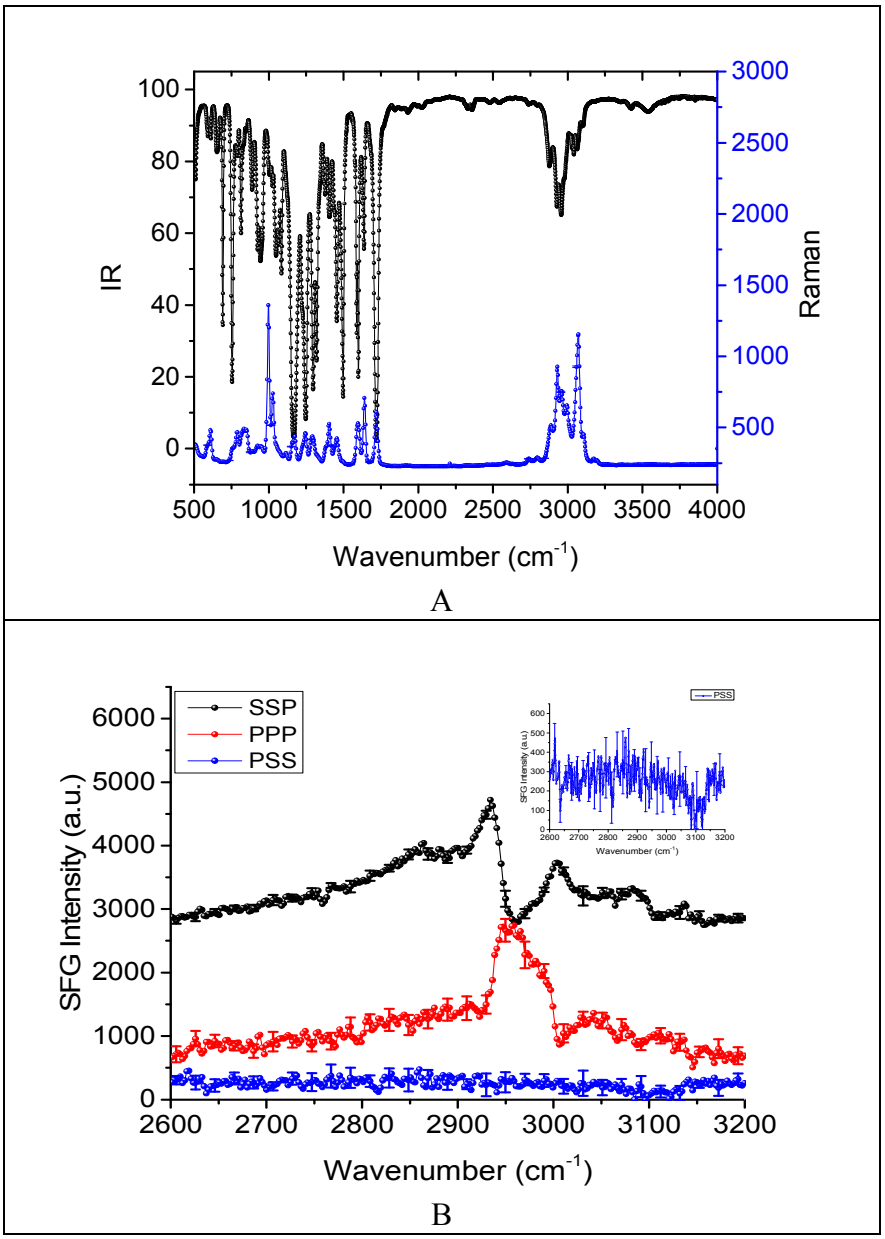

Figure S9. A. IR and Raman spectra of the 2-phenoxyethyl methacrylate (PhEMA) monomer are presented from 500-4000 cm^{-1}. B. SFG spectra of PhEMA monomer at SSP PPP and PSS polarization combinations plotted with vertcicle offset for clarity with SFG spectrum of PSS polarization shown as the inset. The vibrational peak assignments are available in Table S5.

Table S5. List the peak positions of 2-phenoxyethyl methacrylate (PhEMA) including their suggested peak vibrational assignments.

Vibrational Assignment	PhEMA				
	IR	**Raman**	**SSP**	**PPP**	**PSS**
1) Unassigned[1]	2739	2740	2738		
3) CH_2 symmetric stretch[2-3, 7-9]	2876	2866	2861		2859
4) α-CH_3 symmetric stretch[8-9, 12-13]	2879	2885	2902	2902	
5) CH_3 symmetric Stretch (FR) [9, 12-13]/ CH_2 asymmetric Stretch[14, 22]	2928	2930	2934	2934	
6) in-plane αCH_3 asymmetric Stretch	2954	2957		2959	2950
7) out-of-planeα-methyl (-CH_3) asymmetric stretch[3, 7, 11, 14-17]	2979	2980		2985	2978
8) Alkene- methylene CH stretch[18]	3014	3001	3005		
9) Aromatic CH stretch[23]	3043, 3064	3043, 3071	3053	3053	
10) Presence of hydroxyl peaks of adsorbed water[21, 25-27]	3190	3172	3151		

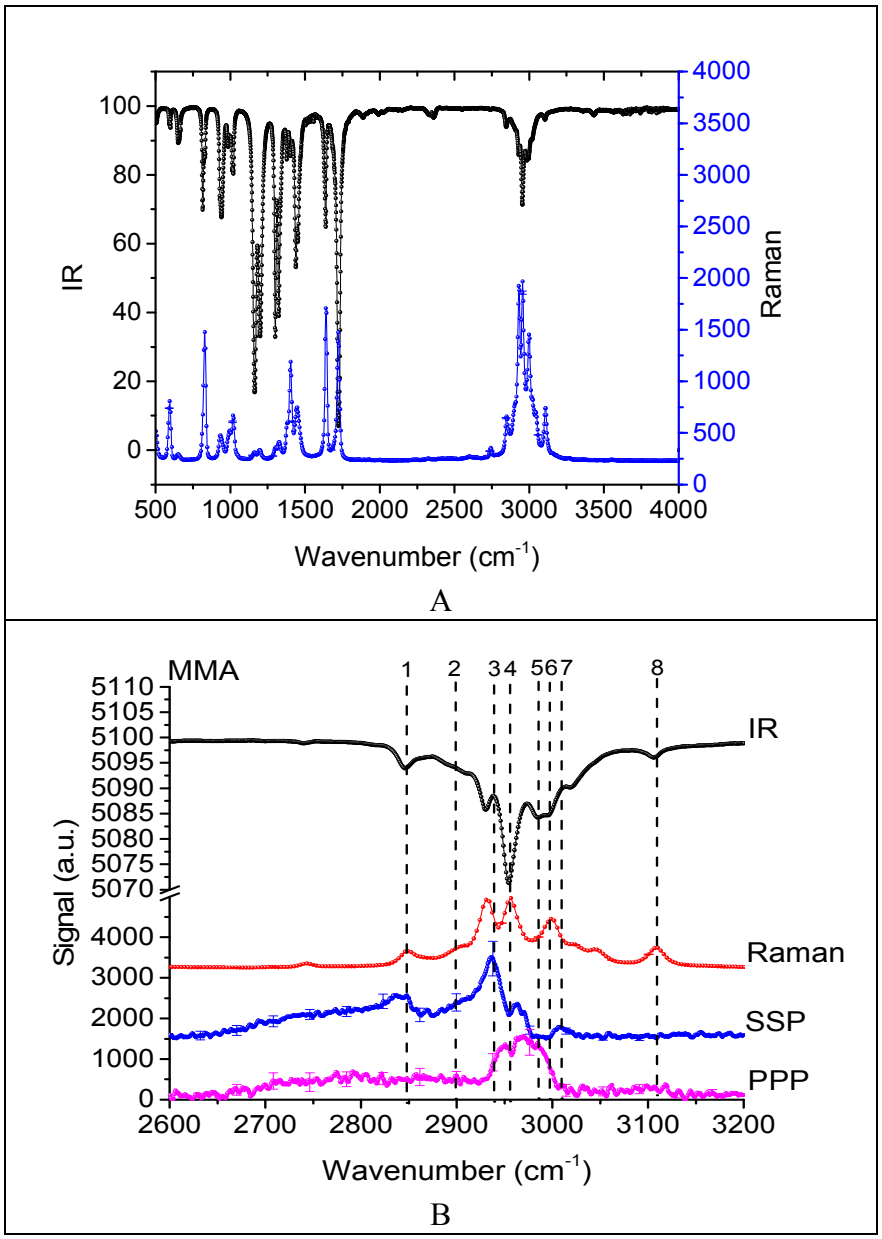

Figure S10. A. IR and Raman spectra of the methyl methacrylate (MMA) monomer are presented from 500-4000 cm^{-1}. B. IR, Raman, and SFG SSP and PPP spectra of MMA monomer are illustrated with the peak positions labeled from 1-8. The vibrational peak assignments are available in Table S6.

Table S6. List the peak positions of methyl methacrylate (MMA) including their suggested peak vibrational assignments.

Vibrational Assignment	MMA			
	IR	Raman	SSP	PPP
1) O-CH_3 symmetric stretch[24]	2844	2850	2840	
2) α-CH_3 symmetric stretch[8-9, 12-13]	2908	2907	2891	
3) α-CH_3 symmetric stretch (FR) [9, 12-13]	2929	2933	2936	
4) α-CH_3 asymmetric stretch (in-plane)[7, 14-15, 24-26]	2955	2957	2963	2957
5) α-CH_3 asymmetric stretch (out-of-plane)[14, 25-26]	2985	2985		2984
6) O- CH_3 asymmetric stretch[5, 7, 14-17]	2996	2999		2997
7) Alkene- methylene CH stretch (=CH_2)[18]	3021	3022	3006	3010
8) Presence of hydroxyl peaks of adsorbed water[21, 25-27]	3106	3109	3113	3098

Table S7. Global Fitting results using Mathematica for MEMA in SSP and PPP polarization combinations

Parameters	Estimated Values		Standard Error		Uncertainty Error with 95% Confidence Level	
	SSP	PPP	SSP	PPP	SSP	PPP
A1	1.011	3.310	0.266	0.0583	±0.532	±1.166
A2	3.504	5.28E-05	0.204	0.171	±0.408	±0.342
A3	2.589	7.092	0.534	0.955	±1.068	±1.911
A4	1.809	0.238	0.383	0.241	±0.765	±0.482
A5	2.472	0.142	0.153	0.259	±0.306	±0.518
A6	0.001	2.720	0.204	0.870	±0.408	±1.740
A7	0.008	0.586	0.113	0.267	±0.225	±0.533
A8	2.420	0.002	0.649	0.433	±1.298	±0.865
A9	5.750	3.136	0.762	0.563	±0.125	±1.127
f1	50		6		±12	
f2	20		1		±1	
f3	46		5		±10	
f4	22		2		±5	
f5	14		0.5		±1	
f6	23		5		±11	
f7	10		2		±5	
f8	32		7		±14	
f9	50		6		±11	
w1	2751		2		±5	
w2	2819		0.5		±1	
w3	2861		2		±3	
w4	2905		1		±2	
w5	2937		1		±1	
w6	2958		2		±3	
w7	2985		1		±2	
w8	3012		4		±7	
w9	3150		6		±13	
n	0.044	0.015	0.004	0.005	±0.007	±0.010
p	2.26		0.20		±0.40	
n1	0.0005	0.0004	0.0004	0.0004	0.0007	±0.0009
R-square value	0.9920					

Table S8. Global Fitting results using Mathematica for EEMA in SSP and PPP polarization combinations

Parameters	Estimated Values		Standard Error		Uncertainty Error with 95% Confidence Level	
	SSP	PPP	SSP	PPP	SSP	PPP
A1	0.001	0.847	0.129	0.385	±0.257	±0.770
A2	2.612	1.217	1.245	0.436	±2.490	±0.872
A3	0.891	0.184	1.797	0.547	±3.593	±1.094
A4	2.753	0.001	0.615	0.173	±1.230	±0.346
A5	0.001	0.166	0.166	0.547	±0.333	±1.094
A6	0.062	1.313	0.173	0.455	±0.346	±0.910
A7	1.240	0.634	0.614	0.641	±1.228	±1.281
A8	2.909	5.205	0.833	1.670	±1.666	±3.341
f1	37		13		±26	
f2	28		5		±11	
f3	29		35		±70	
f4	15		2		±4	
f5	14		4		±8	
f6	11		3		±5	
f7	24		8		±16	
f8	43		7		±13	
w1	2754		10		±20	
w2	2868		4		±8	
w3	2903		12		±24	
w4	2939		1		±2	
w5	2968		2		±4	
w6	2990		1		±2	
w7	3016		4		±8	
w8	3097		6		±13	
n	0.022	0.038	0.004	0.006	±0.007	±0.011
p	2.81		0.68		±1.35	
n1	0.001	0.002	0.0003	0.006	±0.001	±0.001
R-square value	0.9587					

Table S9. Global Fitting results using Mathematica for IEMA in SSP and PPP polarization combinations

Parameters	Estimated Values		Standard Error		Uncertainty Error with 95% Confidence Level	
	SSP	PPP	SSP	PPP	SSP	PPP
A1	0.202	0.001	0.206	0.137	±0.411	±0.274
A2	3.000	0.617	0.654	0.150	±1.308	±0.300
A3	3.915	0.102	1.461	0.163	±2.922	±0.325
A4	3.971	0.001	0.742	1.230	±1.484	±0.260
A5	0.009	6.709	0.210	0.331	±0.421	±0.663
A6	1.577	0.0001	0.453	0.545	±0.905	±1.090
A7	3.671	5.360	0.797	0.993	±1.594	±1.986
f1	31		26		±52	
f2	26		2		±5	
f3	30		6		±12	
f4	18		1		±3	
f5	20		0.5		±1	
f6	23		5		±10	
f7	41		7		±13	
w1	2737		9		±18	
w2	2868		1		±3	
w3	2910		2		±4	
w4	2939		0.5		±1	
w5	2980		1		±2	
w6	3017		3		±5	
w7	3089		7		±15	
n	0.053	0.069	0.006	0.008	±0.014	±0.015
p	2.32		0.20		±0.40	
n1	4.24E-05	0.0027	0.0007	0.0009	0.0013	±0.0018
R-square value	0.9910					

Table S10. Global Fitting results using Mathematica for TEMA in SSP and PPP polarization combinations

Parameters	Estimated Values		Standard Error		Uncertainty Error with 95% Confidence Level	
	SSP	PPP	SSP	PPP	SSP	PPP
A1	0.070	0.207	0.033	0.033	±0.067	±0.065
A2	3.394	0.647	0.470	0.089	±0.941	±0.177
A3	4.251	0.121	0.608	0.052	±1.216	±0.105
A4	2.019	0.031	0.306	0.036	±0.611	±0.072
A5	0.102	6.946	0.187	0.285	±0.373	±0.570
A6	1.724	0.802	0.762	0.662	±1.523	±1.324
A7	3.898	8.631	0.342	0.537	±0.683	±1.075
f1	14		6		±12	
f2	33		2		±4	
f3	24		2		±4	
f4	15		1		±2	
f5	20		0.4		±1	
f6	44		14		±28	
f7	49		3		±5	
w1	2740		3		±7	
w2	2872		1		±2	
w3	2911		1		±1	
w4	2936		0.5		±1	
w5	2982		0.3		±0.6	
w6	3017		7		±15	
w7	3106		4		±7	
n	0.05	0.08	0.002	0.004	±0.01	±0.01
p	2.01		0.05		±0.10	
n1	0.0003	0.0018	0.00022	0.00053	0.0004	±0.001
R-square value	0.9907					

Table S11. Global Fitting results using Mathematica for PhEMA in SSP and PPP polarization combinations

Parameters	Estimated Values		Standard Error		Uncertainty Error with 95% Confidence Level	
	SSP	PPP	SSP	PPP	SSP	PPP
A1	0.020	0.107	0.017	0.048	±0.034	±0.095
A2	2.876	1.561	0.807	0.486	±1.613	±0.972
A3	2.376	1.233	0.728	0.405	±1.456	±0.810
A4	2.514	0.002	0.180	0.121	±0.360	±0.241
A5	0.002	3.471	0.271	0.538	±0.541	±1.076
A6	0.235	1.580	0.171	0.350	±0.342	±0.700
A7	1.716	0.120	0.175	0.153	±0.350	±0.307
A8	4.734	5.830	0.909	1.060	±1.818	±2.120
A9	2.293	1.948	0.687	0.674	±1.374	±1.348
f1	7		4		±8	
f2	41		5		±10	
f3	28		4		±7	
f4	14		0.5		±1	
f5	19		2		±3	
f6	13		2		±3	
f7	15		1		±2	
f8	41		3		±7	
f9	36		7		±14	
w1	2739		3		±6	
w2	2861		3		±6	
w3	2901		1		±2	
w4	2935		1		±1	
w5	2959		1		±2	
w6	2985		1		±1	
w7	3005		1		±2	
w8	3053		3		±7	
w9	3152		6		±14	
n	0.04	0.04	0.01	0.01	±0.02	±0.02
p	2.28		0.45		±0.91	
n1	9.2E-05	0.00293	0.0006	0.0007	0.0013	±0.0015
R-square value	0.9877					

Table S12. Parameter values for generating the simulated SFG curves to obtain the orientation distribution for the monomers.

Parameters	
Refractive indices: n_1(air), n_2(liquid) and n_i(interface)	$n_{1,SFG} = n_{1,vis} = n_{1,IR} = 1.0$ $n_{2,SFG} = 1.4884$ $n_{2,vis} = 1.4848$ $n_{2,IR} = 1.4810$ $n_{i,SFG} = n_{i,vis} = n_{i,IR} = 1.2442$
R-value	3.4(-CH_3)
$\beta_{a,c,a}$	3.4
$\beta_{a,a,c} = \beta_{b,b,c} = \beta_{c,c,c}$	1.0
N_s(number density)	1.0
ω_{vis}(cm^{-1})	12578.6
ω_{IR}(cm^{-1})	2900
ω_{SFG}(cm^{-1})	15478.6
θ_{vis}(°)	50
θ_{IR}(°)	60
θ_{SFG}(°)	51.7
$L_{xx,SFG}$	0.5943
$L_{xx,vis}$	0.6081
$L_{xx,IR}$	0.5228
$L_{yy,SFG}$	0.6578
$L_{yy,vis}$	0.6714
$L_{yy,IR}$	0.5878
$L_{zz,SFG}$	0.5278
$L_{zz,vis}$	0.5216
$L_{zz,IR}$	0.5339
Example: $\chi^{(2)}_{eff,\mathrm{ssp},ss}$	0.117905 (4.4 Cos[θ]+2.4 Cos[θ]^3)

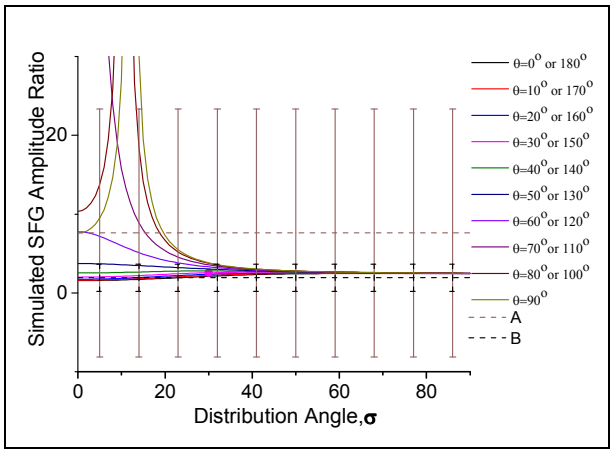

Figure S11. Orientational Analysis obtained from global or simultaneous fitting of SSP and PPP polarization combinations for A) MEMA and B) PhEMA. The simulated SFG amplitude ratios between CH_3 SS (SSP) to CH_3 SS (PPP) are plotted as a function of distribution angle with 95% CL.

Table S13. ST measurements of water, MEMA, PhEMA, EEMA, IEMA, and TEMA using the Du Noüy ring method.[27-28]

			Apparent ST (dynes/cm)		Correction Factor		Real ST (dynes/cm)	
Liquid	Density (g/mL)	Temperature (° C)	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Water	1.000	22.5	80.9	0.1	0.9	9E-05	75.1	0.1
MEMA	0.993	24.3	34.3	0.3	0.9	4E-04	30.5	0.3
PhEMA	1.08	23.5	41.5	0.2	0.9	4E-04	36.9	0.2
EEMA	0.964	24.3	30.2	0.2	0.9	2E-04	26.9	0.2
IEMA	0.961	23.7	28.0	0.3	0.9	4E-04	24.9	0.2
TEMA	0.924	29.9	26.8	0.1	0.9	4E-04	23.8	0.1

<u>*Equations Used:</u>

$$\text{ST } (\Upsilon) = f * P \qquad (1)$$

where

f = correction factor

P = apparent ST

$$\text{Correction factor (F)} = a + \sqrt{\frac{4b}{(\pi R_{mean})^2} * \frac{P}{\Delta\rho} - \frac{1.679r}{R} + 0.04534} \qquad (2)$$

where

R/r = 50.50 (given for the Pt ring)

Mean circumference= $2\pi R_{mean}$ = 6.161 (given for the Pt ring)

$\Delta\rho$ = (D-d) i.e., Density of liquid - density of air (0.001 g/mL)

a = 0.725

b = 0.0009705

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