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Anisotropy of Free Volumes in Uniaxially Oriented Polymer Matrix As Observed by a Polarization-Selective Photochromic Reaction

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I. Introduction

Free volume, i.e., the degree of local mobility, of polymers has been a growing research topic for polymer materials in recent years due to its relation to a number of practically important problems such as physical aging, mobility of additives in polymers, and so on. By use of molecular probes, direct observation of molecular mobilities of the order of several tens of angstroms has been available, allowing the characterization of the distribution of free volumes in polymer.[1] There are also several theoretical models proposed for these distribution functions.[2] Among experiments, the positron annihilation technique provides direct information on the free-volume distribution.[3] Particularly, the angular correlation of positron annihilation radiation (ACAR) was recently demonstrated as a useful technique for monitoring the anisotropy of free volumes in uniaxially and biaxially oriented polymers.[4]

From the viewpoint of molecular probe techniques, fluorescence depolarization[5] or phosphorescence depolarization[6] can be used, in principle, to obtain information on the anisotropy of free volumes in oriented polymers. However, these measurement techniques are limited by either the fluorescence lifetimes or the sensitivity of the triplet state to oxygen and/or impurities. In order to investigate the slow relaxation processes of polymers below the glass transition temperature, we have examined the selectivity of the photocyclization of 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA, Figure 1) in the glassy state of poly(methyl methacrylate) (PMMA) upon irradiation with linearly polarized light.[7] It was found that the selection of this reaction reflects the β-relaxation of the PMMA matrix and also depends strongly on the orientational relaxation of polymer segments in uniaxially oriented PMMA.[8] In this note, the preliminary results of free-volume anisotropy in uniaxially oriented PMMA obtained from the reaction selectivity in the directions parallel and perpendicular to the stretching direction of the polymer matrix are reported and compared with the ACAR data.

II. Experimental Section

Sample Preparation and Experimental Procedure. Samples used in this experiment were prepared as described previously.[8] PMMA doped with HNMA at 10^{-3} M was uniaxially stretched at 120 °C in silicon oil to the appropriate elongation ratio α. Subsequently, the samples were quenched to room temperature with both ends fixed prior to irradiation experiments.

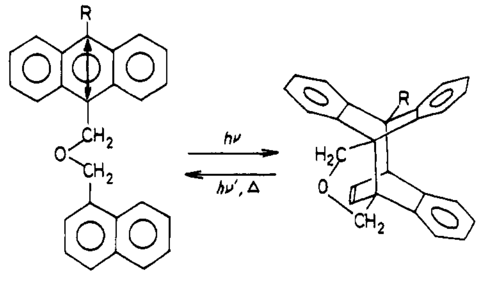

Figure 1. Photocyclization of HNMA: R = CH_2OH.

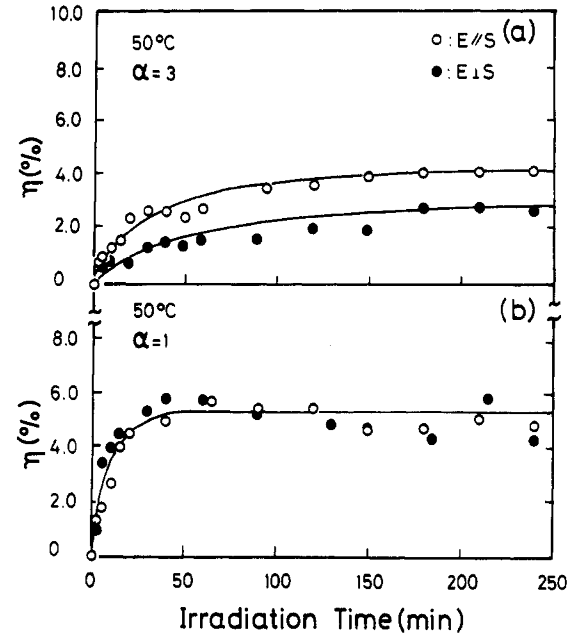

Figure 2. Dependence on irradiation time of the induction efficiency of HNMA at 50 °C: (a) uniaxially oriented PMMA with $\alpha = 3$; (b) as-cast and annealed PMMA, $\alpha = 1$. (○) parallel irradiation; (●) perpendicular irradiation.

The sample was irradiated with linearly polarized light $\vec{E}$ (365 nm) in the direction parallel ($\vec{E}\parallel\vec{S}$) and perpendicular ($\vec{E}\perp\vec{S}$) to the stretching direction $\vec{S}$. The change in absorbance of HNMA at 393.5 nm with irradiation time was followed by using a UV photometer (Shimadzu, Model UV-160). The induction efficiency $\eta(t)$ was calculated from $\eta(t) = 100 \times \{OD_\perp(t) - OD_\parallel(t)\}/OD_0$,[7,8] where $OD_\perp(t)$ and $OD_\parallel(t)$ are the absorbances of HNMA at 393.5 nm in the direction perpendicular and parallel to the polarization of the exciting light. OD_0 is the initial absorbance of the sample at the same wavelength. Both the photostationary and the time-dependent induction efficiency are used to evaluate the anisotropy of free volumes in uniaxially oriented PMMA.

III. Results and Discussion

The time dependence of η using irradiation with linearly polarized light in the directions parallel and perpendicular to the elongational direction of the sample is shown in Figure 2a. Hereafter, these two ways of irradiation are referred to as parallel and perpendicular irradiation. As reported previously,[8] $\eta(t)$ increases with irradiation time and eventually reaches a photostationary state characterized by η_{max}. From these results, it is obvious that the time evolution as well as the photostationary induction

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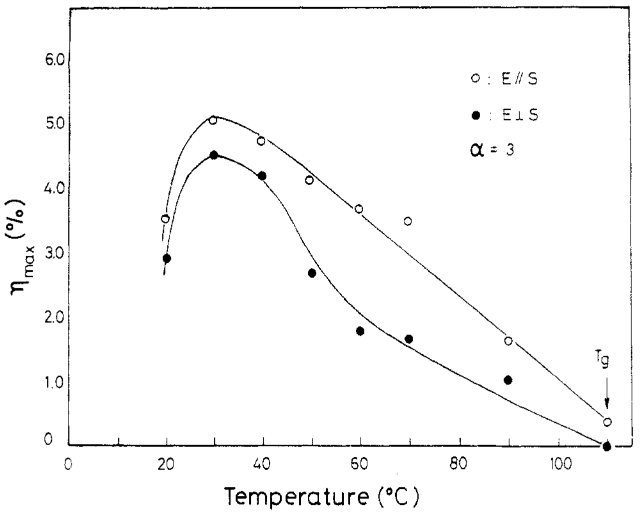

Figure 3. Temperature dependence of the equilibrium induction efficiency η_{max} for uniaxially oriented HNMA with $\alpha = 3$: (○) parallel irradiation; (●) perpendicular irradiation.

efficiency η_{max} for these two cases is different. The η_{max} obtained for parallel irradiation is larger than for perpendicular irradiation. However, almost no difference in η_{max} was observed at the same temperature for an as-cast and annealed PMMA sample as shown in Figure 2b. Therefore, the difference in η_{max} observed for these two irradiations reflects the structural anisotropy of oriented PMMA matrix. The temperature dependence of the photostationary induction efficiency η_{max} for these two cases is shown in Figure 3 for a uniaxially oriented PMMA matrix with $\alpha = 3$. This behavior is similar to those observed with the PMMA matrix without elongation.[7] Namely, η_{max} is small at low temperatures and rapidly increases at temperatures close to the β-relaxation of the polymer matrix. After reaching a maximum, η decreases and eventually approaches a very small value in the vicinity of the T_g of the polymer matrix. As shown in Figure 3, for all temperatures, η_{max} obtained with parallel irradiation is always larger than that observed with perpendicular irradiation. These experimental results also imply that the induction efficiency of HNMA does reflect the anisotropy of free volumes in the glassy state of elongated PMMA over a large range of temperatures. As pointed out in the previous work,[7] the induction efficiency η_{max} of HNMA is determined by the competition between two processes: One is the orientational relaxation of the anthracene moieties and the other is the conformational transitions around the C–O–C linkage. Since the two components of dichroic absorbance are the same before irradiation, it is reasonable to assume that the orientational relaxation of the anthracene moieties is almost unaffected by the stretching process. Therefore, the results shown in Figure 3 imply that the probability for naphthalene to encounter the excited anthracene moieties via conformational transitions along the stretching direction of the polymer matrix is larger than for the perpendicular direction. Similar behavior for the translational diffusion of small aromatic molecules such as azobenzene derivatives in anisotropic media has been observed previously.[10] Subsequently, the growth kinetics is analyzed according to[8]

$$\eta_{max} - \eta(t) = A \exp(-Kt) \qquad (1)$$

where K is the growth rate of the optical anisotropy in the polymer matrix generated by linearly polarized light.

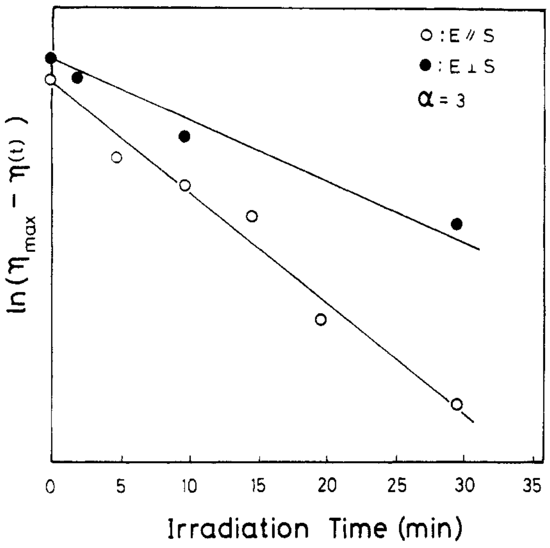

Figure 4. Kinetics of the induction process of HNMA in uniaxially oriented PMMA with $\alpha = 3$ at 50 °C: (○) parallel irradiation; (●) perpendicular irradiation.

Table I
Temperature Dependence of the Anisotropy Ratio γ for PMMA (T_g = 100 °C) with Uniaxial Elongation Ratio $\alpha = 3$

T (°C)	γ	T (°C)	γ
20	1.2	60	2.1
30	1.2	70	2.1
40	1.1	90	1.6
50	1.5		

Since the induction efficiency η eventually approaches the photostationary value η_{max}, the quantity $\eta_{max} - \eta(t)$ becomes very small at a late stage of irradiation and lacks accuracy. As a consequence, only η at the early stage of irradiation was taken into account to analyze the kinetics. Figure 4 shows a plot of eq 1 observed for PMMA with $\alpha = 3$ at 50 °C for the two irradiations. The growth rate K obtained for perpendicular irradiation is found to be smaller than that for parallel irradiation. indicating that the growth of optical anisotropy is larger for the sample irradiated along the stretching direction. The difference in the growth rate K is also due to the more favorable conformational transitions in the direction parallel to the orientation of polymer chains.

In order to relate the induction efficiency obtained by the two irradiations to the anisotropy of free volumes, the ratio γ between the photostationary induction efficiency η_{max} obtained for parallel and perpendicular irradiation is taken as a parameter characterizing the anisotropy of free volumes:

$$\gamma = \eta_{max}(\vec{E}\|\vec{S})/\eta_{max}(\vec{E}\perp\vec{S}) \qquad (2)$$

γ in eq 2 is equal to unity for an isotropic free volume but increases with the free-volume anisotropy. The temperature dependence of the anisotropy parameter γ calculated from the data shown in Figure 3 is summarized in Table I. The γ values increase slightly with increasing temperature and decrease after passing a maximum at temperatures above the onset of the β-relaxation of the polymer matrix. The increase in γ with temperature is probably due to the HNMA with anthracene and naphthalene moieties initially close to each other. Upon irradiation, HNMA with these particular conformations can easily undergo photocyclization without requiring a large change in free volumes. At a temperature close to the glass transition (T_g) of the matrix, the anisotropy still exists because the sample ends are fixed during the experiment. Recently, the ratio of free-volume diameters obtained in the directions parallel and perpendicular to the stretching direction of a biaxially stretched PMMA was directly measured by using the angular correlation of positron annihilation radiation.[4] The value obtained at room temperature was 1.7 at a stretching ratio 4.43. This value is about the same order as the ratio γ between $\eta_{\max}(\vec{E} \parallel \vec{S})$ and $\eta_{\max}(\vec{E} \perp \vec{S})$ shown in Table I. Furthermore, γ obtained for all temperatures in this work is smaller than the elongation ratio α. This result is also consistent with those for the stretched PMMA obtained by ACAR, indicating that PMMA elongated at temperatures above T_g does not follow the affine deformation. From the above results, we conclude that the anisotropy ratio γ defined in eq 2 can be used as a measure of the free-volume anisotropy in oriented polymers. Furthermore, the time dependence of $\eta_{\max} - \eta(t)$ can also provide useful information on these relaxation processes. However, these findings are limited due to the initial distribution of HNMA conformations frozen in the polymer matrix below the β-relaxation temperature. Direct information on the relaxation of free-volume anisotropy can be obtained if naphthalenoanthracenophane,[9] which is known to undergo photocyclization without requiring conformational transition, is used as a probe instead of HNMA. These experiments are currently in progress and will be reported later.

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Registry No. PMMA, 9011-14-7; HNMA, 126666-19-1.