Supplementary Information (SI) for Soft Matter.

Substrate-dependent interfacial structures of ultrathin poly (methyl methacrylate) films upon annealing revealed by sum frequency generation vibrational spectroscopy

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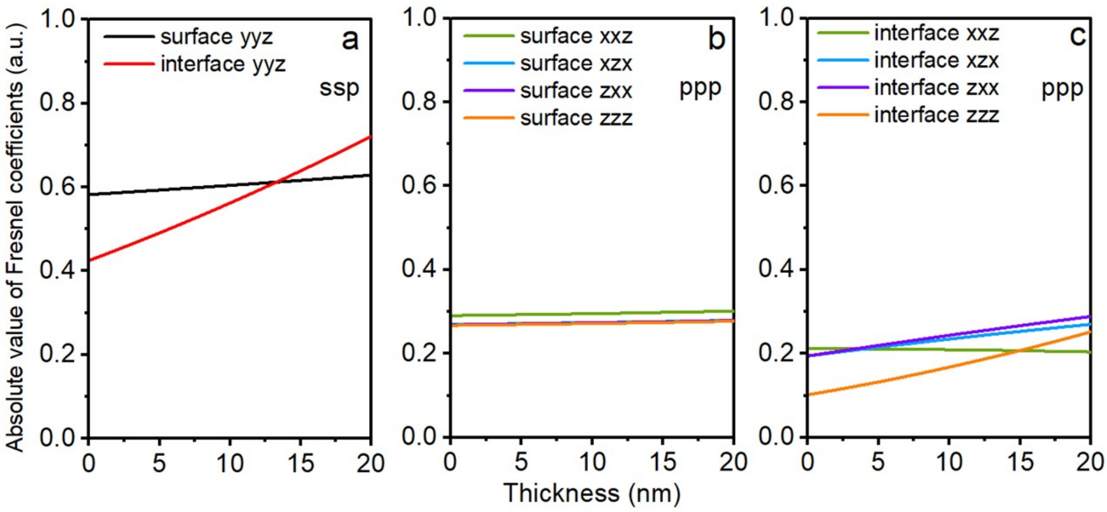

Fig. S1. Calculated thickness-dependent Fresnel coefficients at the PMMA/air surface and the buried PMMA/CaF_2 interface under ssp and ppp polarization combinations.

The calculation of the Fresnel Coefficients of PMMA thin film on the prism

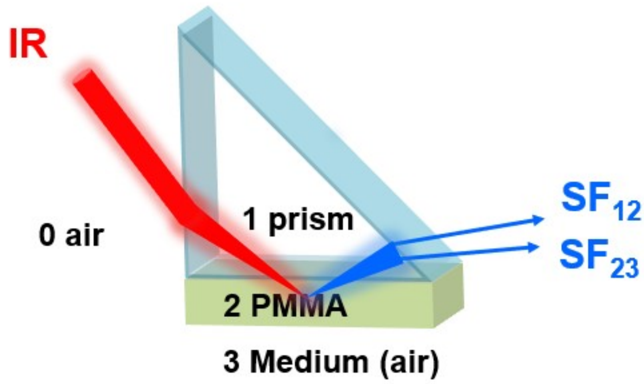

Figure S2. Schematic of the light propagation path in the prism for the SFG experiment. For simplification, only the input infrared beam propagation path was shown here.

For the right-angle prism geometry shown in Figure S2, Media 0 and 3 represent the air. Medium 1 denotes the prism, and Medium 2 signifies the PMMA thin film. For simplification, only the input infrared beam propagation path was shown here. According to the previous publication related to the thin film model[1-10], the Fresnel factors can be expressed as follows:

For the prism/PMMA interface, we have

$$L_{xx}^{prism/PMMA}(\omega_i) = t_p(1 - r_{p23}e^{2i\beta})\frac{cos(\theta_2)}{cos(\theta_1)} \quad \text{(S1)}$$

$$L_{yy}^{prism/PMMA}(\omega_i) = t_s(1 + r_{s23}e^{2i\beta}) \quad \text{(S2)}$$

$$L_{zz}^{prism/PMMA}(\omega_i) = t_p(1 + r_{p23}e^{2i\beta})\frac{n_1 n_2}{n_{12}^2} \quad \text{(S3)}$$

For the PMMA/medium (air) interface, we have

$$I_{xx}^{PMMA/air}(\omega_i) = t_p e^{i\Delta}(1 - r_{p23})\frac{cos(\theta_2)}{cos(\theta_1)} \quad \text{(S4)}$$

$$L_{yy}^{PMMA/air}(\omega_i) = t_s e^{i\Delta}(1 + r_{s23}) \quad \text{(S5)}$$

$$L_{zz}^{PMMA/air}(\omega_i) = t_p e^{i\Delta}(1 + r_{p23})\frac{n_1 n_2}{n_{23}^2} \quad \text{(S6)}$$

where ω_i represents the beam frequency; t_s and t_p denote the overall transmission coefficients at the prism/PMMA interface for the s-and p-polarized beams, respectively; r_{p23} and r_{s23} stands for the linear reflection coefficients of the light beam at the PMMA/medium (air) interface; β signifies the phase difference between a reflective beam and its secondary reflective beam after it propagates across the PMMA thin film and reflects back. θ_1 and θ_2 are the incident angles of the input beam in the silica and PMMA film, respectively. n_1 and n_2 represent the refractive indices of the light beam in the prism and PMMA film, respectively; n_{12} and n_{23} denote the refractive indices of the prism/PMMA and PMMA/air interfaces, respectively. The overall transmission coefficients t_p, t_s and β can be expressed as

$$t_p = \frac{t_{p12}}{1 + r_{p12}r_{p23}e^{2i\beta}} \quad \text{(S7)}$$

$$t_s = \frac{t_{s12}}{1 + r_{s12} r_{s23} e^{2i\beta}} \quad (S8)$$

$$\beta = \frac{2\pi}{\lambda} n_2 d \cos(\theta_2) \quad (S9)$$

where t_{p12} and t_{s12} represent the linear transmission coefficients of the light beam at the prism/PMMA interface; λ is the wavelength of the light beam, and d is the PMMA film thickness. The expressions for the linear coefficients of r_{p23}, r_{s23}, t_{p12}, and t_{s12} are

$$r_{p23} = \frac{n_3 \cos\theta_2 - n_2 \cos\theta_3}{n_3 \cos\theta_2 + n_2 \cos\theta_3} \quad (S10)$$

$$r_{s23} = \frac{n_2 \cos\theta_2 - n_3 \cos\theta_3}{n_2 \cos\theta_2 + n_3 \cos\theta_3} \quad (S11)$$

$$t_{p12} = \frac{2 n_1 \cos\theta_1}{n_2 \cos\theta_1 + n_1 \cos\theta_2} \quad (S12)$$

$$t_{s12} = \frac{2 n_1 \cos\theta_1}{n_1 \cos\theta_1 + n_2 \cos\theta_2} \quad (S13)$$

Here, θ_3 is the incident angle of the light beam in the medium (air). It should be mentioned that the dispersion of the F factors in a narrow frequency range, e.g., 2800-3100 cm^{-1}, could be neglected based on the previous reports in the literature[4-10]. In eqs. (S4)-(S6), the existing Δ, which is the phase difference required when considering the coherence during the addition of the two SHG out beams generated from the prism/PMMA and PMMA/medium (air) interfaces. Since the two output SFG beams are generated by overlapping the input visible and infrared beams at the two interfaces (prism/PMMA and PMMA/air), the propagation phase difference at the two interfaces for the output SFG, the input visible, and the input infrared beams can be described as:

$$\Delta_{SF} = \frac{2\pi n_{2,SF} d}{\lambda_{SF} cos(\theta_{2,SF})} \quad (S14)$$

$$\Delta_{VI} = \frac{2\pi n_{2,VI} d}{\lambda_{VI} cos(\theta_{2,VI})} - \frac{2\pi n_{1,VI} d}{\lambda_{VI}} (tan(\theta_{2,VI}) + tan(\theta_{2,SF})) sin(\theta_{1,VI}) \quad (S15)$$

$$\Delta_{IR} = \frac{2\pi n_{2,IR} d}{\lambda_{IR} cos(\theta_{2,IR})} - \frac{2\pi n_{1,IR} d}{\lambda_{IR}} (tan(\theta_{2,IR}) + tan(\theta_{2,SF})) sin(\theta_{1,IR}) \quad (S16)$$

It should be noted that the overall Fresnel coefficients should include the transmission of the input visible, infrared, and output SFG beams at the top air/silica interface, which means that we need to consider the linear Fresnel coefficients for the two input beams at the air/prism interface (0-1, t_{01}) and one output beam at the same interface (1-0, t_{10}). Now we can write the overall Fresnel coefficients for ssp and ppp polarization combinations, which can be expressed as：

$$F^{prism/PMMA}_{ssp,\,yyz} = L^{prism/PMMA}_{yy,SF} t_{s10.SF} L^{prism/PMMA}_{yy,VI} t_{s01.V} L^{prism/PMMA}_{zz,IN} t_{n01.N} sin(\theta_{1,IN}) \quad (S17)$$

$$F^{PMMA/air}_{ssp,yyz} = L^{PMMA/air}_{yy,SF} t_{s10,SF} L^{PMMA/air}_{yy,VI} t_{s01,VI} L^{PMMA/air}_{zz,IN} t_{p01,IN} sin(\theta_{1,IN}) \quad (S18)$$

$$F^{prism/PMMA}_{ppp,xxz} = - L^{prism/PMMA}_{xx,SF} t_{p10,SF} cos(\theta_{1,SF}) L^{prism/PMMA}_{xx,VI} t_{p01,VI} cos(\theta_{1,VI}) L^{prism/PMMA}_{zz,IN} t_{p01,IN} sin(\theta_{1,IN})$$

$(S19)$

$$F^{prism/PMMA}_{ppp,xzx} = - L^{prism/PMMA}_{xx,SF} t_{p10,SF} cos(\theta_{1,SF}) L^{prism/PMMA}_{zz,VI} t_{p01,VI} sin(\theta_{1,VI}) L^{prism/PMMA}_{xx,IN} t_{p01,IN} cos(\theta_{1,IN})$$

$(S20)$

$$F^{prism/PMMA}_{ppp,zxx} = L^{prism/PMMA}_{zz,SF} t_{p10,SF} sin(\theta_{1,SF}) L^{prism/PMMA}_{xx,VI} t_{p01,VI} cos(\theta_{1,VI}) L^{prism/PMMA}_{xx,IN} t_{p01,IN} cos(\theta_{1,IN})$$

$(S21)$

$$F^{prism/PMMA}_{ppp,zzz} = L^{prism/PMMA}_{zz,SF} t_{p10,SF} sin(\theta_{1,SF}) L^{prism/PMMA}_{zz,VI} t_{p01,VI} sin(\theta_{1,VI}) L^{prism/PMMA}_{zz,IN} t_{p01,IN} sin(\theta_{1,IN})$$

$(S22)$

$$F^{PMMA/air}_{ppp,xxz} = - L^{PMMA/air}_{xx,SF} t_{p10,SF} cos(\theta_{1,SF}) L^{PMMA/air}_{xx,VI} t_{p01,VI} cos(\theta_{1,VI}) L^{PMMA/air}_{zz,IN} t_{p01,IN} sin(\theta_{1,IN})$$

$(S23)$

$$F^{PMMA/air}_{ppp,xzx} = - L^{PMMA/air}_{xx,SF} t_{p10,SF} cos(\phi_{1,SF}) L^{PMMA/air}_{zz,VI} t_{p01,VI} sin(\phi_{1,VI}) L^{PMMA/air}_{xx,IN} t_{p01,IN} cos(\phi_{1,IN})$$

$(S24)$

$$F^{PMMA/air}_{ppp,zxx} = L^{PMMA/air}_{zz,SF} t_{p10,SF} sin(\phi_{1,SF}) L^{PMMA/air}_{xx,VI} t_{p01,VI} cos(\phi_{1,VI}) L^{PMMA/air}_{xx,IN} t_{p01,IN} cos(\phi_{1,IN})$$

$(S25)$

$$F_{ppp,zzz}^{PMMA/air} = L_{zz,SF}^{PMMA/air} t_{p10,SF} sin(\phi_{1,SF}) L_{zz,VI}^{PMMA/air} t_{p01,VI} sin(\phi_{1,VI}) L_{zz,IN}^{PMMA/air} t_{p01,IN} sin(\phi_{1,IN}) \quad (S26)$$

Here, the expressions for t_{10} and t_{01} are similar to eqs S12 and S13. Table S1 shows the refractive indices for the sum-frequency light beam, visible light beam, and infrared light beam.

Table S1. Refractive indices used in this study

Medium	Refractive indices for sum (460 nm)	Refractive indices for visible (532 nm)	Refractive indices for IR (3384 nm)
Air	1	1	1
Silica	1.46	1.46	1.41
CaF_2	1.42	1.44	1.42
PMMA	1.50	1.49	1.46
PMMA/Air	1.25	1.25	1.24
Silica/PMMA	1.48	1.48	1.44
CaF_2/PMMA	1.46	1.47	1.44

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