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Film thickness dependence of photoisomerization for azobenzene chromophores tagged to polystyrene with various molecular weights

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Trans→cis photoisomerization of azobenzene (Az) chromophores in films of polystyrene (PS) with various molecular weights was studied as a function of film thickness at room temperature. The photoisomerization in solid films was composed of fast and slow modes. The fractional amount of the fast mode started to increase with decreasing thickness once the films became thinner than a few hundreds of nanometers. This was interpreted by enhanced mobility at the surface, which becomes remarkable with decreasing thickness. Based on a model analysis, the surface layer thickness was evaluated to be roughly 20 nm. The fractional amount of the fast mode was insensitive to molecular mass of PS at a given thickness, meaning that effects of chain confinement and end groups on it are negligible, if any. Thus, it was finally claimed that there exists a 20 nm-thick surface layer, in which local mobility might be enhanced, in the films.

Key words: Surface, Ultrathin films, Photoisomerization, Azobenzene, Polystyrene

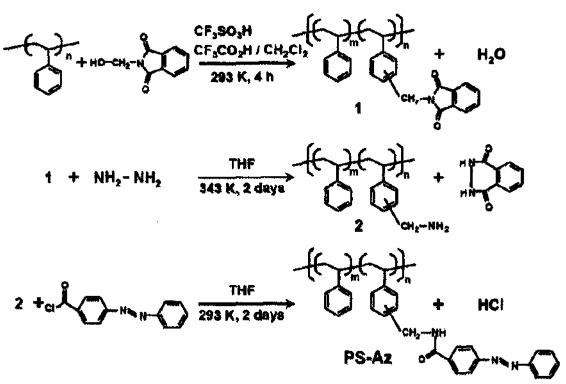
1. INTRODUCTION

Recently, glass transition and dynamics in confined polymer systems have been extensively investigated due to industrial importance as well as scientific interests.[1-11] In the most studied case, polystyrene (PS) thin and ultrathin films, a conclusion obtained thus far is consistently arrived that glass transition temperature (T_g) is lower than that of the corresponding bulk sample,[2,4-9] unless there exists an attractive interaction between the chain and a substrate.[3] Besides, relaxation dynamics for the segmental motion in the PS thin and ultrathin films is recently studied. Consequently, it was revealed that the distribution of the relaxation times became broader with decreasing film thickness due to surface and interfacial effects, once the thickness became thinner than approximately 50 nm.[10]

The objective of this study is to explore how local free volume changes with decreasing film thickness. This would be helpful to understand why the peculiar segmental dynamics must be manifested in such thin and ultrathin states. For this purpose, the most promising way is to use positron lifetime analysis.[12,13] However, the experiments are limited to be carried out because it needs large radioactive facilities. Hence, we adopt a different way, which can be made on a laboratory scale, such as photoisomerization kinetics of azobenzene chromophores. This is based on a notion 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.[14-18]

2. EXPERIMENTAL

As a material, PS containing with Az groups (PS-Az) was used. Scheme 1 shows a synthetic route for PS-Az. At first, monodisperse PSs with various molecular weights were synthesized by a living anionic polymerization using *sec*-butyllithium as an initiator and methanol as a terminator. Then, random amino-methylation of phenyl rings in PS was carried out by the procedure of Mitchell et al. [19] 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 was about 1 mol % to styrene monomers. Table 1 shows number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n), where M_w is weight-average molecular weight, bulk glass transition temperatures (T_g^b), and twice radius



Scheme 1. Synthetic route for PS-Az

Table 1. Characteristics of PS-Az

Sample	Az residue / mol %	M_n	M_w / M_n	T_g^b / K	$2R_g$ / nm
PS-Az-22k	1.2	22k	1.08	375	8.3
PS-Az-59k	1.1	59k	1.06	379	13.6
PS-Az-245k	1.4	245k	1.15	380	26.7

of gyration ($2R_g$) for the PS-Az so obtained. M_n and M_w/M_n were determined by gel permeation chromatography using THF as an eluent. T_g^b was determined by differential scanning calorimetry under dry nitrogen purge at the heating rate of 10 K min^{-1}. Postulating that the chain dimension is not perturbed by the presence of the azobenzene chromophores, the value of $2R_g$ was calculated. 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 393-403 K for 24 hrs. It was experimentally hard to examine the thickness of a film on a quartz plate by ellipsometry. Hence, the thickness of a film prepared under the same condition but on a silicon wafer was assume to be the same as that of the film on the quartz, and was measured by ellipsometry. The plausibility of this assumption was confirmed by different thickness determinations based on absorbance change and interference fringes upon the following absorption measurement.

In order to study kinetic behavior of the trans→cis photoisomerization for the Az groups, 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 a sample at the power of 2 mW•cm^{-2}. Absorption at 336 nm was pursued as a function of time at 298 K by a spectrophotometer (Hitachi U-4100).

3. RESULTS AND DISCUSSION

Figure 1 shows UV spectra for a PS-Az chloroform solution with the concentration of 0.02 wt %, and 17 nm-thick film of PS-Az with M_n= 59k. For a comparison, the spectrum for a 17 nm-thick PS ultrathin film was also shown. An absorption peak observed at 336 nm for the PS-Az solution and the ultrathin film is assigned to the π-π^* transition along the long axis of trans Az molecules.[20] In the case of the control PS ultrathin film, absorbance monotonically increased with decreasing wavelength due to Rayleigh scattering, 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 electron spectra for the PS-Az films were basically the same as that for the solution in shape.

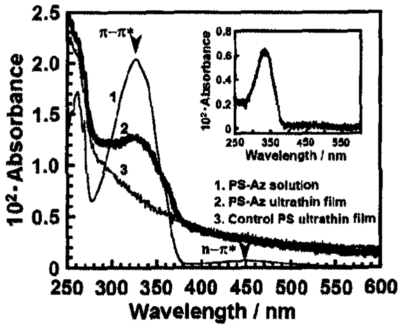


Figure 1. Absorption spectra for a PS-Az dilute chloroform solution, and PS-Az and control PS ultrathin films with the thickness of 17 nm. For the solution, absorbance was reduced to be 1/48 for clarity. The inset shows the difference spectrum between PS-Az and control PS ultrathin films.

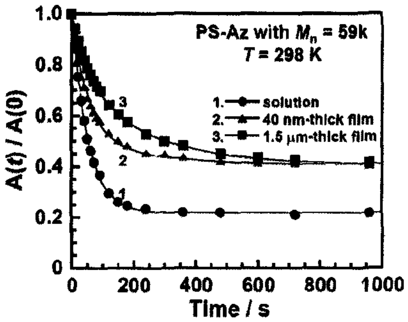


Figure 2. Time dependence of absorbance at 336 nm for PS-Az films. As typical examples, the data sets for the 40 nm and 1.5 μm-thick films are presented. The ordinate was first divided by the absorbance at the time of 0. The solid curves were best-fit ones via equations (1) and (2).

Figure 2 shows time (t) dependence of absorbance (A) at 336 nm for solution and films of PS-Az with M_n= 59k upon 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 equation 1.[18]

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

where τ is time constant for the reaction. And, $A(\infty)$ is A at the photostationary state. The best-fit curve was obtained with τ= 52 s. On the other hand, in the case of the PS-Az films, the time dependence of trans form fraction could not be fitted by equation 1. Instead, the data sets were well fitted using a double exponential equation, as reported.[18] This means that the photochemical trans→cis isomerization was separated into two processes.

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

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 a bulk PS solid film is as fast as in a dilute solution.[21] Hence, fixing τ_1= 52 s, the time variance of $A(t)/A(0)$ for the over 1 μm-thick films were fitted. The best-fit was obtained with τ_2= 222 s and x= 0.38, and the curve was drawn in Figure 2. The slow process with the time constant of 222 s seemed to be characteristic for the photo-isomerization reaction in a solid state, and was assumed to be independent of the thickness. Thus, when the data for thinner PS-Az films were reproduced by eq (2), the two time constants of 52 and 222 s were fixed. This means that only x value was a fitting parameter for the analysis of the thinner films. Data fitting with τ_1= 52 and τ_2= 222 s worked well, as seen in a typical example for the 40 nm-thick.

We now turn to discussion about how the fractional amount of the fast mode depends on the film thickness. Figure 3 shows the film thickness dependence of x for the films of PS-Az with M_n= 22k, 59k and 245k. While the x value was invariant with respect to the thickness down to a few hundreds of nanometers, it started to increase with decreasing thickness for much thinner films. Then, the value reached a constant of 0.7-0.8 at approximately 40 nm. This inclination seems to be independent of molecular weight of PS.

So far, it has been widely accepted that there exists a liquid-like surface layer of the PS films.[2,4] And thus, it is plausible 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 results.

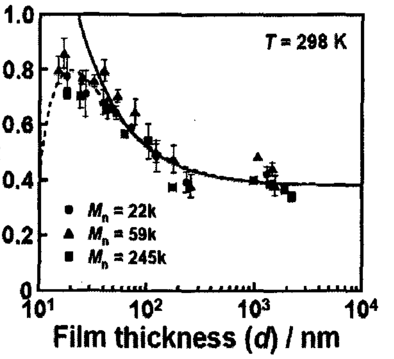


Figure 3. Relation between fraction of the fast component and film thickness. The solid and broken curves were drawn by fitting procedures mentioned in the text.

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

where x_b and x_s are x values in the bulk and surface regions, respectively. And, α_s and d are surface layer and film thickness, respectively. Since surface mobility is enhanced in comparison with the internal bulk region, the x_s value was here assumed to be 1.00 and was invariant with respect to the thickness. Fixing x_b= 0.38 and x_s= 1.00, best-fit curve was obtained with α_s= 22.6 nm, provided that data points for the films thinner than 32 nm were not counted. While equation (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 on account of a contribution from a less mobile layer at the substrate interface. If the interfacial effect is incorporated to the model, the experimental d vs. x relation could be well fit in the entire thickness range employed, as drawn by the dot curve in Figure 3.

$$x(d)=x_b\left\{1-\frac{(\alpha_s+\alpha_i))}{d}\right\}+x_s\frac{\alpha_s}{d}-x_i\left(\frac{\alpha_i}{d}\right)^2 \qquad (4)$$

Here, α_i and x_i are layer thickness and x value at the substrate interface. The meaning of the third term is that the presence of the substrate deactivates the trans→cis photoisomerization in the films, and corresponds well to a recent finding that chain mobility in the interfacial region with the solid substrate is depressed in comparison with the internal region of the film. However, since a fitting procedure with many parameters would make discussion ambiguous, further discussion on the basis of equation 4 was truncated.

We successfully presents that the surface region dynamically behaves as liquid for the photoinduced trans→cis isomerization of the Az probes, and that the thickness is approximately 20 nm. However, this value is much larger than the reported thicknesses of the surface layers, in which the segmental mobility is enhanced,[22] and in which the excess free volume is induced.[12,13] A simple but possible explanation for this is that molecular motion with a relatively small scale for PS is activated in the surface region down to about 20 nm. 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, related to motion of the side chains.

We finally come to molecular weight dependence of the *x*-*d* relation. As seen in Figure 3, the *x*-*d* relation was not directly correlated to the chain length of PS-Az. This implies that the fractional amount of the fast component is not so sensitive to an effect of chain confinement. In the case of PS-Az with M_n= 245k, two thinnest films were thinner than the chain dimension, resulting in apparent distortion of chains. Nevertheless, the x values for the films were comparable to those for other M_n samples with the corresponding thicknesses. In addition, the M_n independence of the *x*-*d* relation indicates that the photoisomerization is not motivated only by local free volume in the films. The number density of chain ends is given by $N/2$, where N is degree of polymerization. Hence, the number density of chain ends for the PS-Az with M_n of 22k is larger than that for the PS-Az with M_n of 245k by more than 10 times. Nonetheless, the clear effect of M_n on the x value at a given thickness was not discerned. These are quite consistent with our tentative conclusion that molecular motion with a relatively small scale for PS is a key to rationalize the 20 nm-thick surface layer, in which the photoisomerization is fast. 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.

4. CONCLUSIONS

We studied on isomerization kinetics for azobenzene probes in thin and ultrathin films of PS with various molecular weights. Consequently, the reaction rate increased with decreasing thickness once the films became thinner than a few hundreds of nanometers. Besides, no molecular weight dependence was observed. These results were explained in terms of the surface layer, in which molecular motion with a relatively small scale rather than the segmental motion was activated.

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