Supporting Information:

Impact of the Alpha-Methyl Group (α-CH_3) on the Aggregation States and Interfacial Isotherms of Poly(acrylates) Monolayers at the Water Surface

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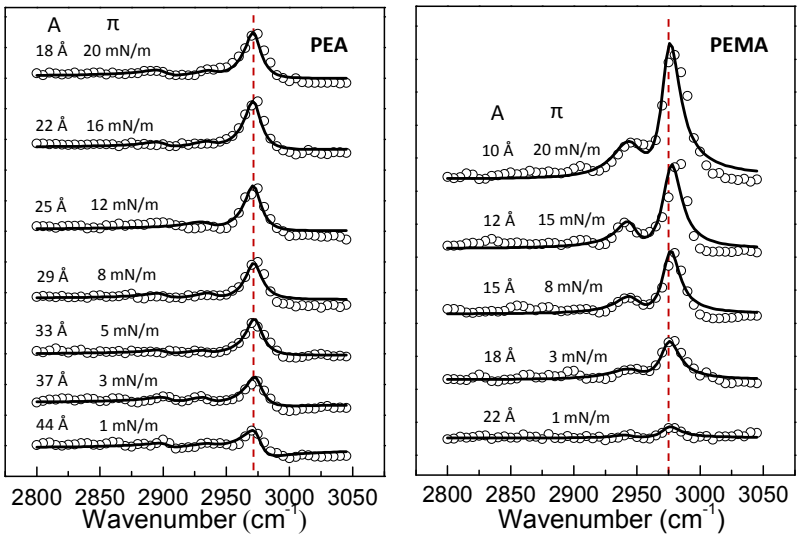

Figure S1. SFG spectra of PEA and PEMA monolayers at various surface areas. (*ppp* polarization combination)

Table S1. Fitting results of SFG spectra shown in Figure 3 for PMA and PMMA at selected surface pressures.

ω_i (cm^{-1})	Γ	assignment	1 mN/m		4 mN/m		13 mN/m		18 mN/m	
			A_{ssp}		A_{ssp}		A_{ssp}		A_{ssp}	
			PMA	PMMA	PMA	PMMA	PMA	PMMA	PMA	PMMA
2910	8	-CH_2 *ss*	12	0	9	4	-	7	8	-
2955	9	-OCH_3 *ss*	32	27	45	56	-	106	78	-
2991	8	-OCH_3 *as*, α-CH_3 *as*	6	5	8	8	-	16	9	-
3020	8	-OCH_3 *as*	6	4	6	8	-	15	6	-

Table S2. The values of $\chi_{eff,ssp,ss}^{(2)}/\chi_{eff,ssp,as}^{(2)}$ for the ester CH_3 groups of PMA and PMMA at various surface areas

PMA		PMMA	
surfaces areas ($Å^2$/units)	$\chi_{eff,ssp,ss}^{(2)}/\chi_{eff,ssp,as}^{(2)}$	surfaces areas ($Å^2$/units)	$\chi_{eff,ssp,ss}^{(2)}/\chi_{eff,ssp,as}^{(2)}$
47	2.4	16	3.0
32	3.3	15	3.3
21	3.8	14	3.3
19	4.7	13	3.2
16	5.4	12	3.1
12	5.8	10	3.1

Table S3. Fitting results of SFG spectra shown in Figure 3 and Figure S1 for PEA at selected surface pressures.

ω_i (cm^{-1})	Γ	assignment	1 mN/m		5 mN/m		12 mN/m		20 mN/m	
			A_{ss}	A_{ppp}	A_{ssp}	A_{ppp}	A_{ssp}	A_{ppp}	A_{ssp}	A_{ppp}
2872	9	s-CH_3 *Fermi*	9	-	14	-	21	-	27	-
2902	9	-CH_2 *as*	5	3	9	6	16	0	17	5
2937	10	s-CH_3 *ss*	19	4	48	4	72	7	90	6
2973	9	s-CH_3 *as*	7	19	27	30	26	34	31	32

Table S4. Fitting results for SFG spectra shown in Figure 3 and Figure S1 for PEMA at selected surface pressures.

ω_i (cm^{-1})	Γ	assignment	1 mN/m		3 mN/m		15 mN/m		20 mN/m	
			A_{ss}	A_{ppp}	A_{ssp}	A_{ppp}	A_{ssp}	A_{ppp}	A_{ssp}	A_{ppp}
2847	9	-CH_2 *ss*	8	-	16	-	13	-	17	-
2874	9	s-CH_3 *Fermi*	8	-	12	-	18	-	35	-
2940	12	s-CH_3 *ss*	26	5	44	9	56	13	74	17
2974	10	s-CH_3 *as*	-4	12	-5	22	-6	27	-5	43

Table S5. The values of $\chi_{eff,ssp,ss}^{(2)}/\chi_{eff,ppp,as}^{(2)}$ for the ester side chains CH_3 groups of PEA and PEMA at various surface areas

PEA		PEMA	
surfaces areas (Å^2/units)	$\chi_{eff,ssp,ss}^{(2)}/\chi_{eff,ppp,as}^{(2)}$	surfaces areas (Å^2/units)	$\chi_{eff,ssp,ss}^{(2)}/\chi_{eff,ppp,as}^{(2)}$
44	1.2	-	-
37	1.6	24	2.4
33	1.9	22	2.5
29	2.1	18	2.3
25	2.5	15	2.3
22	2.7	12	2.5
18	3.3	10	2.7

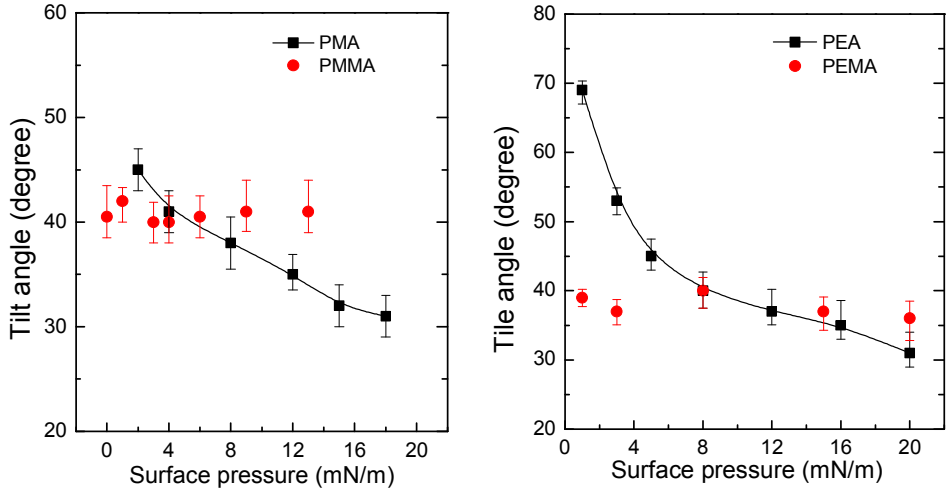

Figure S2. Tile angle (θ) of side-chain methyl groups as functions of the surface pressure.

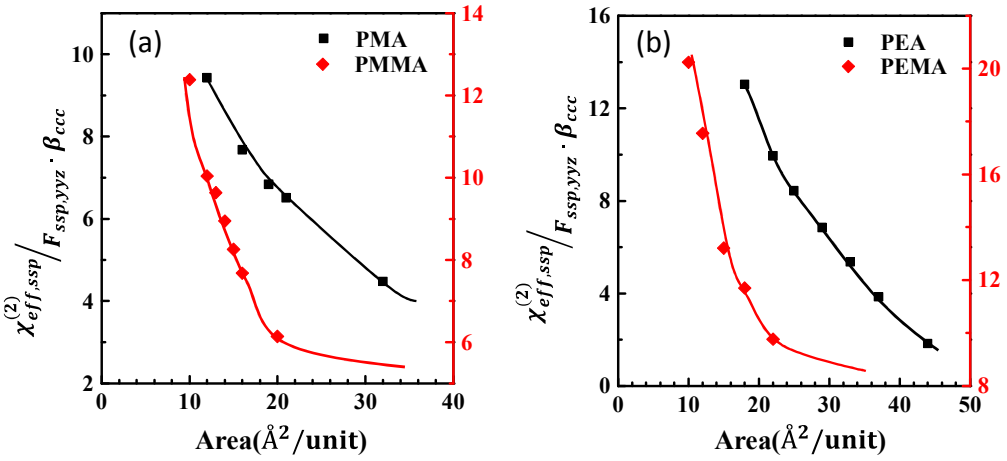

Figure S3. Simulated SFG intensity of PMA, PMMA (a) and PEA, PEMA (b) as a function of the surface areas.

Based on the orientation angle shown in Figure 5 and molecular density which is inverse of the surface areas, we can theoretically calculate the SFG intensity of s-CH_3. We have the following relation for *ss* mode of s-CH_3 in the *ssp* spectra:

$$I_{\mathrm{SFG,\,ssp}}^{1/2} \propto \left|\chi_{\mathrm{eff,\,ssp}}^{(2)}\right| \propto F_{\mathrm{ssp,\,yyz}}\chi_{\mathrm{yyz,\,ss}} \propto \frac{1}{2}F_{\mathrm{ssp,\,yyz}}N\beta_{ccc}\left[\cos\theta(1+r)-\cos^3\theta(1-r)\right]$$

where $F_{\mathrm{ssp,yyz}}$ is the Fresnel factor; N is the surface density; θ is the tilt angle of -CH_3 with respect to the surface normal and $r = \beta_{\mathrm{aac}}/\beta_{\mathrm{ccc}}$. Since β_{ccc} and $F_{\mathrm{ssp,yyz}}$ are constant,

irrelative with the surface pressure or surface area, here we use $\chi_{eff,ssp}/F_{ssp,yyz}\cdot\beta_{ccc}$, instead of $I_{SFG,ssp}$, to investigate the changes of the relatively simulated SFG intensity with decreasing the surface areas.

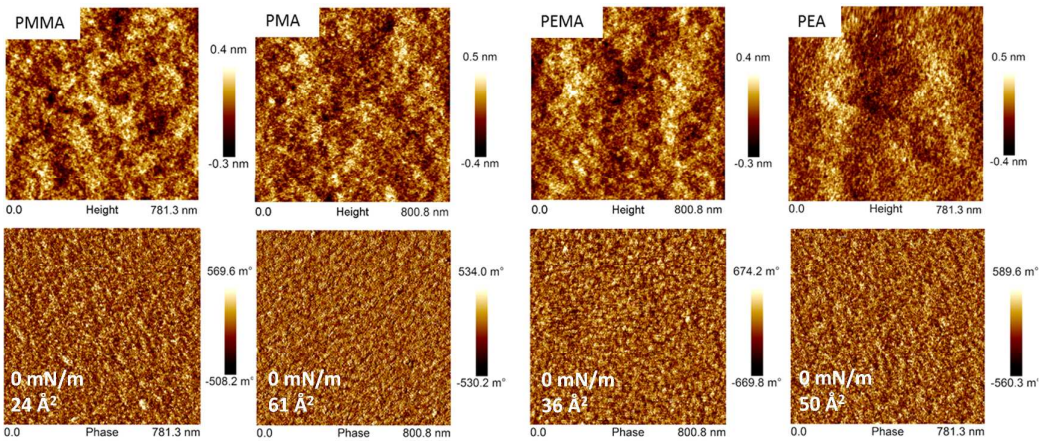

Figure S4. AFM images of the LB films transferred from the water surface at 0 mN/m.

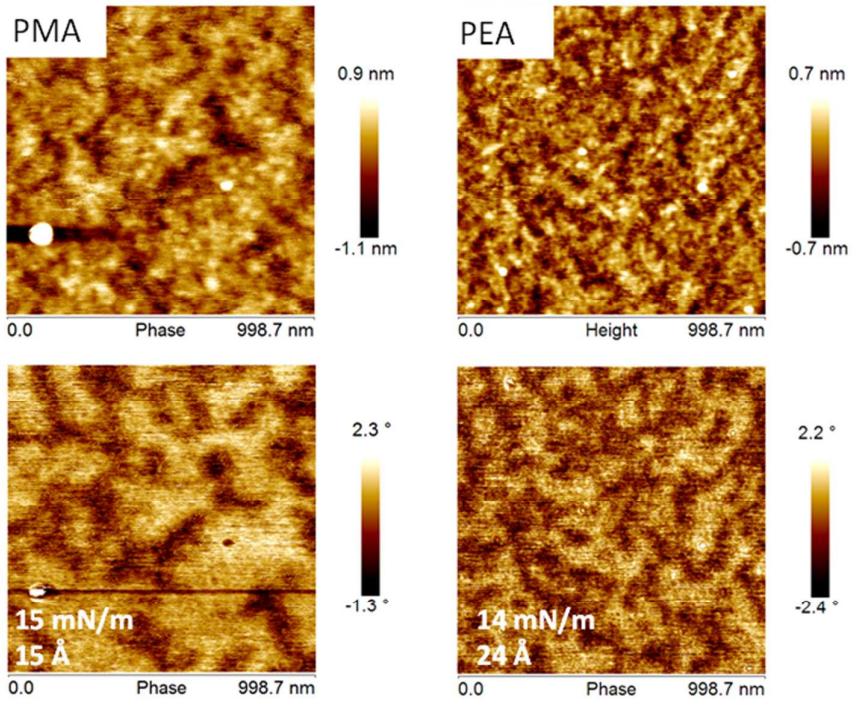

Figure S5. AFM images of the LB films of PMA and PEA transferred from the water surface at surface pressures of 15 and 14 mN/m, respectively.