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Time-resolved fluorescence analysis for dye-labeled polystyrene in thin films[☆]

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ABSTRACT

Time-resolved fluorescence spectroscopy and anisotropy were applied to dye-labeled polystyrene in thin films. Both fluorescence lifetime and rotational relaxation time decreased with decreasing thickness once the film became thinner than approximately 100 nm. The results could be well reproduced by a tri-layer model composed of surface, interface and bulk regions. The model analysis clearly indicates that the chain dynamics in the surface and substrate interfacial regions is, respectively, faster and slower than that in the internal bulk phase.

1. Introduction

Polymer dynamics in confined systems have been widely studied by many research groups over the world using various experimental methods [1–9]. This is because it will lead to a better understanding of hierarchical polymer dynamics and a novel guideline to design functional materials such as multi-layer organic electronics devices, organic–inorganic hybrid materials, and polymeric biomaterials etc.

Glass transition temperature (T_g) of a polymer in thin films supported on solid substrates is one of the most studied subject in the field [10–24]. In general, T_g decreases with decreasing film thickness when the film becomes thinner than 100 nm [11–13,16,17,20,21,23]. On the other hand, if there is a strong interaction between polymer chains and the substrate surface, T_g increases with decreasing film thickness [2,23,25–27]. A simple bilayer model incorporating an effect of surface, at which mobility is enhanced [28–35], succeeded to reproduce the experimental T_g-thickness relation [13,21].

Temperature-dependent fluorescence spectroscopy for a polymer with a dye enables us to gain access to T_g of the polymer [36–44]. Thus, if such an experiment can be combined with a space-resolved technique, T_g can be measured at a desired position. This was realized by inserting a layer containing fluorescence probes into desired position of the film [40] and also by using the evanescent-wave-excitation method [42,44].

So far, there are many reports dealing with chain mobility in the interfacial region with a solid substrate that is less enhanced than that in the bulk [44–47]. This would be the case even for a polymer which doesn't possess a special attractive interaction with the substrate. If this is the case, the bilayer model should be improved after incorporating an effect of the interfacial layer. That is, the trilayer model should be used. We have previously used this model to fit the film thickness dependence of photo-isomerization for azobenzene tagged to polystyrene (PS) and made a great success to reproduce the experimental data [48].

The objective of this study is to apply time-resolved fluorescence spectroscopy and anisotropy to 6-(*N*-(7-nitrobenz-2-oxa-1,3-diazol-4-yl)amino)hexanoic acid (NBD) tagged to PS in thin films. The fluorescence anisotropy enables us to gain direct access to the local dynamics of the dye via the rotational relaxation, to polymer thin films [49,50]. The information so obtained is compared with that by the former one, which we have already applied to PS thin films [48]. The experimental results are analyzed with the trilayer model to extract the effects of surface and substrate interface on the chain dynamics in thin films.

2. Experiments

PS was synthesized by living anionic polymerization using *sec*-butyllithium and methanol as an initiator and a terminator, respectively. The number-average molecular weight (M_n) and the polydispersity index evaluated by gel permeation chromatography with PS standards were 53.4 k and 1.03, respectively. The bulk glass transition temperature

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(T_g^b) measured by differential scanning calorimetry (DSC) was 375 K. The phenyl ring of PS was aminomethylized by the procedure of Mitchell et al. [51] and subsequently labeled by NBD. NBD was randomly introduced in the side chain of PS and the fraction was 5.9×10^{-2} mol% which is sufficiently low to avoid the self-quenching of the dyes [52]. The maximum absorption and fluorescence emission wavelengths of NBD tagged to PS (PS-NBD) in a dilute tetrahydrofuran solution were 457 and 517 nm, respectively.

PS-NBD films with various thicknesses (h) were prepared by spin-coating from toluene solutions onto quartz substrates. The films were then annealed at 393 K for 24 h under vacuum. Their thicknesses were evaluated by ellipsometry in conjunction with atomic force microscopy (AFM). For AFM observation, a film was partly scratched by a blade so that the silicon substrate was exposed to the air. The thickness was determined based on the topographic AFM image of the partly scratched film. The NBD dyes were excited with the second-harmonic generation of a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami; full width at half-maximum (fwhm) = 1.5 ps; wavelength = 430 nm) equipped with a pulse selector and a harmonic generator. A streakscope (Hamamatsu Photonics, C4334-01) was used to detect the time-resolved fluorescence from excited NBD molecules. The exciting light was irradiated from the substrate side.

3. Results and discussion

3.1. Fluorescence lifetime

In general, the fluorescence lifetime (τ) is proportional to fluorescence intensity (I). This is because I is proportional to fluorescence quantum yield given by $k_f / (k_f + k_{nr})$, where k_f and k_{nr} are rate constants of radiative (fluorescence transition) and non-radiative pathways to the ground state for excited species, respectively. Taking into account that the τ value is given by $(k_f + k_{nr})^{-1}$, it is apparent that τ is proportional to I. What is the advantage of measuring τ over I is that the data among different measurements can be simply compared.

The τ value is affected by many factors such as temperature and polarity, density, and dynamics of the surrounding medium. Thus, the absolute value of τ does not directly reflect the dynamics of the matrix polymer. However, when the τ value for a probe in a polymer matrix is measured as a function of X, which is an experimental variable, and if the value is changed at a given X, it can be claimed that the dynamics of the matrix film is changed at the X value. For example, once the temperature goes beyond the relaxation temperature of the matrix, the dynamic environment of probe molecules is definitely altered via the change in the dynamics of the matrix.

In our experimental system, NBD and PS were used as fluorescence probe and matrix polymer, respectively. We have previously studied the temperature dependence of τ for PS-NBD [44]. In this case, the variable of X was temperature. As a result, while NBD was insensitive to the β-relaxation process, it was sensitive to the α-one. That is, once the temperature goes beyond the T_g of PS, the dynamic environment of NBD is altered via the change in the dynamics of PS, leading to the determination of T_g [44]. Actually, this is essentially the same as the way to determine T_g on the basis of the temperature-dependence of fluorescence intensity [39–44]. Therefore, it seems reasonable to infer that the segmental dynamics can be discussed by fluorescence lifetime measurement. In the current study, the experimental variable of X is the film thickness. Thus, measuring τ as a function of film thickness, we can discuss the relation of the segmental dynamics of PS to the film thickness.

Postulating that chain dynamics in the surface and interfacial regions is different from that in the bulk, the light emission behavior of NBD tagged to PS in thin film should differ from that in a thick film. This is because the ratio of the surface and interfacial areas to the total volume increases with decreasing film thickness. To confirm this, the fluorescence decay curves for PS-NBD in thick and thin films were examined.

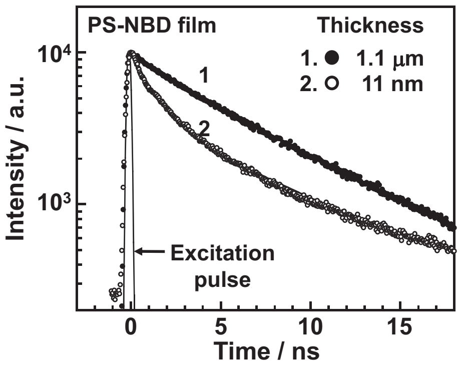

Fig. 1. Decay curves of fluorescence from NBD tagged to PS in films.

Fig. 1 shows the results. When a pulse was irradiated onto a film, the fluorescence intensity abruptly increased and then decreased with increasing time. The decay became faster for the thinner film, as shown in Fig. 1. The τ was extracted by fitting the fluorescence decay curve using the following equation,

$$I = I_0\{x \cdot \exp(-t/\tau_{fast}) + (1-x) \cdot \exp(-t/\tau_{slow})\} \tag{1}$$

where t, I_0, τ_{fast} and τ_{slow} and x are time, I right after the excitation, τ of the fast and slow components and fraction of the fast component, respectively.

Fig. 2 shows the h dependence of $<\tau>$ for NBD tagged to PS in films. The $<\tau>$ value was given by

$$\langle\tau\rangle = x \cdot \tau_{fast} + (1-x) \cdot \tau_{slow} \tag{2}$$

and decreased with decreasing h once the film thickness fell short of approximately 100 nm. This implies that the fractional amount of non-radiative pathways to the ground state for excited NBD species increased with decreasing thickness.

What is a discrepancy between thin and thick films is the surface area to the total volume of the film. So far, it has been widely accepted that the molecular mobility in the surface region is much more enhanced than that in the internal region of the film. Postulating that the fractional amount of the non-radiative pathways is larger in the surface than in the internal region due to the enhanced surface mobility, the thickness dependence of $<\tau>$ could be understood.

We tried to reproduce the $<\tau>$ vs. thickness relation using Eq. (3) based on the bi-layer model, in which the film is composed of the surface layer with a thickness of α_s and the bulk layer with thickness of $(h - \alpha_s)$,

$$\langle\tau\rangle = \langle\tau_{surf}\rangle \cdot (\alpha_s/h) + \langle\tau_{bulk}\rangle \cdot \{1-(\alpha_s/h)\} \tag{3}$$

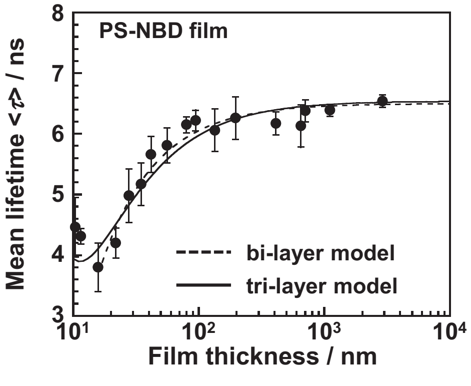

Fig. 2. Thickness dependence of mean-lifetime for NBD tagged to PS in films.