

Supporting Information

Locally favored two-dimensional structures of block copolymer melts on non-neutral surfaces

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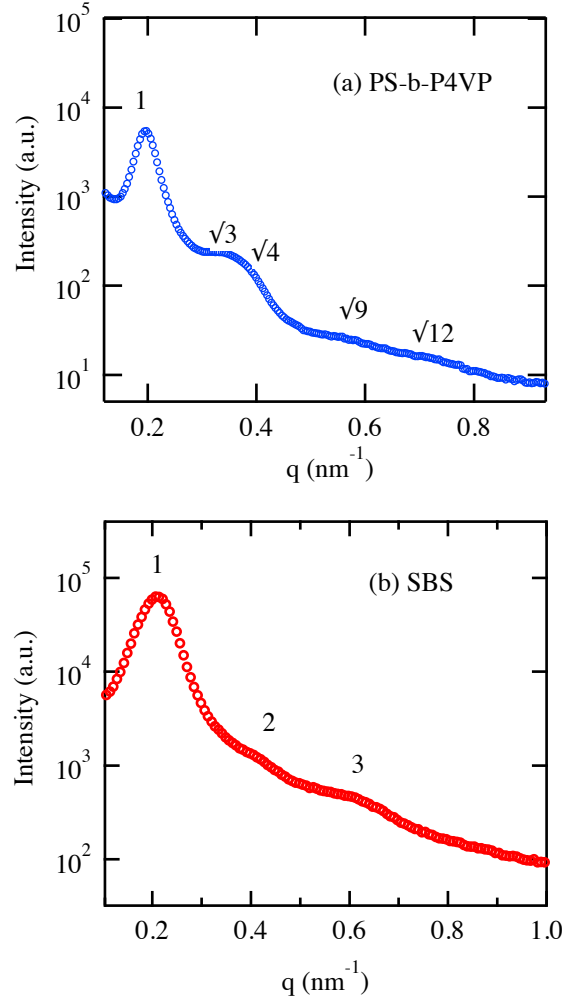


Fig. S1: Small angle x-ray scattering (SAXS) profiles of the bulk (a) PS-*block*-P4VP and (b) SBS samples measured at 25 °C. The measurements were performed at the X27C beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) at the X-ray wavelength (λ) of 0.1371nm. The peak positions relative to the first order maximum (q_m) are also indicated in the graph. The domain spacing (L_d) was calculated by $L_d=2\pi/q_m$.

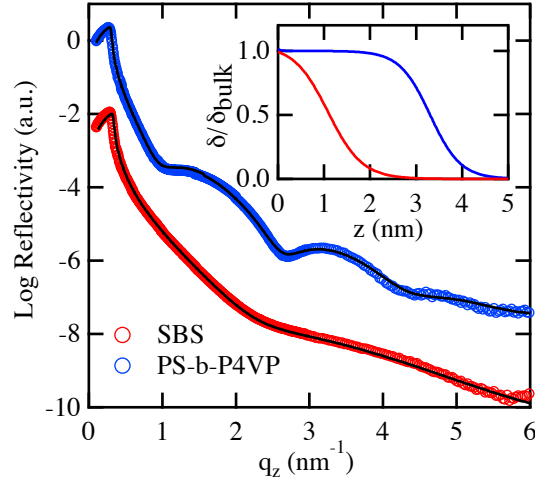


Fig. S2: XR profiles of the SBS and PS-*block*-P4VP flattened layers derived from the annealed SBS and PS-*block*-P4VP thin films for 100 h. We utilized a three-layer model (a Si substrate, a SiO_x layer, and a polymer layer) to fit the XR data. A least-square fit (the black solid lines) to the XR profiles were performed using the dispersion (δ) profile shown in the inset. The dispersion values, which depend on the density values of the films¹, were normalized by the bulk dispersion (δ_{bulk}) values. The thickness the SBS flattened layer and the roughness of the air-polymer interface was 1.6 ± 0.2 nm and 0.6 nm; the thickness the PS-*block*-P4VP flattened layer and the roughness of the air-polymer interface was 3.5 ± 0.2 nm and 0.2 nm from the best-fitting results.

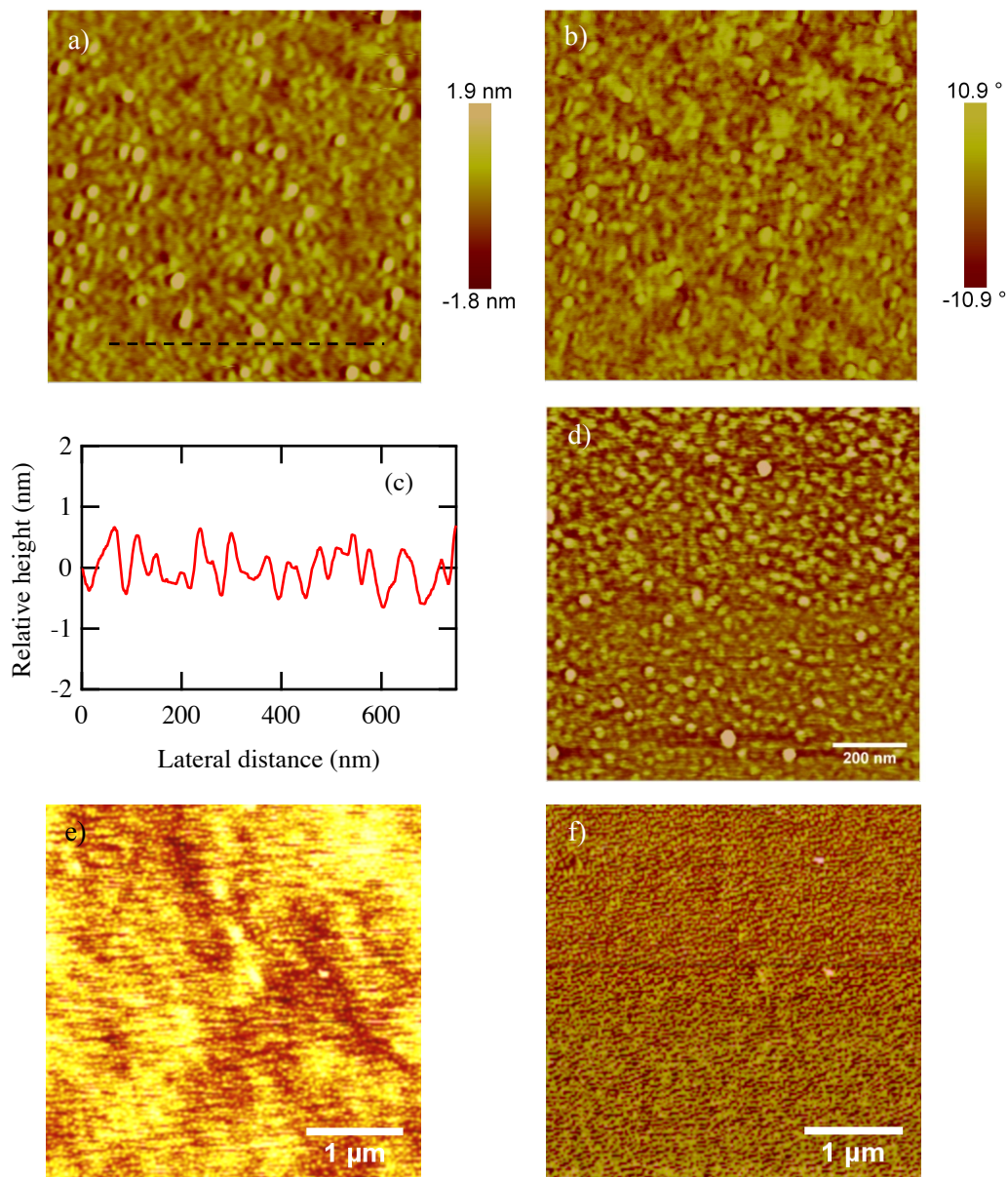


Fig. S3: AFM images (1μm x 1μm) of the PS-*block*-P4VP flattened layer: a) height image; b) phase image; c) height profile along the black dashed line shown in (a). The RMS roughness of the PS-*block*-P4VP flattened layer was estimated to be about 0.2 nm. (d) AFM phase image (1μm x 1μm) of the SBS flattened layer. In comparison of the SEM image shown in Fig. 2a, the bright region can be identified as the PB-rich region. To verify the homogeneity of the film surface, enlarged AFM images of the PS-*block*-PMMA flattened layer are shown: (e) height image; (f) phase image. The height scale is 0 - 4 nm.

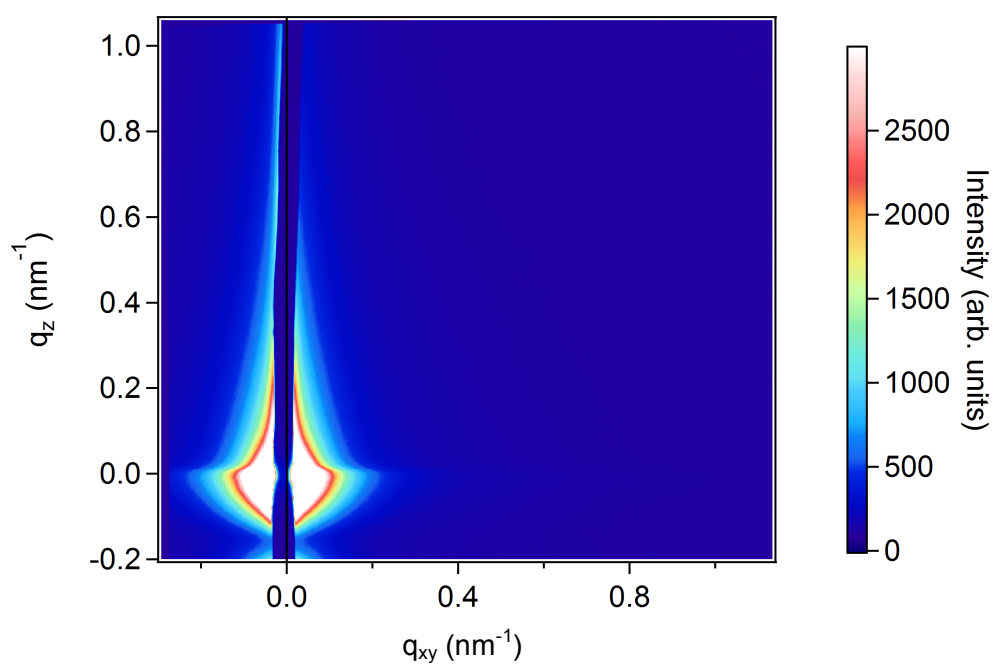


Fig. S4. 2D GISAXS image of the PS-*block*-P4VP flattened layer. The in-plane GISAXS profile was extracted at the exit angle (between the scattered beam and the film surface) of $\alpha_f = 0.17^\circ$, which corresponds to the q_{xy} -value of $q_z = 0.15 \text{ nm}^{-1}$.

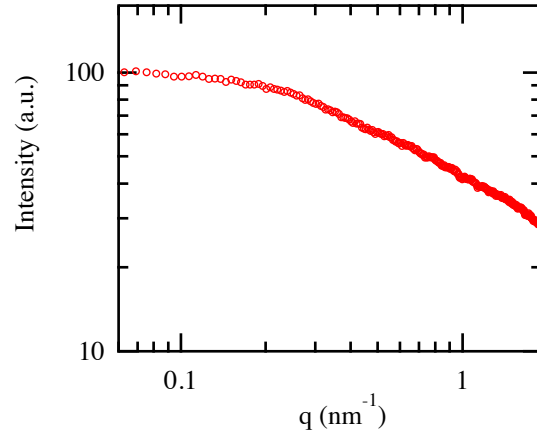


Fig. S5. Fourier transform profile of the SEM image of the PS-*block*-P4VP flattened layer shown in Fig. 2. There is a broad peak at around $q = 0.2$ nm⁻¹. When compared it to the GISAXS profile shown in Fig. 3, there are clear differences between them: an up-turn at $q_{xy} < 0.1$ nm⁻¹ and the lack of the broad peak in the GISAXS profile. This upturn suggests the presence of a larger structure composed of the percolating structure and would make the broad peak invisible.

Orientation of phenyl groups: The intensity of SFG signal (I^{SFG}) is proportional to the absolute value of the effective sum-frequency susceptibility tensor of the interface ($\chi_{\text{eff}}^{(2)}$):

$$I^{\text{SFG}} \propto |\chi_{\text{eff}}^{(2)}|^2 = \left| \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \right|^2 \quad (\text{S1})$$

where $\chi_{\text{NR}}^{(2)}$ is the non-resonant background contribution. A_q , ω_q and Γ_q are strength, resonant frequency and damping coefficient of the q^{th} vibration mode, respectively. Each peak on the SF spectra was fitted by eq. S1 using A_q , ω_q and Γ_q as fitting parameters. Panels (a) and (b) of Fig. S4 show the curve-fitting results of the SFG spectra for the annealed SBS film with the *ssp* and *ppp* polarization combinations, respectively. The peak assignment was described in the main text.

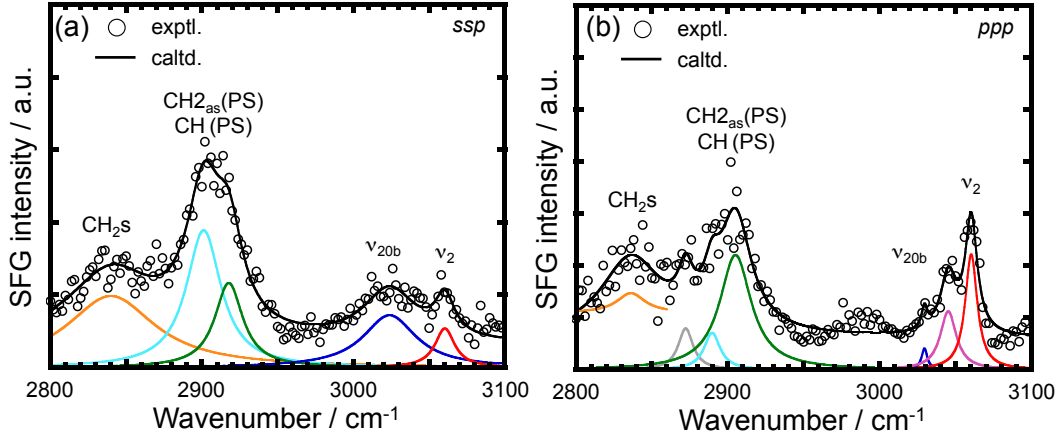


Fig. S4. SFG spectra with (a) the *ssp* and (b) *ppp* polarization combinations for the annealed SBS film. Open circles and solid lines denote experimental and calculated data, respectively.

The macroscopic sum-frequency susceptibility tensor χ_{ijk} is related to the microscopic hyperpolarizability tensor elements $\beta_{ijk'}$ in the molecular coordinate system defined by a , b , c axes. Phenyl groups can be treated as C_{2v} symmetry^{3,4}. In this case,

$$\chi_{xxz} = \chi_{yyz}, \chi_{xzx} = \chi_{yzy}, \chi_{zxx} = \chi_{zyy}, \chi_{zzz} \quad (\text{S2})$$

There exist two methods to analyze the orientation of phenyl rings. One is based on the SFG intensity ratio of two different vibration modes for phenyl groups with the *ssp* polarization combination. Another is the calculation from the SFG intensity ratio of the *ssp* polarization combination over the *ppp* one for the ν_2 vibration mode, $(I_{\text{ssp},\nu_2}/I_{\text{ppp},\nu_2})^{3,5,6}$. In this study, the latter method was adopted because unknown parameters are involved in the former one.

In general, $\chi_{\text{eff},\text{ssp}}^{(2)}$ and $\chi_{\text{eff},\text{ppp}}^{(2)}$ can be expressed as follows;

$$\begin{aligned} \chi_{\text{eff},\text{ssp}}^{(2)} &= F_{\text{ssp},\text{yyz}} \chi_{\text{yyz}} \\ &= L_{\text{yy}}(\omega_{\text{SF}}) L_{\text{yy}}(\omega_{\text{Vis}}) L_{\text{zz}}(\omega_{\text{IR}}) \sin \theta_{\text{IR}} \chi_{\text{yyz}} \end{aligned} \quad (\text{S3a})$$

$$\begin{aligned} \chi_{\text{eff},\text{ppp}}^{(2)} &= F_{\text{ppp},\text{xxz}} \chi_{xxz} + F_{\text{ppp},\text{xzx}} \chi_{xzx} + F_{\text{ppp},\text{zxx}} \chi_{zxx} + F_{\text{ppp},\text{zzz}} \chi_{zzz} \\ &= -L_{\text{xx}}(\omega_{\text{SFG}}) L_{\text{xx}}(\omega_{\text{Vis}}) L_{\text{zz}}(\omega_{\text{IR}}) \cos \theta_{\text{SF}} \cos \theta_{\text{Vis}} \sin \theta_{\text{IR}} \chi_{xxz} \\ &\quad - L_{\text{xx}}(\omega_{\text{SFG}}) L_{\text{zz}}(\omega_{\text{Vis}}) L_{\text{xx}}(\omega_{\text{IR}}) \cos \theta_{\text{SF}} \sin \theta_{\text{Vis}} \cos \theta_{\text{IR}} \chi_{xzx} \\ &\quad + L_{\text{zz}}(\omega_{\text{SFG}}) L_{\text{xx}}(\omega_{\text{Vis}}) L_{\text{xx}}(\omega_{\text{IR}}) \sin \theta_{\text{SF}} \cos \theta_{\text{Vis}} \cos \theta_{\text{IR}} \chi_{zxx} \end{aligned} \quad (\text{S3b})$$

$$+L_{zz}(\omega_{\text{SFG}})L_{zz}(\omega_{\text{Vis}})L_{zz}(\omega_{\text{IR}})\sin\theta_{\text{SF}}\sin\theta_{\text{Vis}}\sin\theta_{\text{IR}}\chi_{zzz}$$

where $L_{ii}(i = x, y, z)$ are Fresnel coefficients. The angle between surface normal and beam is expressed as θ . The subscripts Vis and IR denote the input beams. To calculate Fresnel factors for the interfaces, the following equations are used⁷,

$$L_{xx}(\omega) = \frac{2n_1(\omega)\cos\theta_1}{n_2(\omega)\cos\theta_1+n_1(\omega)\cos\theta_2} \times \frac{2n_2(\omega)\cos\theta_2}{n_3\cos\theta_2+n_2(\omega)\cos\theta_3} \times \frac{\cos\theta_3}{\cos\theta_1} \quad (\text{S4a})$$

$$L_{yy}(\omega) = \frac{2n_1(\omega)\cos\theta_1}{n_1(\omega)\cos\theta_1+n_2(\omega)\cos\theta_2} \times \frac{2n_2(\omega)\cos\theta_2}{n_2\cos\theta_2+n_3(\omega)\cos\theta_3} \quad (\text{S4b})$$

$$L_{zz}(\omega) = \frac{2n_1(\omega)\cos\theta_1}{n_2(\omega)\cos\theta_1+n_1(\omega)\cos\theta_2} \times \frac{2n_2(\omega)\cos\theta_2}{n_3\cos\theta_2+n_2(\omega)\cos\theta_3} \times \frac{n_1}{n_3} \times \left(\frac{n_3(\omega)}{n'(\omega)}\right)^2 \quad (\text{S4c})$$

where n' is the refractive index of the SBS/SiO_x interfacial layer. The value of 1.50 was here used. In eq. S4, q_i is the incidence angle in the medium i . For the ν_2 mode, the component of c for an isotropic interface are given by Refs. 3 and 5,

$$\begin{aligned} \chi_{yyz,\nu_2} &= \chi_{xxz,\nu_2} \\ &= \frac{1}{4}N_s(\beta_{aac,\nu_2} + \beta_{bbc,\nu_2} + 2\beta_{ccc,\nu_2})\langle\cos\phi\rangle + \frac{1}{4}N_s(\beta_{aac,\nu_2} + \beta_{bbc,\nu_2} - 2\beta_{ccc,\nu_2})\langle\cos^3\phi\rangle \end{aligned} \quad (\text{S5})$$

$$\chi_{zyy,\nu_2} = \chi_{zyx,\nu_2} = \chi_{xzx,\nu_2} = \chi_{zxx,\nu_2} = -\frac{1}{4}N_s(\beta_{aac,\nu_2} + \beta_{bbc,\nu_2} - 2\beta_{ccc,\nu_2})(\langle\cos\phi\rangle - \langle\cos^3\phi\rangle) \quad (\text{S6})$$

$$\chi_{zzz,\nu_2} = \frac{1}{2}N_s(\beta_{aac,\nu_2} + \beta_{bbc,\nu_2})\langle\cos\phi\rangle - \frac{1}{2}N_s(\beta_{aac,\nu_2} + \beta_{bbc,\nu_2} - 2\beta_{ccc,\nu_2})\langle\cos^3\phi\rangle \quad (\text{S7})$$

Using eqs from S3 to S7, the $(I_{ssp,n2}/I_{ppp,n2})$ value can be obtained. Postulating that $F_{ppp,xzx}$ and $F_{ppp,zxx}$ are comparable with opposite signs and that χ_{xzx} is equal to χ_{zxx} for the ν_2 mode, eq. S3b is simplified to be;

$$\chi_{\text{eff},ppp}^{(2)} \cong F_{ppp,xzx}\chi_{xxz} + F_{ppp,zzz}\chi_{zzz} \quad (\text{S8})$$

Thus, the $(I_{ssp,n2}/I_{ppp,n2})$ value is given by,

$$\frac{I_{ssp,n2}}{I_{ppp,n2}} = \left| \frac{\chi_{\text{eff},ssp,\nu_2}}{\chi_{\text{eff},ppp,\nu_2}} \right|^2 \cong \left| \frac{F_{ssp,yyz}\chi_{yyz,\nu_2}}{F_{ppp,xzx}\chi_{xxz,\nu_2} + F_{ppp,zzz}\chi_{zzz,\nu_2}} \right|^2 \quad (\text{S9})$$

Functional groups existed at the interface generally possess an orientation angle with a certain distribution. Here the angle distribution (σ) was defined by Gaussian and applied to eq.S9⁸.

$$\langle\cos^n\phi\rangle = \int_0^\pi \cos^n\phi f(\phi) \sin\phi d\phi \quad (\text{S10})$$

$$f(\phi) = N \exp\{-(\phi-\phi_0)^2/2\sigma^2\} \quad (\text{S11})$$

where ϕ_0 is the averaged tilt angle of phenyl groups.

Fig. S5 shows the calculated $I_{ssp,n2}/I_{ppp,n2}$ as a function of ϕ with a tilt angle distribution (σ). Comparing the experimental $I_{ssp,n2}/I_{ppp,n2}$ value of 1.63 with those shown in Fig. S8, we can claim that f is possibly 55° with $\sigma = 0^\circ$ or 90° with $\sigma = 30^\circ$ for the two extreme cases. Hence, the phenyl rings roughly orient themselves parallel to the substrate surface.

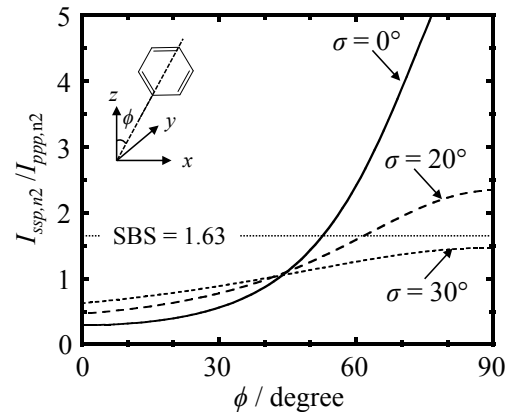


Fig. S5. SFG intensity ratio of the ν_2 mode with ssp over ppp polarization combinations as a function of averaged tilt angle (ϕ).

References:

- [1] P. Gin, N. S. Jiang, C. Liang, T. Taniguchi, B. Akgun, S. K. Satija, M. K. Endoh, and T. Koga, Revealed Architectures of Adsorbed Polymer Chains at Solid-Polymer Melt Interfaces *Phys. Rev. Lett.* **2012**, 109, 265501.
- [2] Z. Chen, Y. R. Shen, and G. A. Somorjai, Studies of Polymer Surfaces by Sum Frequency Generation Vibrational Spectroscopy, *Annu. Rev. Phys. Chem.* **2002**, 53, 437-465.
- [3] C. Hirose, N. Akamatsu, and K. Domen, Formulas for the Analysis of the Surface SFG Spectrum and Transformation Coefficients of Cartesian SFG Tensor Components, *Appl. Spectrosc.* **1992**, 46, 1051-1072.
- [4] K. S. Gautam, A. D. Schwab, A. Dhinojwala, D. Zhang, S. M. Dougal, and M. S. Yeganeh, Molecular Structure of Polystyrene at Air/Polymer and Solid/Polymer Interfaces, *Phys. Rev. Lett.* **2000**, 85, 3854.
- [5] X. Lu, J. N. Mayers, and Z. Chen, Molecular Ordering of Phenyl Groups at the Buried Polystyrene/Metal Interface, *Langmuir* **2014**, 30, 9418-9422.
- [6] Y. Tateishi, N. Kai, H. Noguchi, K. Uosaki, T. Nagamura, and K. Tanaka, Local Conformation of Poly(methyl methacrylate) at Nitrogen and Water Interfaces, *Polym. Chem.* **2010**, 1, 303-311.
- [7] H. Noguchi, H. Minowa, T. Tominaga, J. P. Gong, Y. Osada, and K. Uosaki, Interfacial Water Structure at Polymer Gel/Quartz Interfaces Investigated by Sum Frequency Generation Spectroscopy, *Phys. Chem. Chem. Phys.* **2008**, 10, 4987-4993.
- [8] X. Wei, X. Zhuang, S.-C. Hong, X. Zhuang, T. Goto, and Y. R. Shen, Sum-Frequency Vibrational Spectroscopic Study of a Rubbed Polymer Surface, *Phys. Rev. Lett.* **1999**, 82, 4256.