Supplementary Information for:

Depth Profile of the Segmental Dynamics of at a Poly(methyl methacrylate) Film Surface

Biao Zuo, Yingjun Liu, Lin Wang, Yumei Zhu, Yifan Wang, Xinping Wang*

Department of Chemistry, Key Laboratory of Advanced Textile Materials and Manufacturing Technology of the Education Ministry, Zhejiang Sci-Tech University, Hangzhou 310018, China

*Email: wxinping@yahoo.com or wxinping@zstu.edu.cn

Section 1: Depth sensitive techniques for surface characterization

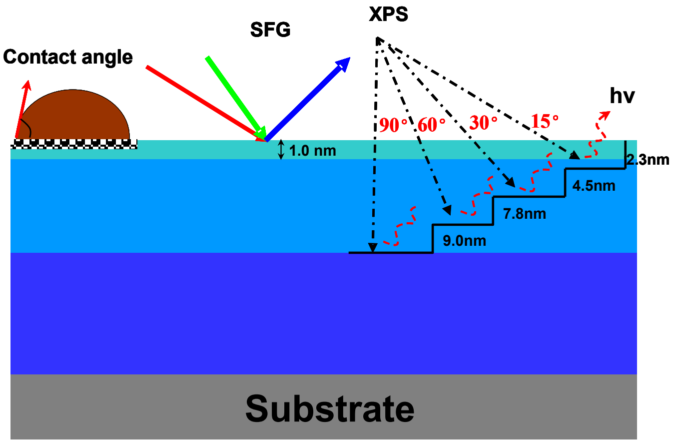

Figure. S1. Schematic representation of the sampling depths of SFG, contact angle measurement and angle resolved XPS, respectively.

Contact angle measurement is a sensitive surface technique for reflecting the chemical composition and molecule structures on surfaces. The contact angle is determined only by the short-range interactions between film surface and the testing liquid. Whiteside and his coworkers firstly demonstrated that the analytical depth of the contact angle is about ***0.5 nm***,[1,2] which was further confirmed by various other experiments.[3-8] Angle resolved XPS is a well- known surface technique which is able to distinguish the chemical composition in depths from 2~10 nm by altering the emission angle of the photoelectron (θ). The analytical depth of XPS analysis can be defined by $d = 3\lambda\sin\theta$, where θ is the emission angle of the photoelectron to the surface plane, and 3λ is the sampling depth where 95% of the electrons escape. In this experiment, θ values of 15°, 30°, 60° and 90° were chosen, corresponding to the integrated depths about ***2.3, 4.5, 7.8 and 9.0 nm***, respectively.[9,10]

SFG is a recently developed secondary nonlinear optical spectroscopy. From the physics of SFG, it has been widely accepted that SFG detects structural information on the sub-monolayer surface.[11-14] For an isotropic amorphous polymer surface, the SFG signal was proven to be merely from the top 0.5-1.0 nm of a surface.[15] To facilitate comparisons with other techniques, we herein estimated the analytical depth of SFG probing amorphous polymer surfaces to be about ***1.0 nm***. Therefore, combined with SFG, contact angle measurements and angle-resolve XPS, the structural information of films from 0.5 nm of a surface to the depth of 9.0 nm can be acquired. The sampling depth of the respective techniques is shown in Figure S1.

Section 2: DSC measurement of PMMA$_{430}$-ec-FMA$_4$

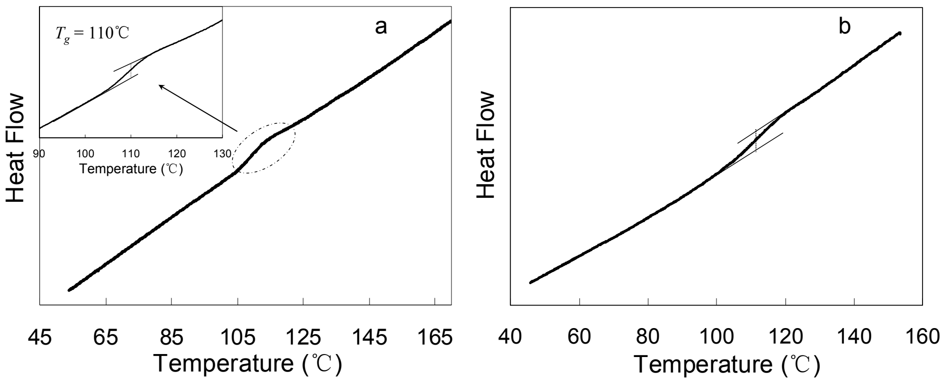

Figure S2. DSC curves of PMMA$_{430}$-ec-FMA$_4$ (a) and PMMA$_{430}$ (b) bulk sample.

The curve of PMMA$_{430}$-ec-FMA$_4$ (Figure S2-a) only shows a slight endothermic transition near 110°C and is without any other heating events for melting, crystallization or other phase transitions in the temperature range from 50°C to 170 °C. The T_g of PMMA in PMMA$_{430}$-ec-FMA$_4$ was determined to be 110°C from the temperature at the half-height of the heat capacity increase (1/2ΔCp), which was same as the T_g of PMMA$_{430}$ homo-polymer (Figure S2-b). These facts demonstrate that the introduction of very small amounts of FMA units at the PMMA chain end does not influence the association behavior of PMMA chains, and the crystallization of FMA units was not observed for the bulk sample.

Section 3: Surface topographies of PMMA$_{430}$-ec-FMA$_4$ films

The surface AFM topography images of the PMMA$_{430}$-ec-FMA$_4$ spin-coated and cast films are shown in Figure S3, and can be seen to exhibit very smooth surfaces with RMS roughness below 1 nm. This indicates that the polymer chains randomly distribute on the surface without aggregation or phase separation, and further confirms the fact that the introduction of very few FMA units at the PMMA chain end does not influence the aggregation behavior of PMMA chains on the surface.

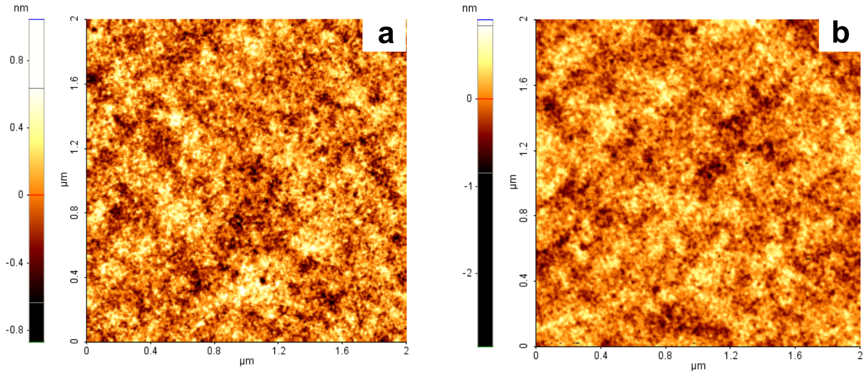

Figure S3. AFM topography images of the PMMA$_{430}$-ec-FMA$_4$ spin-coated (a) and cast (b) films.

Section 4: Variation of SFG 2960 cm^{-1} peak intensities with heating

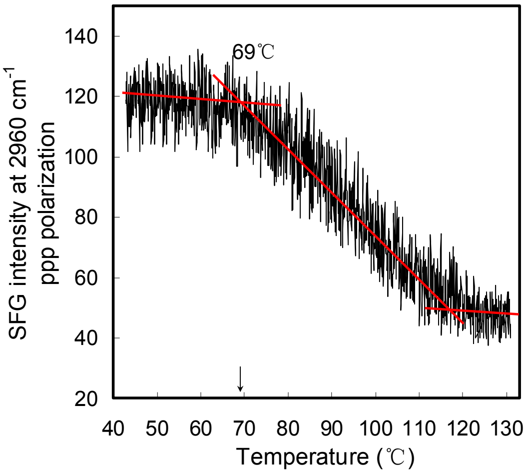

Figure S4. SFG intensity of the peak at 2960 cm^{-1} in the *ppp* polarization for PMMA$_{430}$-ec-FMA$_4$ film as the film was heated at a rate of 0.5 °C/min.

To further investigate the surface structural transition during annealing, we monitored the SFG intensities of the peak at 2960 cm^{-1} in *ppp* polarization (Figure S4) during heating of the sample at 0.5 °C/min *in situ*. It is obvious that the first intersection temperature between the linear fits is about 69°C (T^{onset} = 69 °C).

Section 5: SFG *ssp* spectra of PMMA$_{430}$-ec-FMA$_4$ spin-coated film as a function of temperature

The changes of SFG *ssp* spectra of PMMA$_{430}$-ec-FMA$_4$ spin-coated film as a function of annealing temperature are displayed in Figure S5. The SFG spectra of the films annealed at 55, 60 and 70°C remain unchanged. When the temperature is higher than 70°C, the peak at 2910 cm^{-1} from the CH_2 groups in the chain backbone starts to decrease with increasing temperature, indicating a T^{onset} near 70°C. This decrease in 2910 cm^{-1} peak is indicative of the gradually depleting of PMMA backbone from the outmost surface in the course of thermal annealing. The SFG technique has been utilized to measure the surface T_g by detecting the surface structural changes caused by temperature change.[16,17] The T^{onset} obtained by the mobility change of CH_2 groups in the PMMA backbone (2910 cm^{-1} peak in *ssp* spectra) is the same as the T^{onset} obtained from the methyl side groups (2960 cm^{-1} peak in *ppp* spectra), which suggests that the T^{onset} is attributed to the PMMA segmental motion involved in both backbone and side groups.

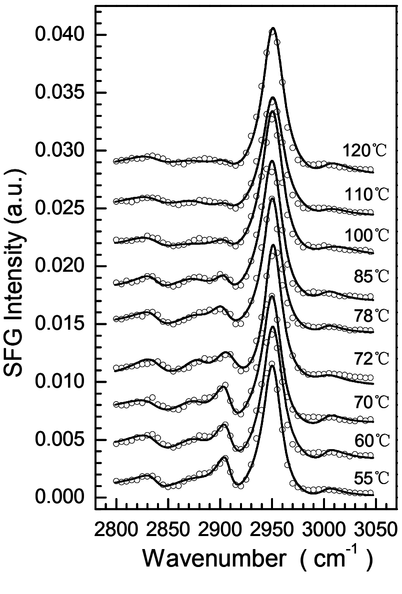

Figure S5. SFG spectra of the $PMMA_{430}$-ec-FMA_4 spin-coated films as function of temperature. (*ssp*)

Section 6: Surface T^{onset} of PMMA$_{430}$-ec-FMA$_2$ measured by contact angle

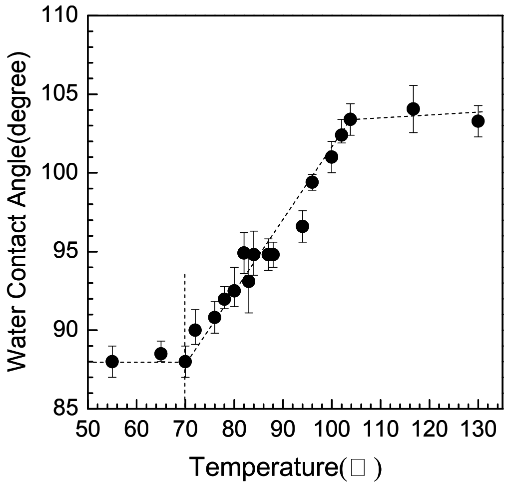

Figure S6. Change of the contact angle of the PMMA$_{430}$-ec-FMA$_2$ spin-coated films as a function of temperature.

Section 7: Surface T^{onset} of PMMA$_{430}$-ec-F6MA$_5$ film measured by contact angle

Figures S6 and S7 display the temperature dependence of the contact angle for two PMMA$_{430}$ samples end capped with two FMA or five CH_2-$C(CH_3)COOCH_2CH_2$ $(CF_2)_5CF_3$ moities. The results show that the two samples have the same T^{onset} (70°C) as PMMA$_{430}$-ec-FMA$_4$ at the depth at which the contact angle was explored. This result suggests that the variance of the structure of the end groups does not affect the surface T^{onset} and also affirms that the measured relaxation temperature (T^{onset}) is explicitly due to the mobility transition of PMMA segments from a glass state to a rubbery state.

Section 8: Surface T^{onset} of PMMA$_{430}$-ec-F6MA$_5$ film measured by contact angle

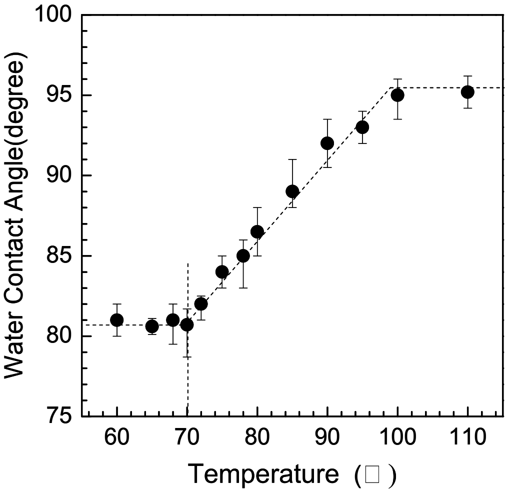

Figure S7. Change of the contact angle of the PMMA$_{430}$-ec-[(CH$_2$-C(CH$_3$)COO CH$_2$CH$_2$ (CF$_2$)$_5$CF$_3$]$_5$ spin-coated films as a function of temperatures.

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