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Retarded local dynamics of single fluorescent probes in polymeric glass due to interaction strengthening

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ABSTRACT

The effect of strengthening of interaction between single fluorescent probes and polymer matrix to the probes' dynamics is investigated using single molecule fluorescence defocus microscopy. By introducing multiple hydroxyl groups to the fluorescent probes (perylene diimide derivatives) which builds up hydrogen bonds between the probe and polymer matrix, the dynamics is discovered to be retarded. This is evidenced by the lowering of the frequency of the vibrational modes in the power spectra of the rotation trajectories of individual fluorescent probes, and also by the decrease in population of rotating probes. The results show that by strengthening the probe-matrix interaction, the local dynamics detected by the probes is equivalent to that detected by a bigger probe, due to the enhanced friction between the probe and the polymer matrix.

1. Introduction

Microscopic picture of dynamics is the key knowledge to the understanding of polymer properties in many aspects, especially rheological properties [1–3] and glass transition [4–7]. Among the methods probing local dynamics, single molecule fluorescence has been proved to be very effective because of its high detection sensitivity, excellent spatial resolution and suitable time resolution [8–11]. By these powerful methods, translational diffusion and rotational diffusion of individual fluorescent probes can be clearly visualized and monitored, from which the information on the local dynamics is extracted [12–17]. For example, it has been demonstrated that the motion of single fluorescent probes reflects the dynamical heterogeneity that exists widely in glass [8,14,18,19]. The activation of local molecular motion due to external deformation has been visualized [20,21]. The correlation of the probes' rotation with the α-relaxation modes in polymer melts have also been clearly exposed [8,11,15,22,23]. Much more promising information on local dynamics is expected to be revealed by investigations using single molecule fluorescence.

In the investigations, fluorescent molecules are employed as probes of the local dynamics, either doped in the matrix or chemically connected to the polymers [8–17]. Because the probes are chemically different to the polymer matrix and due to the fact that the probes have finite molecular size, the dynamics probed by them might be different to the intrinsic dynamics of the polymer matrix. This issue has been drawing attention for decades and efforts have been put to investigate the effect of probes' finite size and its interaction with the polymer matrix. Investigations have been conducted using a number of methods including nonlinear optical spectroscopy [24–26], dielectric spectroscopy [27,28], as well as single molecule fluorescence microscopy [15,29]. In a recent study [30], a systematic investigation was performed to look into the effect of probes' finite size to the local dynamics it probed by defocus single molecule fluorescence microscopy. In this study, power spectral analysis of the rotation trajectories was conducted, revealing local vibration modes inside the polymer matrix. The dependence of the dynamics probed by fluorophores on their size was investigated and the characteristic length scale of glass transition was discovered.

Motivated by the powerfulness of defocus single fluorescence microscopy and the rich information deducted from the power spectra of rotation trajectory, the effect of interaction between the probe and the polymer matrix is investigated in the current study. Interaction is tuned by adjusting the amount of hydrogen bonds

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formed between the probes and the matrix. The results clearly demonstrate the strong effect of the probe-matrix interaction on the dynamics detected by the probes.

2. Experimental section

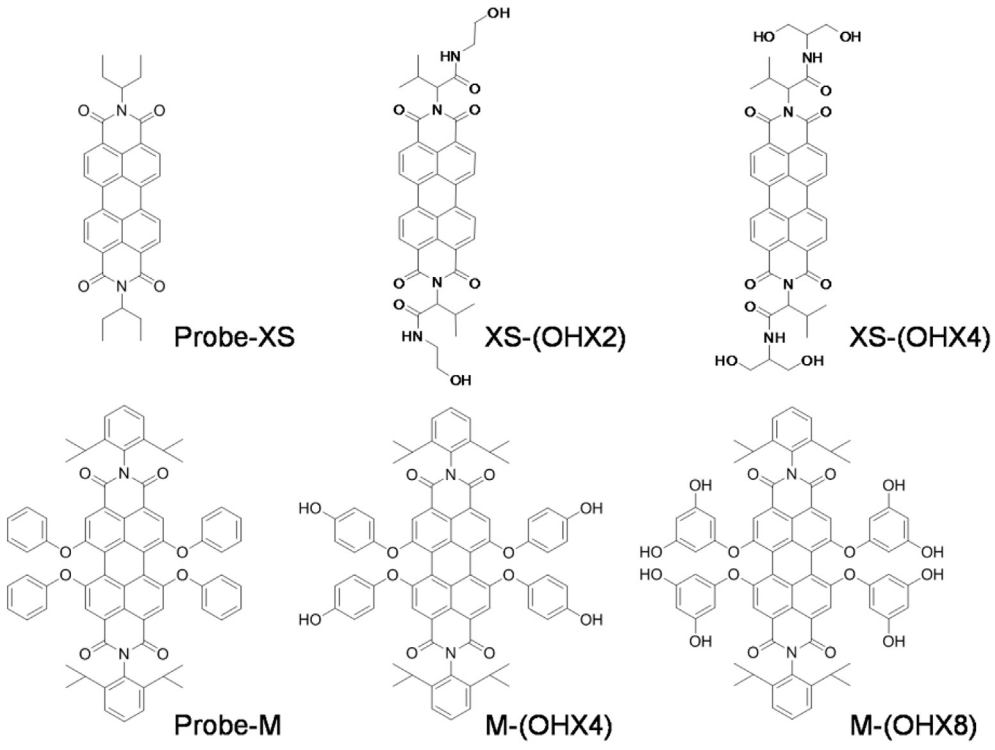
Polyvinylacetate (PVAc) was purchased from Sigma-Aldrich and poly n-propyl methacrylate (PnPMA) and poly n-butyl methacrylate (PnBMA) from Polymer Source (Quebéc, Canada) and were used as received. The glass transition temperatures of these three polymer samples are 42.5 °C, 60.0 °C and 39.0 °C, respectively, as measured by a differential scanning calorimeter (TA Instruments Q2000) at a heating rate of 10 °C·min^{-1}.

Samples were prepared by spin-casting polymer solution onto 0.17 mm-thick glass coverslips (Thermo Fisher). PVAc was dissolved in ethyl acetate (spectroscopic grade, Acros) at a concentration of 1.7 wt%. PnPMA and PnBMA were dissolved in toluene (spectroscopic grade, Acros) at the concentration of 2.4 wt% and 2.3 wt%, respectively. Tracer amount of fluorescent molecules (perylene diimide derivatives) was dissolved in the solution at the concentration of ~10^{-9} M. After spin-coating, the sample films were annealed in vacuum at 100 °C for 12 h to remove the residual solvent and stress. The thickness of the resulted samples was 96.0, 102.0 and 120.0 nm, respectively, as measured by ellipsometry (J. A. Woollam, M-2000V). The distribution of the probes along the normal direction was checked by secondary ion mass spectroscopy measurement and the results show uniform distribution of the probes with moderate segregation to polymer-substrate interface, as detailed in the Supplementary Materials.

A number of perylene diimide derivatives were chosen as fluorescent probes. These molecules were adopted due to their high photo-stability and also relative ease of modification of their chemical structures by introducing hydroxyl groups to the molecules. The chemical structures of all probes adopted are shown in Scheme 1.

The perylene diimide derivatives adopted are of two series – one with a smaller core (the original probe is denoted as Probe-XS, and the derivative modified with *n* hydroxyl groups denoted as XS-(OH×n)) and another one with a bigger core (denoted as Probe-M and M-(OH×n)). These fluorescent probes were synthesized according to the published protocols [31,32], and their final chemical structures are verified by the spectroscopic characterizations.

Single molecule defocused fluorescence microscopy was performed using a home-built set-up based on an inverted microscope (IX-71, Olympus) in a total internal reflection configuration [14,30,33]. The 532 nm output of a solid laser was used as the excitation source, which is introduced into the sample through the objective lens (PlanApo×100, oil immersion, numerical aperture = 1.45). The laser was tuned to be circularly polarized so that equal probabilities of excitation are guaranteed for the fluorescent molecules inside the sample having different spatial orientations. The power intensity of the laser at the sample was 9.0–16.0 W·cm^{-2} for high enough signal-to-noise ratio and minimal effect of photobleaching. The fluorescence images were recorded with an EMCCD camera (Andor DV 897) with the exposure time of 0.5 s for the best image contrast and good enough time resolution. The temperature of the sample and the objective lens were controlled separately by two heating stages – HCS60 (INSTEC) for the sample and TC-HLS-025 (Bioscience Tools) for the objective lens, with the accuracy of 0.1 °C. The temperature was adjusted at the interval of 2 °C and the sample was equilibrated for 10 min at each temperature before the measurement was conducted. Special care was taken to avoid the effect of water adsorption into the sample, as water absorption may change the glass transition temperature, especially for PVAc. After annealed in vacuum, the samples were transferred to the microscope using desiccators. In single molecule microscopy experiments, the samples were mounted in the tightly sealed HCS60 heating stage so that it is isolated from the ambient humidity (<10%). Defocus microscopy geometry was adopted – the focal position of the objective lens was adjusted



Scheme 1. Chemical structure of fluorescent probes (perylene diimide derivatives) adopted in the current study. (OH×n) denotes the probe having *n* hydroxyl groups.