

Supplementary Materials for “Examining dynamics in a polymer matrix by single molecule fluorescence probes of different sizes” by Hao Zhang et al,

1. Defocused single molecule fluorescence microscopy videos

Videos are provided for Probe-M recorded at 34.2 and 43.6°C. The dimension of the images is 27.4×27.4 μm.

2. Assemblies of 50 typical power spectra of the probes adopted

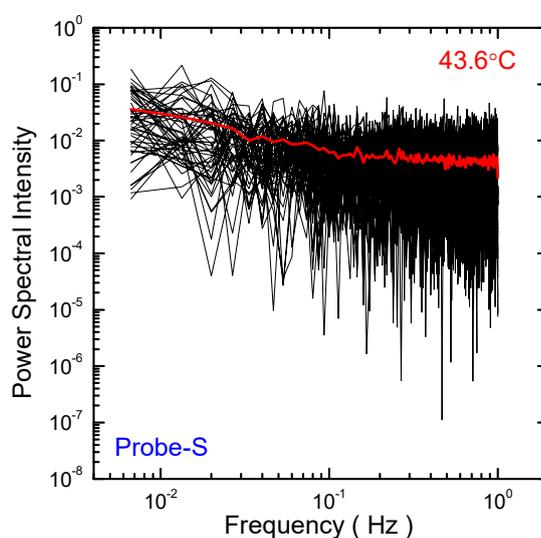


Figure S1 Assembly of 50 power spectra of Probe-S doped in the 96 nm-thick PVAc film measured at 43.6°C. The red line denotes the average of these 50 power spectra.

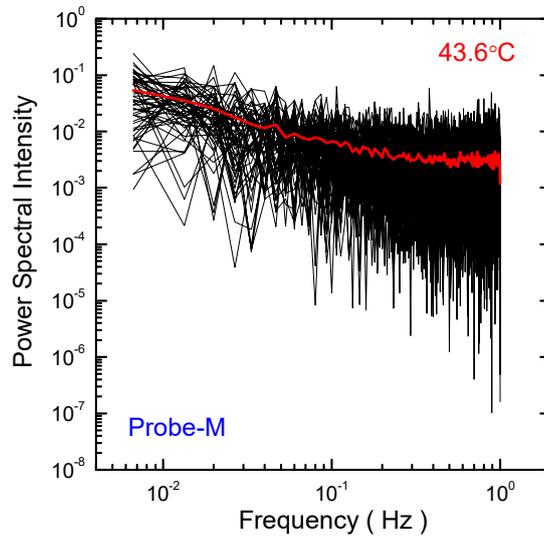


Figure S2 Assembly of 50 power spectra of Probe-M doped in the 96 nm-thick PVAc film measured at 43.6°C. The red line denotes the average of these 50 power spectra.

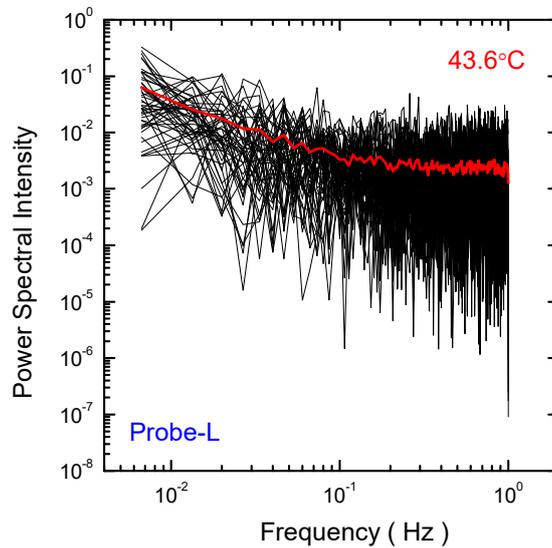


Figure S3 Assembly of 50 power spectra of Probe-L doped in the 96 nm-thick PVAc film measured at 43.6°C. The red line denotes the average of these 50 power spectra.

3. Dielectric loss spectra of PVAc film

For the impedance measurement presented here, the samples, which are 0.5 mm in thickness and 10.0 mm in diameter, are sandwiched between two gold electrodes. The sample is housed inside a home-made sample cell, equipped with heating device and proper thermo-insulation. The sample's temperature is precisely controlled using LakeShore 335 controller. The impedance analysis is conducted by Solartron SI-1260 Impedance/Gain-Phase Analyzer with the SI-1296 Dielectric Interface. The measurements were performed in the frequency range 0.01 Hz – 1.0 MHz at temperatures between 313 and 353 K. The typical loss spectra are displayed in Figure S4. It is noted that no reliable measurement can be conducted below frequency of 10^{-1} Hz.

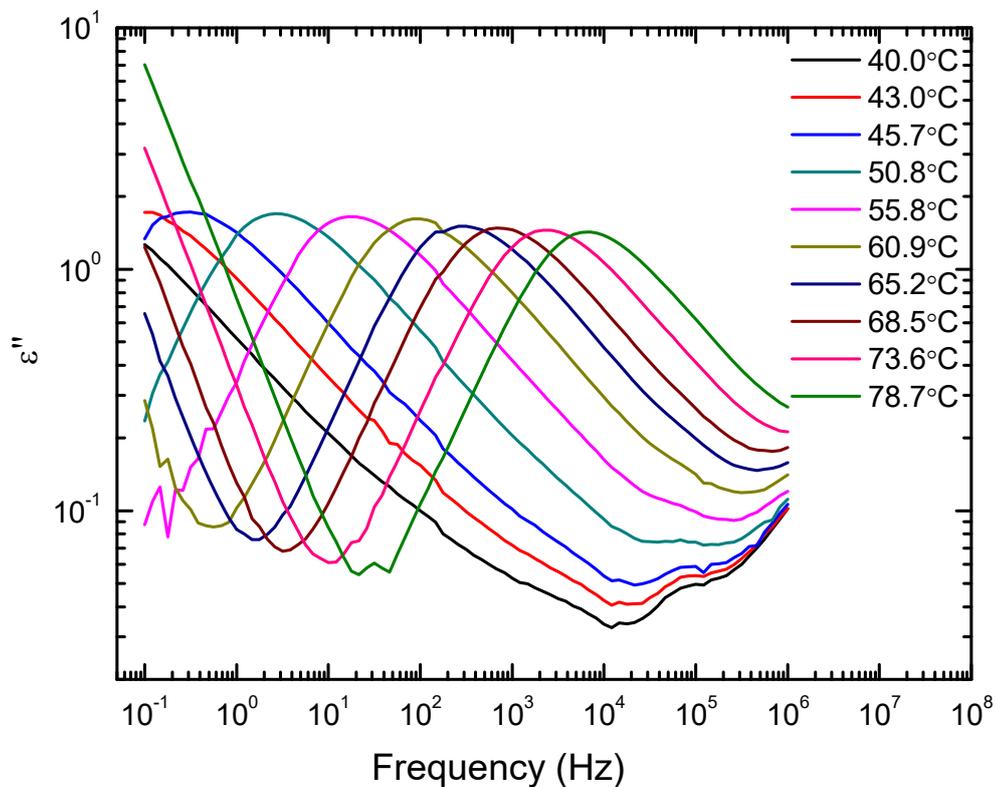


Figure S4 Dielectric loss spectra of PVAc film measured under different temperatures. The value of sample's temperature is displayed in the figure.

4. Comparison of temperature dependence of f_r and power spectral intensity

The integrated area of the power spectra density data (therefore the spectral intensity) was calculated as the indication of energy taken by the rotating fluorescent probes,

and it is plotted together with the data of temperature dependence of f_r (Figure S5). It is observed that the spectral intensity keeps increasing even after the f_r value reaches unity. For example, for Probe-S, its power spectral intensity is still increasing way beyond its T_u temperature. This is also true for Probe-M but with a larger slope compared with Probe-S. For Probe-L, the increase in spectral intensity is much lower at lower temperature ($<39.8^\circ\text{C}$) where the increase of f_r value is also small, while the increase in spectral intensity is much sharper at higher temperature ($>39.8^\circ\text{C}$) where the increase of f_r value is also bigger. This is a clear indication that the temperature for f_r value to reach unity (T_u) is the starting of significant occurrence of glass transition, i.e. the starting of vast increase of heat flow in the DSC measurements.

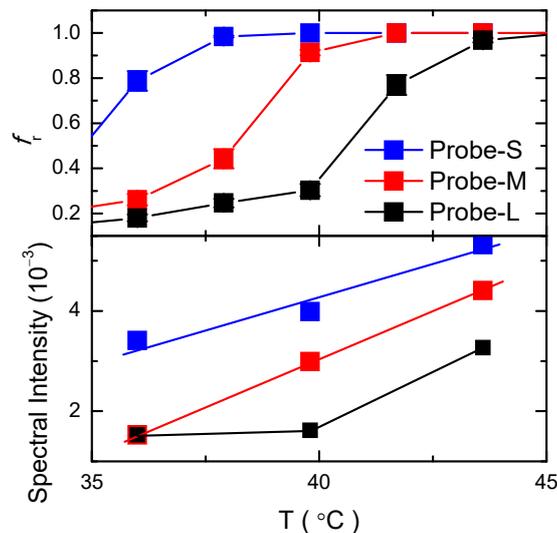


Figure S5 The f_r value as a function of temperature is plotted together with power spectral intensity for comparison. For Probe-S, even after the f_r value reaches unity, its power spectral intensity is still increasing at the same rate.

5. Distribution of fluorescence probes inside the PVAc film

Secondary ion Mass Spectroscopy (SIMS) was employed to investigate the distribution of fluorescence probes along the direction normal to the film's plane. SIMS measurement was performed on a standard commercial TOF-SIMS v(ION-TOF GmbH, Münster, Germany). The experimental condition is: Ion beam: Ar^+ , incident angle: 45° . The depth profiling experiment was performed with an analyzed area of $100 \times 100 \mu\text{m}$ inside an etching area of $300 \times 300 \mu\text{m}$. All analyses were carried out at 256×256 pixels. Figure S6 shows the results, in which the intensity of CN group representing the fluorescence probes (perylendiimide) exhibits a slight and gradual increase in intensity near polymer-air and polymer-substrate interfaces – the intensity at polymer-air is about 10% higher than the middle of the film while that at polymer-substrate interface is about 60% higher. The results indicate segregation of the probes does exist but is not severe.

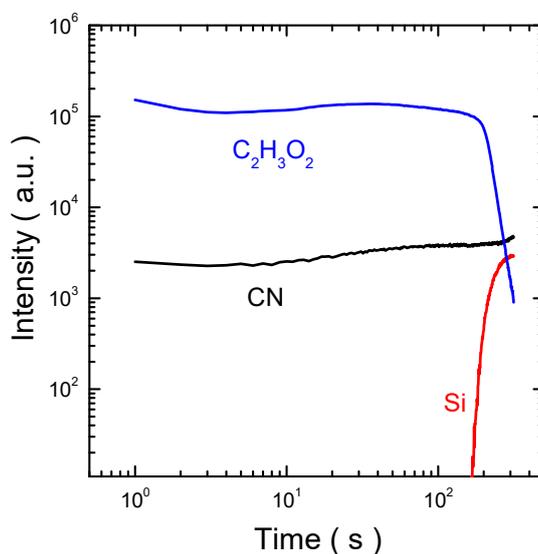


Figure S6 Intensity of signal from CN group representing the fluorescence probe (perylendiimide) and $\text{C}_2\text{H}_3\text{O}_2$ group representing the polymer (PVAc) as a function of experimental time.

6. Surface morphology characterization by atomic force microscopy

The surface morphology of the film is characterized by an atomic force microscope (AFM, Multimode 8, Digital Instruments). The scan size is $10 \times 10 \mu\text{m}$. The typical result is shown in Figure S7. No dewetting was observed at elevated temperatures.

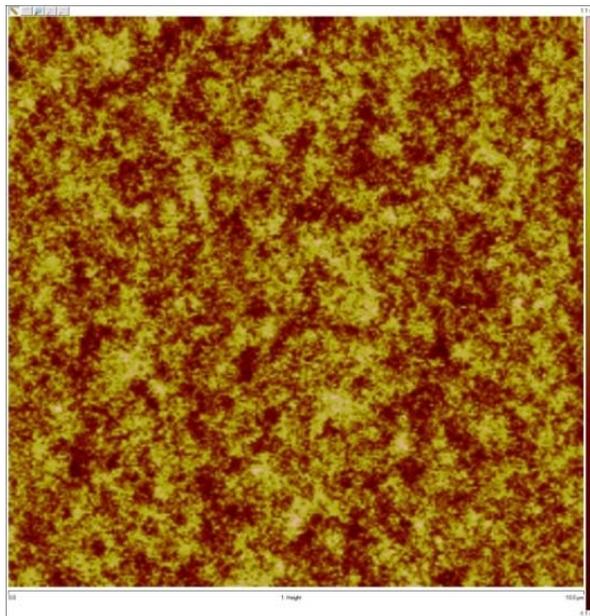


Figure S7 The surface morphology of a 96 nm-thick PVAc film deposited on a glass cover slip after the single molecule fluorescence experiment was conducted. No dewetting was observed at elevated temperatures.

7. *Single molecule dynamics at polymer-air and polymer-substrate interfaces*

Control experiments were conducted to compare the dynamics of fluorescence probes located at polymer-air or polymer-substrate interfaces. The probes are allocated to these interfaces by depositing them using selective solvent. Cyclohexane was chosen to dissolve the probes because it is a poor solvent for the polymer (PVAc). To allocate the probes at polymer-air interface, the probes were spin-casted onto the pre-deposited PVAc film. To allocate the probes at polymer-substrate interface, the probes were spin-casted on the substrate at first, and the PVAc films were spin-casted on top of it afterwards. The power spectra of rotational motion of Probe-S and Probe-M at these two interfaces at 39.8°C are displayed in Figure S8, together with the data for the same probe doped in the film. The data show that the power spectra of Probe-S and Probe-M at polymer-air interface show no significant difference to those doped in the films while much slower and less activated dynamics is found at polymer-substrate interface.

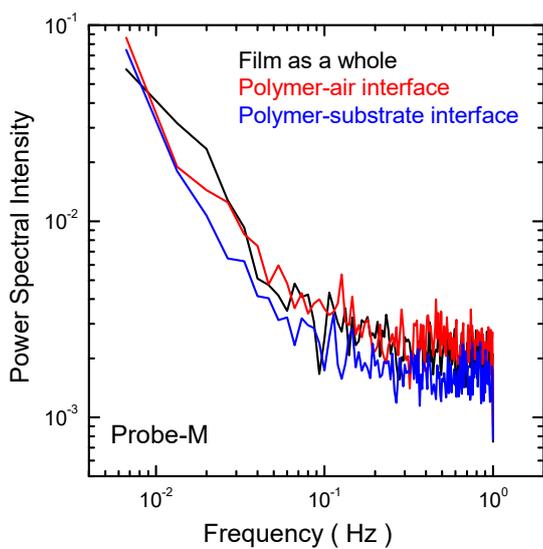
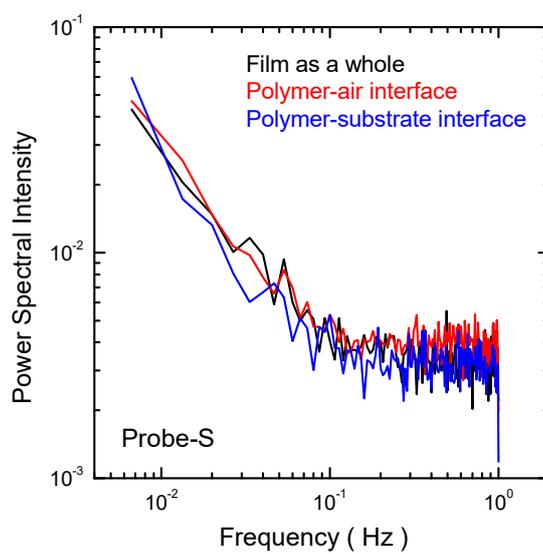


Figure S8 Averaged power spectra of Probe-M and Probe-S deposited at the polymer-air and polymer-substrate interfaces recorded at 39.8°C. The data for probes doped in the film as a whole is displayed together as a comparison. The film thickness is 96.0 nm.