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Photoisomerization of Azobenzene Probes Tagged to Polystyrene in Thin Films

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Introduction. For the past decade, glass transition and mobility in confined polymer systems have been extensively studied due to industrial importance as well as scientific interests.[1−10] In the most studied case, polystyrene (PS) thin and ultrathin films, a conclusion obtained is consistently arrived that glass transition temperature (T_g) of the PS thin and ultrathin films differs from the corresponding bulk value, unless there exists an attractive interaction between the chain and a substrate. Although why the enhanced mobility must be manifested in the thin and ultrathin states is far from clear on molecular level for the moment, it is no wonder the presence of the free surface is one of responsible factors in the active molecular motion.[11−15]

In this study, photoisomerization kinetics of azobenzene (Az) chromophores tagged to PS in thin films was studied as a function of thickness. Invoking that the rate is mainly governed by the number density of sites where local free volumes are greater than a critical size necessary for the photoisomerization[16−20] and/or by molecular motion of PS with a relatively small scale,[20−22] local free volume and local mode relaxation in the surface region were discussed. Such a study enables us to gain access to information about hierarchical molecular motion in the surface region of polymer films, resulting in an understanding why polymer dynamics becomes faster with decreasing size of the system.

Experimental Section. Films of PS tagged with Az groups (PS-Az) were used as specimens. First, monodisperse PS with the number-average molecular weight (M_n) of 59K was synthesized by a living anionic polymerization using *sec*-butyllithium as an initiator and methanol as a terminator. The bulk glass transition temperature (T_g^b) was determined to be 376 K by differential scanning calorimetry. The labeling procedure started with random aminomethylation of phenyl rings in PS by the procedure of Mitchell et al.[23] with some modifications. The aminomethyl groups were subsequently reacted with an appropriate amount of the Az chromophores to complete the labeling procedure. The Az fraction of a PS chain estimated by elemental analysis was 1 mol % to styrene monomers. The PS−Az films with various thicknesses were prepared onto quartz plates by a spin-coating or a solvent-casting method and then were annealed in vacuo at 393 K for 24 h.

To study kinetic behavior of the trans → cis photoisomerization for the Az groups, the absorption band at 336 nm arisen from the Az trans form was measured. A mercury−xenon lamp (Hamamatsu L8333-01) was used as a light source. Using a band-pass filter, ultraviolet (UV) light with the wavelength centered at 350 ± 5 nm was irradiated onto the samples at a power of 2 mW cm^{-2}. Absorption at 336 nm was pursued as a function of time at room temperature of 298 K by a spectrometer (Hitachi U-4100).

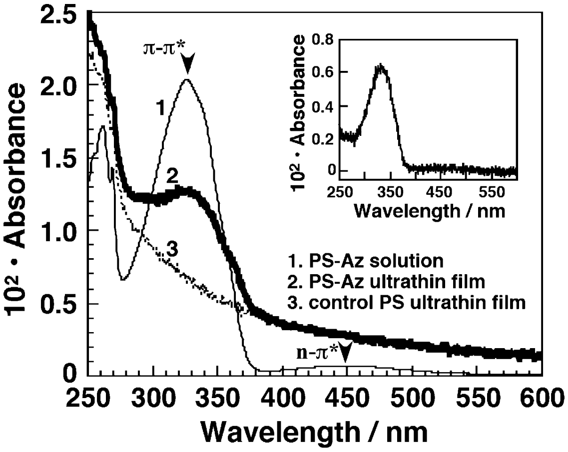

Figure 1. Absorption spectra for a PS−Az dilute chloroform solution and PS−Az and control PS ultrathin films with the thickness of 17 nm. For the solution, absorbance was reduced to be 1/48 for clarity. The inset shows the difference spectrum between PS−Az and control PS ultrathin films.

Results and Discussion. Figure 1 shows UV spectra of a PS−Az chloroform solution with the concentration of 0.02 wt % and a PS−Az ultrathin film with the thickness of 17 nm. For comparison, the spectrum for a 17 nm thick PS ultrathin film was also presented. An absorption peak observed at 336 nm for the PS−Az solution and an ultrathin film is assigned to the $\pi-\pi^*$ transition along the long axis of trans Az molecules.[24] In the case of the control PS ultrathin film, absorbance monotonically increased with decreasing wavelength, even though the Az probes were not existed in the film. Hence, the spectra of the PS−Az films were subtracted by each spectrum of the corresponding control PS films. The inset of Figure 1 shows the difference spectrum for the PS−Az ultrathin film with the thickness of 17 nm. After the subtraction process, the absorption spectra for the PS−Az films were basically the same as that for the solution in shape.

Figure 2 shows time (t) dependence of absorbance (A) at 336 nm during the photoisomerization. The ordinate was normalized by A at $t = 0$ ($A(0)$). The A value exponentially decreased with t for the PS−Az chloroform solution. In general, the photoisomerization of chromophores in a dilute solution proceeds on the first-order reaction. Hence, the experimental result was tried to fit by eq 1.[20]

$$\frac{A(t)}{A(0)} = y_0 \exp\left(-\frac{t}{\tau}\right) + (1 - y_0) \qquad (1)$$

where τ and y_0 are time constant for the reaction and fraction amount of trans form photoisomerized after reaching the photostationary state. The best-fit curve was obtained with $\tau = 52$ s. On the other hand, in the case of the PS−Az films, the time dependence of the trans form fraction could not be fit by eq 1. Instead, the

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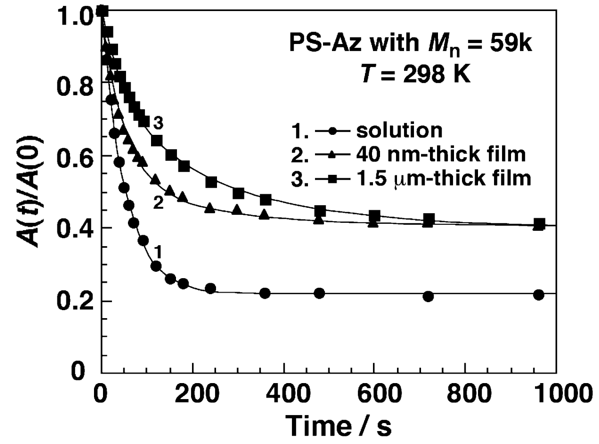

Figure 2. Time dependence of absorbance at the wavelength of 336 nm for PS−Az films. As typical examples, the data sets for the 40 nm and 1.5 μm thick films are presented. The ordinate was first divided by the absorbance at the time of 0. The solid curves were best-fit ones via eqs 1 and 2.

data sets were well fit using a double-exponential equation, as reported.[20] This means that the photochemical trans → cis isomerization was separated into two processes.

$$\frac{A(t)}{A(0)} = y_0\left[x \exp\left(-\frac{t}{\tau_1}\right) + (1-x)\exp\left(-\frac{t}{\tau_2}\right)\right] + (1-y_0) \qquad (2)$$

where τ_1 and τ_2 are time constants for the fast and slow modes of the reaction. Also, x denotes fractional amount of the fast mode. According to extensive works by Sung and co-workers, the fast process in bulk PS solid films is as fast as in a dilute solution, and the fractional amount decreased with physical aging but increased with temperature, plasticization, or tensile deformation.[25] This is because the fraction is correlated to the amount of sites where local free volumes are greater than a critical size necessary for the photoisomerization of the Az groups. Hence, fixing τ_1 = 52 s, the time variance of $A(t)/A(0)$ for the 1.5 μm thick film was fit. The best fit was obtained with τ_2 = 222 s and x = 0.38, and the curve was drawn in Figure 2. In the following, these two time constants of 52 and 222 s were used to fit the data for thinner PS−Az films. Data fitting with τ_1 = 52 and τ_2 = 222 s works well, as seen in a typical example for the 40 nm thick film.

We now come to discussion about how the fractional amount of the fast mode depends on the film thickness, which is shown in Figure 3. While x was invariant with respect to the thickness down to a few hundreds of nanometers, the value started to increase with decreasing thickness for thinner films. Then, the value reached a constant of approximately 0.8 at around 40 nm. When a film becomes thinner and thinner, the following two factors should be considered to affect physicochemical properties of the film.

At first, a chain confinement effect is discussed. Assuming that the chain dimension is not perturbed by the presence of the azobenzene chromophores, twice the radius of gyration for a PS−Az chain used was calculated to be 13 nm. Since this value was much smaller than the thickness at which the x value started to change, the PS−Az chains would not be seriously distorted in the films. Thus, this leads to a conclusion that the chain confinement effect can be excluded from the reason why the x value increased for the thinner films.

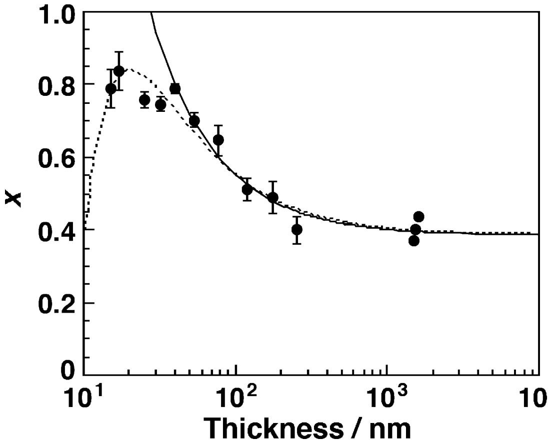

Figure 3. Relation between fraction of the fast component and film thickness. The solid and broken curves were drawn by fitting procedures mentioned in the text.

Second, a surface effect is discussed. So far, it has been widely accepted that there exists a liquidlike surface layer of the PS films.[2,3] And thus, it seems most likely that the photochemical trans → cis isomerization of the chromophores in the surface region proceeds as fast as in a dilute solution. Taking into account such, a model composed of the surface layer and the bulk phase is made to reproduce the experimental result.

$$x(d) = x_b\left(1 - \frac{\alpha_s}{d}\right) + x_s\frac{\alpha_s}{d} \qquad (3)$$

where x_b and x_s are x values in the bulk and the surface regions, respectively, namely 0.38 and 1.00. And, α_s and d are surface layer and film thicknesses, respectively. The solid curve in Figure 3 was the best-fit one with α_s = 27.3 nm, provided that four data points for the films thinner than 32 nm were not counted. While eq 3 well reproduced the experimental data over a broad range of thickness down to 40 nm, this was not the case for much thinner films due probably to a contribution from a less mobile layer at the substrate interface. If the interfacial effect is incorporated to eq 3 as the third term, the experimental d vs x relation could be well fit in the entire thickness range employed, as drawn by the dotted curve in Figure 3. However, since a fitting procedure with many parameters makes discussion ambiguous, we discarded such an approach. Recently, it has been prevailed that T_g in the interfacial region with the solid substrate is higher than the T_g^b. The plausibility of the third term should be correlated to the thickness of the interfacial region, in which molecular mobility is depressed. This is challenging but will be addressed in the near future.

To confirm whether the presence of the surface layer truly accelerates the trans → cis photoisomerization, a 160 nm thick film of PS with M_n of 59K was put onto the PS−Az film with the thickness of 40 nm, and the time dependence of the trans fraction was examined. In this case, the surface effect should be weakened. Although the x value for the 40 nm thick PS−Az film was 0.80 ± 0.02 as shown in Figure 3, it decreased to be 0.72 ± 0.02 after the PS top layer was laminated. Moreover, the bilayer was annealed at 393 K for 24 h to diffuse the interface between PS and PS−Az, resulting in decrease in the surface layer thickness of the PS−Az film. The interfacial width after the annealing was evaluated to be 15.4 ± 0.4 by dynamic secondary ion mass spectroscopy.[26] The decrement of the surface layer might be a half of the interfacial width. For the annealed bilayer, the x value again decreased to 0.67 ± 0.01 because the interfacial region was composed of the two original surfaces. These results strongly advocate our argument that the surface effect is the responsible factor in what is seen in Figure 3.

Here, as a general concern, an effect of residual strain on the photoisomerization kinetics is addressed. When residual strain imposed by, mostly, the spin-coating process remained, the surrounding environment for the Az probes is different from that being in a quasi-equilibrium state. Such an effect would cause that the value of x_b itself increases with decreasing thickness. However, since all films examined were annealed under the condition that chains were fully relaxed, the effect should be ignored for our case. In addition, using the same film used as before, different trials to examine $A(t)/A(0)$ vs t were made after 3 months. Even in that case, the x values obtained were not changed, meaning that not only the residual strain effect but also physical aging were trivial for our study, if any.

In this communication, we successfully present that the surface region dynamically behaves as liquid for the photoinduced trans → cis isomerization of the Az probes and that the thickness is 27 nm. However, this value seems to be too large in comparison with reported thicknesses of the surface layer, in which the segmental mobility is enhanced. A simple but plausible explanation for this is that local free volume starts to deviate from the bulk distribution in a region deeper than the surface layer in which the segmental mobility is enhanced. On the other hand, Algers and co-workers have recently studied density gradient in the surface region of poly(methyl methacrylate) films by pulsed low-energy positron lifetime analysis in conjunction with some theoretical treatments.[27] They claimed that the density gradient width in the surface region should be within a few nanometers. If this is the case even for our study, our explanation mentioned above is supposed to be denied. In that case, there should exist other responsible factors for the faster photoisomerization in the surface region in addition to the enhanced local free volume. A tentative candidate for it is molecular motion of PS with a relatively small scale.[28] That is, the surface depth in which the local motion is enhanced would be deeper than the depth of the enhanced segmental mobility. In our experiment, the Az probes were tagged to the side chain parts, and thus, what we observed in the photoisomerization kinetics would be, in part, correlated to local motion of the side chains. In any event, it is too early to conclude the issue for the moment. More conclusive work based on further experiments will be reported in the near future.

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