

Segment Dynamics in Thin Polystyrene Films Probed by Single-Molecule Optics

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Polymers have recently been demonstrated to exhibit different chain dynamic behavior, as compared to the bulk, when confined into the geometry of ultrathin films.^{1,2} Investigations of the glass transition temperature (T_g) of thin, supported, polystyrene films by ellipsometry,³ Brillouin light scattering,⁴ dielectric spectroscopy,⁵ or positron annihilation lifetime spectroscopy (PALS),⁶ among others, showed large T_g depressions. This behavior is thought to be due to the existence of a surface layer where the polymer chain dynamics is enhanced over that in the bulk. This layer becomes dominant for very thin films, thereby shifting T_g of the films toward lower temperatures. The existence of such a surface layer is also supported by measurements of T_g for free-standing polymer films⁷ and by a direct examination of the polymer surface by PALS.⁸ However, all experimental techniques mentioned provide ensemble-averaged information. Furthermore, the depth at which deviation between the surface and the bulk dynamics becomes significant could not be addressed in detail due to the lack of depth resolution of these techniques on the nanometer scale.

Single molecule fluorescence detection (SMD) intrinsically avoids ensemble averaging. In combination with high spatial and temporal resolution, SMD is an ideal tool for investigating structure and dynamics of the probe environment on the nanoscale. Through the use of different approaches, SMD has already been employed with success to study macromolecular systems^{9,10} and inorganic/organic composite films.¹¹ In a recent study¹² we have introduced a new single-molecule approach based on fluorescent lifetime fluctuations to give direct insight into local, nanoscale dynamics of the polymer matrix surrounding a chromophoric probe on the segmental level.

In this communication we report, for the first time, on the use of single-molecule fluorescence lifetime to investigate thin film effects in a glassy polymer system at temperatures far below bulk T_g . We find that the dynamics of the surroundings of the probe becomes enhanced when the constituent macromolecules are confined into a thin film. The characteristic film thickness at which this behavior becomes noticeable is several times larger than the radius of gyration (R_g) of the polymer chain used. Our result points toward the existence of interfacial regions with enhanced dynamics and represents the first step toward depth-resolved studies of polymer films on the nanoscale using SMD.

Thin-film samples were prepared by spin coating DiD (1,1'-dioctadecyl-3,3,3',3'-tetramethylindodicarbocyanine, Molecular Probes D-307)/polystyrene (PS, $M_n = 89300$ g/mol, $M_w/M_n = 1.06$, Polymer Standard Service) solutions onto cleaned glass cover slides. The films were subsequently annealed, first for 12 h at 60 °C and later for 3 h at 105 °C in order to remove the residual solvent and relax all stresses induced by the spin coating procedure. The

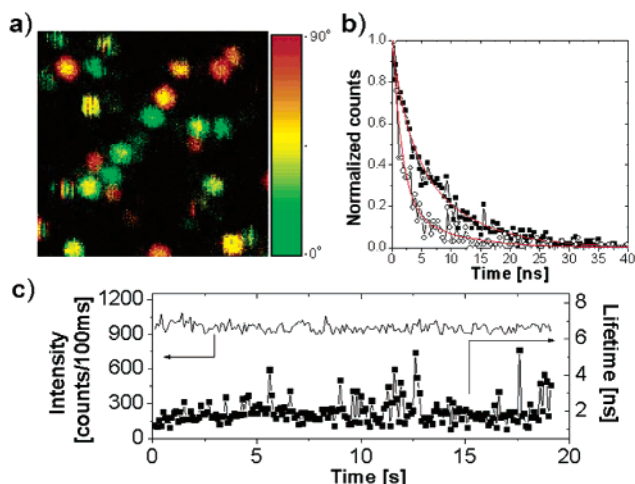


Figure 1. (a) $5 \times 5 \mu\text{m}^2$ fluorescence intensity scan of single DiD molecules in a 110 nm thick PS film at 22 °C. The color scale indicates the polarization of the fluorescence, which is a measure for the in-plane orientation of the molecules. Constant color confirms that the molecules are not rotating in the matrix. (b) Fluorescence decays of one DiD molecule from which a short (2.5 ns, ○) and long (6 ns, ■) fluorescence lifetime was extracted. The red lines correspond to single-exponential fits to the data. (c) Fluorescence intensity and lifetime traces for a single DiD in PS. Excursions to longer lifetimes (up to 5 ns) are clearly visible.

concentration of the dye was 10^{-9} M in the resulting PS films, and the thickness was varied between 10 and 200 nm. A NanoScope III Atomic Force Microscope (Digital Instruments, Santa Barbara) was used to estimate the planarity and the roughness of the samples (<2 nm) before and after the measurements, respectively. No dewetting of the thin films was observed at any stage. To detect the individual molecules within the polymeric matrix, we used a scanning fluorescence confocal microscope (custom built) equipped with suitable dichroic, excitation, and emission filters. A picosecond pulsed laser (PicoQuant, 800-B) was employed to excite the molecules at the wavelength of 635 nm. Fluorescence photons were collected by two avalanche photodetectors (SPCM-AQ-14, EG&G Electro Optics) placed after a polarization beam splitter. An SPC 500 time-correlated single-photon counting card (Becker & Hickl) was used for time-resolved lifetime measurements.¹² For higher temperature measurements, a custom-built hot stage was placed below the sample and the temperature was monitored with an accuracy of ± 2 °C. For each film thickness, 400 probe molecules were analyzed for two different temperatures, 22 and 35 °C, respectively.

Figure 1a depicts a $5 \times 5 \mu\text{m}^2$ fluorescence intensity scan. Characteristic on–off behavior and single-step photobleaching observed confirm that the spots on the image correspond to single emitters. For each single molecule, we collected intensity and

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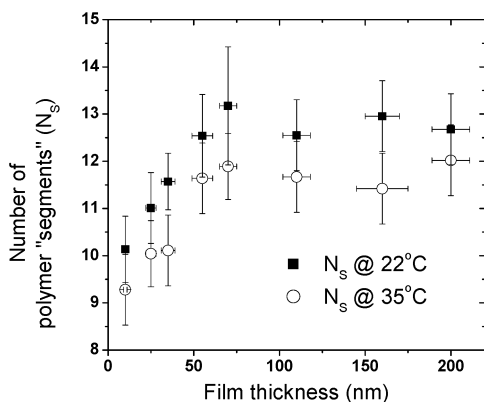


Figure 2. Mean value of the effective number of polymer “segments” in the rearrangement volume around the single-molecule probes as a function of PS film thickness for two different temperatures.

fluorescence lifetime traces with 100 ms time intervals, during 20–60 s total observation time. The accuracy of lifetime determination is on the order of 300 ps. Examples of decay curves (two snapshots at different times for the same molecule) are presented in Figure 1b. In Figure 1c, fluorescence intensity and lifetime traces are shown. Changes in the lifetime as a function of time for the same molecule are clearly visible. From the lifetime trajectory of each molecule we built lifetime distributions, which were fitted with a distribution function.¹³ From the fitting parameters we determine the effective number of polymer “segments” (N_S) taking part in the rearrangement volume around the single probe using the method described in detail in ref 12. N_S determined by this procedure provides direct information concerning local, segmental scale polymer dynamics and its spatial distribution. The value of N_S is very sensitive for small density fluctuations around the probe within the probed time interval. Higher values of N_S can be visualized as a larger collection of polymer segments, which must move cooperatively during segmental relaxation around the probe, therefore indicating slower system dynamics.

In Figure 2, we present the mean of N_S values for single molecules as a function of PS film thickness for two different temperatures. The effect of temperature on N_S is consistent with our earlier results showing a decrease of N_S with increasing temperature.¹² The behavior of N_S as a function of film thickness can be divided into two regions. One region can be assigned to film thickness above a certain threshold value h_0 , where N_S remains essentially constant. Below h_0 , N_S becomes a function of thickness and decreases with decreasing film thickness. The transition (h_0) between the two regions is estimated from the graph to be around 50–60 nm.

Two main effects are known to be responsible for the observed decrease of N_S with decreasing film thickness: chain confinement (when the characteristic length scale of the polymer chain is comparable to the dimensions of the system) and the presence of interfaces with modified dynamics. However, for the molar mass of the polymer used here, the average radius of gyration (R_g) of the macromolecules is 9–10 nm assuming a chain conformation as in the θ state, i.e., 6 times smaller than the value of h_0 . Thus, chain confinement is not expected to play a major role in our case. For a similar system consisting of air/polystyrene/glass, it was reported that the polymer/glass interface does not perturb the film dynamics.¹⁴ Therefore, we attribute the decrease of N_S for small film thickness to modified polymer dynamics induced by the presence of a free polymer surface.¹⁵ We also conclude that in such thin films, the dynamics of the polymer is modified far below the

bulk glass transition temperature ($T_{g,b} = 100$ °C as measured by DSC) even though a large fraction of the macromolecules cannot “sense” the possible effect of the interfaces nor are they forced to adopt a different conformation due to the confinement represented by the thin film. Apparently due to the connectivity and interpenetration of polymer chains, surface-induced enhancement of polymer dynamics propagate into the sample. The temperature dependence of N_S for PS films yields $dN_S/dT = -0.11$ [segments/deg]¹² thus the dynamics in the thinnest film is equivalent to the dynamics in thicker films (thickness $> h_0$) if it was observed at temperatures elevated by as much as 30 °C.

From the mean lifetime of a collection of single molecules as a function of film thickness (not presented here), we rule out any dye segregation to one of the interfaces or at a certain depth within the samples. Also, from the stability of the fluorescence polarization state and from the mean fluorescence lifetime for each molecule during the observation time, we excluded the possibility that the decrease of N_S is caused by an increased rotational or translational activity of the probe in thinner films at the experimental temperatures (65 and 80 °C below $T_{g,b}$, respectively) that could cause lifetime fluctuations¹⁶ and thus influence N_S .

In conclusion, we used a single-molecule lifetime technique to study the influence of the film thickness on local polymer dynamics on the nanometer length scale at temperatures far below the glass transition temperature. We find modified segment scale dynamics when the polymer is confined into films with thicknesses below 50–60 nm corresponding to 6 times the radius of gyration. In the future, we intend to extend our investigations to a controlled, depth-resolved dynamics study in thin polymer films from the surface to the bulk using NSOM-based approaches.

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Supporting Information Available: Representative histograms of the width parameter and the corresponding N_S distributions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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