

Supporting Information (SI)

Effect of Interfacial Local Conformation of Polymer Chains on Adhesion Strength

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1. Local conformation of carbonyl groups by molecular dynamics simulation

To discuss the interfacial orientation of side chain carbonyl groups of PMMA, all-atom molecular dynamics (MD) simulations were conducted. The initial structure was created by placing 5 PMMA (rr triads: 100%) chains with a molecular weight of 15k at 1 nm from the quartz surface. The structural relaxation of the PMMA chains on the surface at 600 K was then evaluated using MD simulations. According to the Vogel–Fulcher–Tammann (VFT) equation,¹ 100 ps at 600 K is considered a sufficient time scale for the segmental relaxation. The simulations were performed using the Forcite module of Materials Studio 2023 (Dassault Systèmes) with the COMPASSIII force field. The PMMA chains reached the surface at approximately 15 ps at 600 K, and after 100 ps they were fully adsorbed onto the quartz surface. Panels (a) and (b) of Figure S1 show the distribution of tilt angle of carbonyl groups ($\theta_{C=O}$) at $t = 15$ and 100 ps. Here, $\theta_{C=O}$, defined as the angle relative to the interface normal, was extracted from the 0.5 nm depth region from the quartz surface. In the bulk of isotropic material, where carbonyl groups are randomly oriented, a histogram of $\theta_{C=O}$ representing the probability of occurrence at each angle should follow a sine function. However, the actual distribution deviated from a sine curve. The two types of local conformation observed at $t = 100$ ps could be attributed to carbonyl groups directly interacting with silanol groups on the quartz surface, and to carbonyl groups where ester methyl groups interacted with silanol groups following interfacial reorientation during annealing.² A prominent $\theta_{C=O}$ peak observed at 40° after 15 ps shifted to 30° after 100 ps, and the peak became sharper in shape after 100 ps. Considering that the aforementioned sine function is convoluted with the actual orientation distribution of functional groups, the actual orientation angle is likely to be smaller than the obtained value of 30° . Indeed, when examining snapshots, there are many carbonyl groups with orientation angles much smaller than 30° . These results indicate that

carbonyl groups tilted more toward the quartz interface to more effectively form hydrogen bonds and the population of interacted carbonyl groups increased.² This observation qualitatively aligns with the SFG results shown in Figure 3.

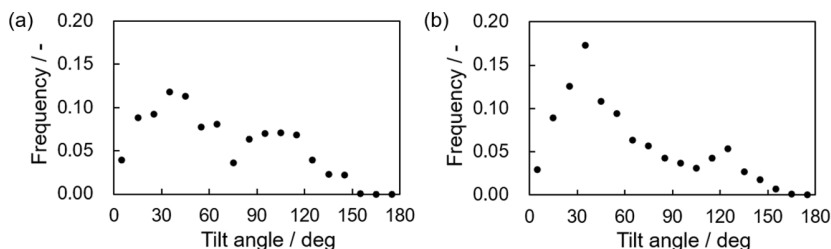


Figure S1 Tilt angle distribution for C=O groups at (a) 15 ps and (b) 100 ps.

2. SFG spectra in carbonyl and hydroxyl regions for PS/PMMA on SiO_x

To discuss hydrogen bonds between ester methyl groups and hydroxyl groups on the SiO_x surface, SFG spectra were collected with the *ssp* polarization combination. Panels (a) and (b) of Figure S2 show the SFG spectra in the carbonyl and hydroxyl stretching regions for PS/PMMA blends with various bulk compositions at the SiO_x interface. A broad peak corresponding to the stretching vibration of side chain carbonyl groups of PMMA was observed for PS/PMMA (25/75), (50/50), and (75/25), indicating the presence of PMMA at the interface. This result is in good accordance with the SFG spectra in the CH stretching vibrational region shown in Figure 5 (a). Notably, the peak position shifted to a lower wavenumber with increasing PMMA fraction.³ A similar peak shift associated with the PMMA fraction was also observed in the OH stretching vibrational region. Moreover, the shape of both peaks in the carbonyl and hydroxyl regions became sharper with increasing PMMA fraction. These results make it clear that hydrogen bonds became more prominent at the PS/PMMA interfaces as well as SiO_x surfaces with increasing bulk PMMA fraction.

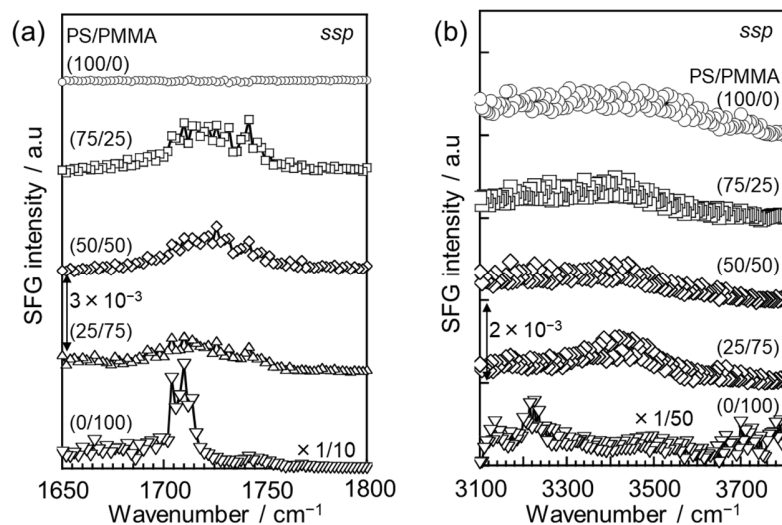


Figure S2 SFG *ssp* spectra in (a) carbonyl and (b) hydroxyl stretching region vibration regions.

References

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