Probing Molecular Structures of Poly(dimethyl siloxane) at Buried Interfaces *in Situ*

(Supporting information)

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1. Refractive Index and Fresnel Coefficient

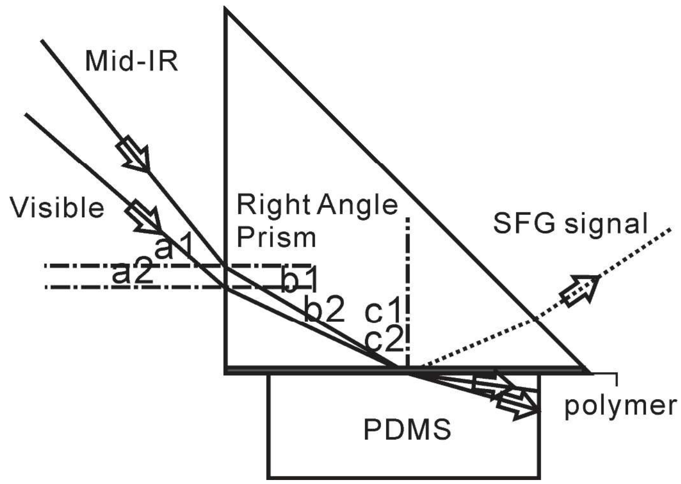

Figure s1. The near total reflection geometry used in the SFG experiment.

The refractive index of air is 1.00 at all frequencies. The refractive indices of the silica prism are 1.41, 1.46, and 1.47 at 2900 cm^{-1} (IR), 532 nm (visible), and 461 nm (signal), respectively. The refractive indices of PDMS are 1.37 (IR), 1.43(visible) and 1.43(signal). The refractive indices of PET are 1.47 (IR), 1.57 (visible) and 1.59 (signal). The input angles of the visible and IR beams were 60.0° and 57.0° vs. the surface normal in the lab frame. Therefore, the incident angle of the input IR beam at the prism/air interface (angle a1) was 33.0°, while the incident angle of the input visible beam (angle a2) at the same interface was 30.0°.

(1) At the silica PDMS interface:

We calculated the refractive angles for both the IR and visible beams inside the prism (angles b1 and b2), which were 22.7° and 20.0°, respectively. We then deduced that the incident angles of the two input beams at the silica/PDMS interface were 67.3° and 70.0° respectively.

We can use the following equation to calculate Fresnel coefficients:

$$L_{yy}(\omega) = \frac{2n_1(\omega)\cos\beta}{n_1(\omega)\cos\beta + n_2(\omega)\cos\gamma}, \quad L_{zz}(\omega) = \frac{2n_2(\omega)\cos\beta}{n_1(\omega)\cos\gamma + n_2(\omega)\cos\beta}\left(\frac{n_1(\omega)}{n'(\omega)}\right)^2$$

where β is the incident angle at the interface, and γ is the refractive angle at the interface and can be calculated using β and refractive indices of both materials forming the interface. $n'(\omega)$ is the refractive index of the interface, which can be approximated by averaging the refractive indices of the two materials forming the interface. At silica/PDMS interface, the values of n' equal to 1.39 (IR), 1.445 (visible), 1.45 (signal), respectively.

Along with the following two equations,

$$\chi_{eff,ssp} = L_{yy}(\omega_{SF}) L_{yy}(\omega_{vis}) L_{zz}(\omega_{IR}) \sin\theta_{i,IR} \cdot \chi_{yyz}$$
$$\chi_{eff,sps} = L_{yy}(\omega_{SF}) L_{zz}(\omega_{vis}) L_{yy}(\omega_{IR}) \sin\theta_{i,vis} \cdot \chi_{yzy}$$

We calculated the effective Fresnel coefficients at the silica/PDMS interface to be:

$$\chi_{eff,ssp} = 1.31 \cdot \chi_{yyz}$$
$$\chi_{eff,sps} = 1.33 \cdot \chi_{yzy}$$

(2) At the d_4-PET/PDMS interface:

The d_4-PET layer was between the silica and PDMS. The IR and visible input beams at the d_4-PET/silica interface were still 67.3° and 70.0°, respectively. Passing through the d_4-PET film, the incident angles of IR and visible beams at the d_4-PET/PDMS interface can be calculated as 54.4° and 59.0°, respectively. At the d_4-PET/PDMS interface, the values of n' equal to 1.42 (IR), 1.50 (visible), 1.51 (signal), respectively. Similar to the silica/PDMS interface, we can calculate at the d_4-PET/PDMS interface:

$$\chi_{eff,ssp} = 1.48 \cdot \chi_{yyz}$$
$$\chi_{eff,sps} = 1.58 \cdot \chi_{yzy}$$

Compared to the silica/PDMS interface, IR and visible beams reaching the d_4-PET/PDMS interface were attenuated by the silica/d_4-PET interface due to the reflection. Similarly, the signal generated from the d_4-PET/PDMS interface was also attenuated by silica/d_4-PET interface. Base on Snell's law, we can calculate that the transmission ratio for s polarized signal is 0.962, for s polarized visible beam is 0.957, for p polarized IR is 0.995. Therefore, the ssp polarization attenuation factor is A=0.962*0.957*0.995=0.915. This factor was used in the paper for narrowing the possible orientation of PDMS methyl group at the silica interface. In ssp polarization, we have:

$$\frac{A \cdot \chi_{ssp,PDMS/Silica}}{\chi_{ssp,PDMS/dPET}} = \frac{1.31 \cdot \chi_{yyz,PDMS/Silica}}{1.48 \cdot \chi_{yyz,PDMS/dPET}}$$

Therefore,

$$\frac{\chi_{yyz,PDMS/Silica}}{\chi_{yyz,PDMS/dPET}} = \frac{1.48 \cdot A}{1.31} \frac{\chi_{ssp,PDMS/Silica}}{\chi_{ssp,PDMS/dPET}} = \frac{1.48 \cdot 0.915}{1.31} \frac{\chi_{ssp,PDMS/Silica}}{\chi_{ssp,PDMS/dPET}} = 1.03 \frac{\chi_{ssp,PDMS/Silica}}{\chi_{ssp,PDMS/dPET}}$$

2. Possible Orientation Angle Ranges of PDMS $Si(CH_3)_2$ Groups

At the d_4-PET/uncured PDMS interface, from the spectral fitting results and considering the Fresnel coefficients, we have

$$\chi_{yyz,s} / \chi_{yyz,as} = 1.24 \pm 0.17$$
$$\chi_{yyz,as} / \chi_{yzy,as} = \pm 0.51 \pm 0.06$$

The possible ranges of orientation angles for PDMS $Si(CH_3)_2$ groups deduced using $\chi_{yyz,s} / \chi_{yyz,as} = 1.24$ and $\chi_{yyz,as} / \chi_{yzy,as} = -0.51$ are shown in Figure s2a and s2b, respectively. Figure s2c shows the overlapping area of the two ranges in Figure s2a and s2b. Clearly that if $\chi_{yyz,as} / \chi_{yzy,as} = -0.51$, no possible orientation angle for PDMS methyl groups satisfies both measured values. Therefore, we believe that $\chi_{yyz,as} / \chi_{yzy,as} = 0.51 \pm 0.06$, as we presented in the text.

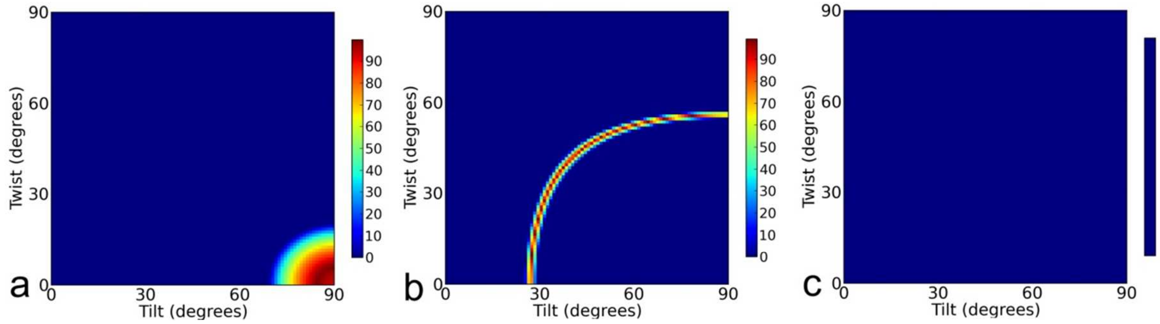

Figure s2. Plot $\chi_{yyz,s} / \chi_{yyz,as}$ and $\chi_{yyz,as} / \chi_{yzy,as}$ values obtained from SFG experiment in Figure 3c and 3d (in the paper text) respectively to obtain: (a) Orientation range of $Si(CH_3)_2$ group at the d_4-PET/uncured PDMS interface using $\chi_{yyz,s} / \chi_{yyz,as} = 1.24$; (b) Orientation range of $Si(CH_3)_2$ group at the d_4-PET/uncured PDMS interface using $\chi_{yyz,as} / \chi_{yzy,as} = -0.51$; (c) Overlapping area of (a) and (b). No possible orientation angle range can be identified in (c). The error bar presented here is 20%.

Similarly, the orientation ranges deduced using $\chi_{yyz,s} / \chi_{yyz,as} = 1.35$ and $\chi_{yyz,as} / \chi_{yzy,as} = -0.51$ are shown in Figure s3a and s3b. The overlapping area is shown in Figure s3c. No possible orientation range can be identified in (c). Therefore, we believe that $\chi_{yyz,as} / \chi_{yzy,as} = 0.51 \pm 0.05$ at the d_4-PET/cured PDMS interface, as we presented in the text.

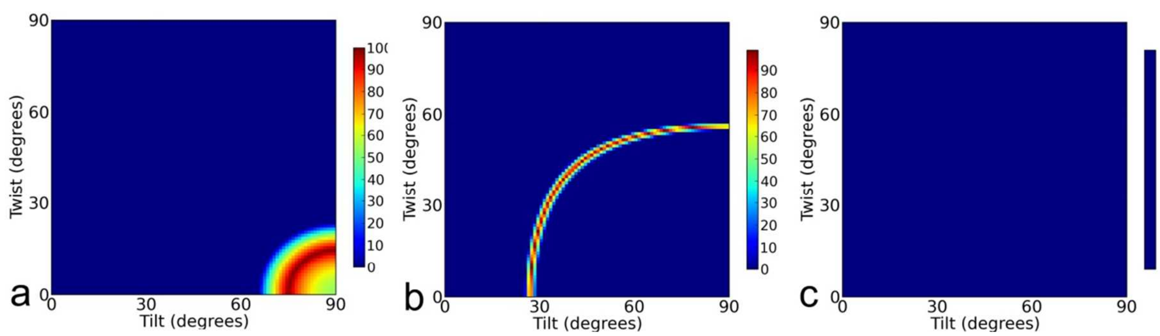

Figure s3. Plot $\chi_{yyz,s} / \chi_{yyz,as}$ and $\chi_{yyz,as} / \chi_{yzy,as}$ values obtained from SFG experiment in Figure 3c and 3d (in the paper text) respectively to obtain: (a) Orientation range of $Si(CH_3)_2$ group at the d_4-PET/cured PDMS interface using $\chi_{yyz,s} / \chi_{yyz,as} = 1.35$; (b) Orientation range of $Si(CH_3)_2$ group at the d_4-PET/cured PDMS interface using $\chi_{yyz,as} / \chi_{yzy,as} = -0.51$; (c) Overlapping area of (a) and (b). No possible orientation angle range can be identified in (c). The error bar presented here is 20%

Similarly, we can obtain at the silica/uncured PDMS interface, $\chi_{yyz,as} / \chi_{yzy,as} = -2.71 \pm 0.31$ rather than 2.71±0.31; at the silica/cured PDMS interface, $\chi_{yyz,as} / \chi_{yzy,as} = -1.83 \pm 0.23$ rather than 1.83±0.23. These results can be easily obtained because in Figure 3d (in the paper text), there's no possible orientation range satisfies $\chi_{yyz,as} / \chi_{yzy,as} > +1$.