Supporting Information

Method to Probe Glass Transition Temperatures of Polymer Thin Films

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Figure S1 shows the chemical formulas of PMMA, PBMA and PEMA.

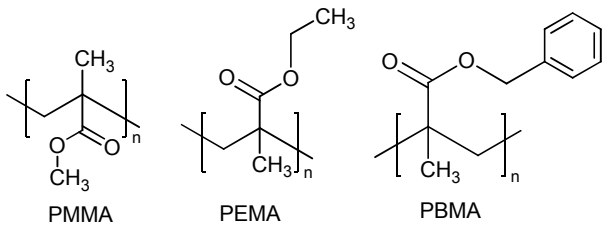

Figure S1. Chemical formulas of the polymers employed in this study.

Figure S2 shows the SFG *ppp* spectra collected at 298 K and 393 K for a 30-nm-thick PMMA thin film sample on a Au substrate.

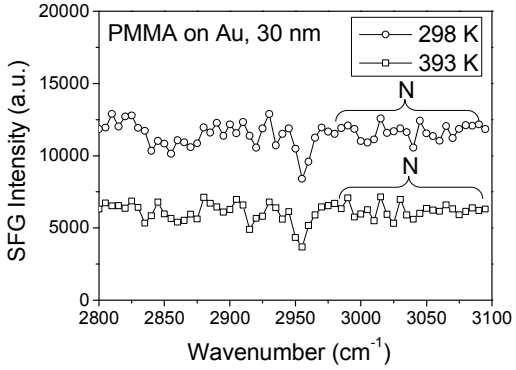

Figure S2. SFG *ppp* spectra collected at 298 K and 393 K for a 30-nm-thick PMMA thin film sample on a Au substrate.

Figure S3 shows SFG *ppp* spectra of a 27-nm-thick PBMA film on a Au substrate (A) and a 17-nm-thick PEMA film on a Au substrate (B).

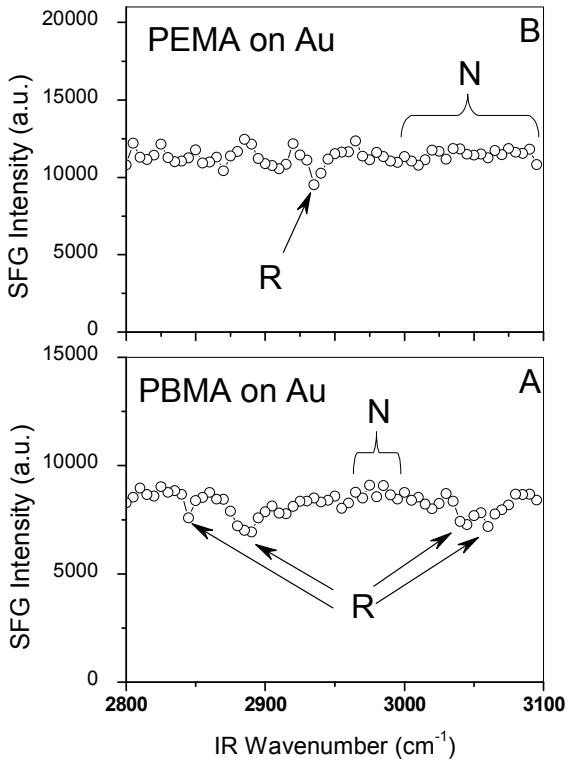

Figure S3. SFG *ppp* spectra of a 27-nm-thick PBMA film on a Au substrate (A) and a 17-nm-thick PEMA film on a Au substrate (B). The molecular vibrational signals appeared as the distinct resonant peaks (denoted by "R") while the SFPP signals appeared as the nonresonant backgrounds (denoted by "N").

Similarly, the molecular vibrational signals appeared as distinct resonant peaks denoted by "R" while the SFG SFPP signals appeared as the nonresonant backgrounds denoted by "N" in Figure S2. The temperature-dependent SFG SFPP signals for PBMA thin films with thicknesses of 27 nm, 34 nm, 45 nm and 80 nm and for PEMA thin films with thicknesses of 17 nm, 44 nm, 70 nm, and 125 nm were recorded, which were shown in Figure S3A and S3B, respectively. The results

indicated that the T_g decreased with decreasing the film thicknesses for both PBMA and PEMA thin films, consistent with the PMMA thin films.

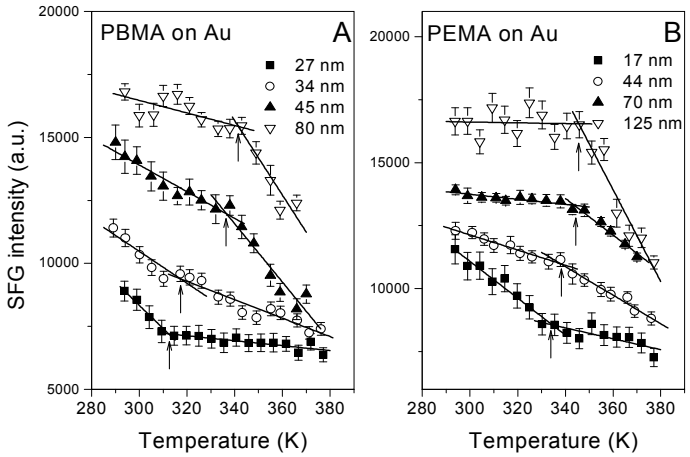

Figure S4. SFG SFPP signals as a function of temperature for PBMA (A) and PEMA (B) thin films on Au substrates. The measured transition temperatures (intersection points) were indicated by arrows. Dots were experimental data and straight lines were fitted results. Data were offset for clarity.

The thickness-dependence of T_g for both PBMA and PEMA thin films was shown in Figure S5. The data points suggested that the magnitude of the T_g decrease for PEMA thin films is much smaller than that for the PBMA thin films. This may reflect the different effects of the side pendent groups on the dynamic behaviors of polymer thin films.[1–5]

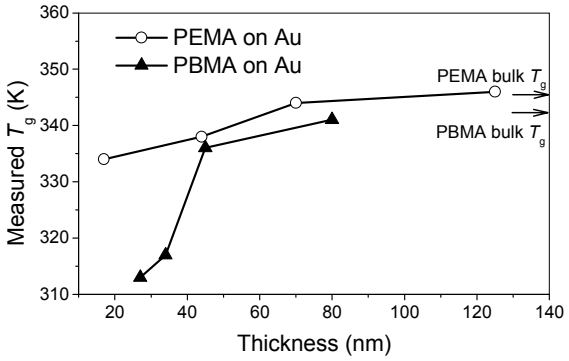

Figure S5. Detected glass transition temperatures as a function of film thickness for PBMA and PEMA polymer thin films on Au substrates; the bulk T_gs of PBMA and PEMA measured by DSC were indicated by arrows.

For DSC experiments, the temperature of all the powder samples (PMMA, PEMA and PBMA) was ramped at 2 K/min. The glass transition temperatures (T_gs) of PMMA, PEMA and PBMA were measured to be 385K (half C_p extrapolated), 345K (half C_p extrapolated) and 341K (half C_p extrapolated), respectively. The experimental results were shown in Figure S6. Before DSC scans, all the samples were heated up above their own T_gs. Then the PMMA, PEMA and PBMA samples were annealed at 365 K, 325 K, and 321 K, respectively, for 4 hours. Therefore the enthalpy relaxation peaks were observed.

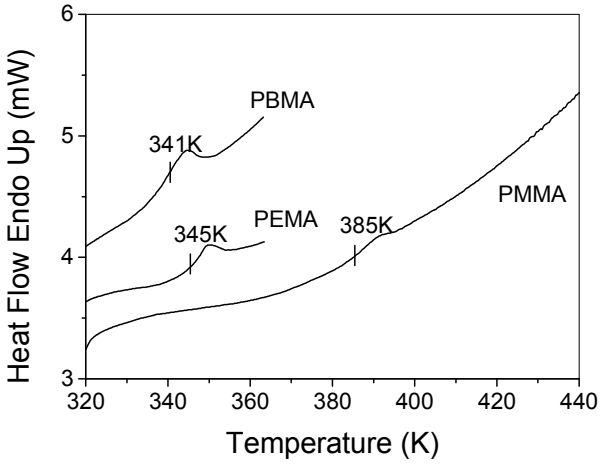

Figure S6. Bulk T_gs for PMMA, PBMA and PEMA measured by DSC.

SFG experimental details of sandwiched geometry.

For the sandwiched geometry, the PMMA thin film was firstly spin coated onto a transparent silica window surface and then a 500-nm-thick silver (Ag) layer was electron-beam evaporated onto the PMMA thin film surface. Before and after the electron-beam evaporation, all the samples were annealed at 120 °C for 4 hours. The two input laser beams for SFG study came from the silica window side, went through the silica window and overlapped spatially and temporally at the PMMA/Ag interface. The SFPP signal from the Ag surface was generated and monitored at different temperatures.

Temperature calibration for these two experimental geometries.

For the PMMA thin films supported on Au, the temperature was directly calibrated at the Au surface using crystalline small molecules (Dodecylamine, hexanamide, DL-hydroxy succinic acid, benzoic acid, paranitroaniline and p-phenylenediamine) with sharp melting temperatures. For the sandwiched geometry, the temperature was calibrated at the silica top surface, which is farther away from the

heating device compared to the polymer film (see TOC graphic, heating is from the metal side).

References:

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(3) Mattsson, J.; Forrest, J. A.; Börjesson, L. *Phys. Rev. E* **2000**, *62*, 5187–5200.

(4) Roth, C. B.; Pound, A.; Kamp, S. W.; Murray, C. A.; Dutcher, J. R. *Eur. Phys. J. E* **2006**, *20*, 441−448.

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