polymer communications

Relationship between reorientational motions of a photochromic dopant and local relaxation processes of a glassy polymer matrix

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The reorientational relaxation process of the photochromic molecule 9-hydroxymethyl-10-[(naphthylmethoxy)-methyl]anthracene (HNMA) was observed in glassy poly(methyl methacrylate) (PMMA). For this purpose, the intramolecular photodimerization of HNMA incorporated in a PMMA matrix was selectively induced by irradiation with linearly polarized light. The optical anisotropy created in this way in the sample was allowed to relax to equilibrium by annealing at different temperatures. The reorientational relaxation of HNMA associated with this thermal treatment was subsequently observed by monitoring the time dependence of the two dichroic absorbance components of the anthracene moieties of HNMA. It was found that this relaxation process is well described by the sum of an exponential function of annealing time and a baseline which strongly depends on temperature. This fact implies that HNMA was not completely randomized in the glassy state of PMMA upon annealing. Furthermore, within the range of experimental temperatures, the activation energy of the reorientational relaxation rates of HNMA is close to that of the γ-process of the PMMA matrix, suggesting that the relaxation of the anthracene moieties is affected by the rotational motions of the α-methyl groups on the PMMA chain backbone. These preliminary results might provide some helpful guiding principles for controlling the stability of host/guest polymer materials using non-linear optical dyes.

(Keywords: reorientational relaxation; photochromic dopant; glassy polymer matrix)

Introduction

The transport process of small molecules in bulk polymer matrix has been an important area of research in polymer materials science for the last few decades because of its relationship to a variety of practical problems such as sorption phenomena of gas or simple liquids in glassy polymers, membrane permeability or problems related to the control and release processes of drugs[1]. Recently, the interest in this area has been extended to the reorientational relaxation of small molecules in glassy polymer matrices because this information is crucially important for the understanding of the temporal destabilization mechanism of non-linear optical materials prepared by poling amorphous polymers doped with non-linear optical dyes[2]. In general, both the translational diffusion and reorientational relaxation of diffusants or dopants in polymer matrices share a common feature that the transport coefficients of these small molecules are governed by the local relaxation processes of polymer chains. For temperatures above the glass transition temperature (T_g) of the polymer matrix, it is widely accepted that polymer segmental free volumes are the principal control parameter of these transport coefficients. These conclusions have been drawn from a number of experiments in which the translational as well as rotational diffusion coefficients were directly measured[3–5]. On the other hand, below T_g in the glassy region, the experimental techniques for the direct observation of these transport phenomena become quite limited except for a few methods such as modified fluorescence depolarization[6] or intramolecular reaction kinetics associated with conformational rearrangements[7–9]. According to these experiments, the free volume distribution of polymer matrices is the main driving force for these transport processes[10]. Recently, in an effort to understand the reorientational randomization of non-linear optical dyes incorporated in polymer matrices after poling, a number of experiments has been reported for the temporal behaviour of the second harmonic generation (SHG) signals of dye/polymer systems below T_g[11–14]. In order to establish the long-term stability of the non-linear optical properties of these materials, it is necessary to understand the correlation between the local relaxation processes of the polymer matrix and the reorientational relaxation of these dopants. The main purpose of this communication is to establish this relationship.

We have studied, in recent years, the selectivity of photochromic reaction kinetics upon irradiation with linearly polarized light in a glassy polymer matrix[15]. According to the results, the intramolecular photodimerization of the bichromophoric molecule 9-hydroxymethyl-10-[(naphthylmethoxy)methyl]anthracene (HNMA) can be selectively induced by irradiation with linearly polarized light in the glassy state of poly(methyl methacrylate) (PMMA). The induction efficiency $\eta(t)$, i.e. a measure of the optical anisotropy, is defined as:

$$\eta(t)=\frac{\mathrm{OD}_{\perp}(t)-\mathrm{OD}_{\parallel}(t)}{\mathrm{OD}_0}\times 10^2 \qquad (1)$$

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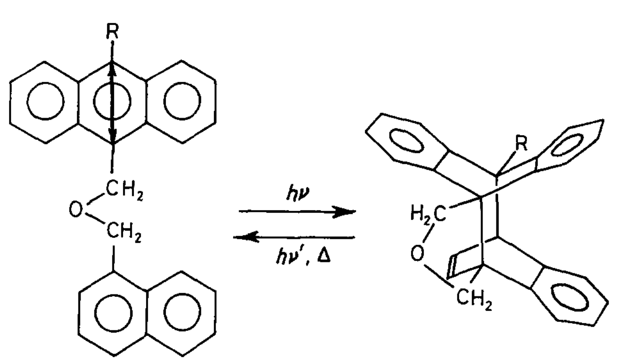

Figure 1 Chemical structures and the intramolecular photodimerization of 9-hydroxymethyl-10-[(naphthylmethoxy)methyl]anthracene (HNMA). The arrow on the anthracene ring indicates the absorption transition moment of the molecule

where $OD_{\parallel}(t)$ and $OD_{\perp}(t)$ are the absorbance components in the directions parallel and perpendicular to the polarization of the exciting light, respectively, and OD_0 is the initial absorbance before irradiation.

The induction efficiency shows several features such as exhibiting a maximum at the temperature of the β-relaxation process of PMMA and rising exponentially with irradiation time. Based on this information, the reorientational relaxation of HNMA has been observed in the isotropic[16] as well as in the anisotropic PMMA matrix[17]. However in these experiments, the information on the reorientational relaxation of HNMA was indirectly obtained because the intramolecular photodimerization kinetics involved the time evolution of the induction efficiency $\eta(t)$. In order to eliminate the effects of reaction kinetics and extract the reorientational relaxation of HNMA in glassy PMMA, photochromic molecules without conformational transitions such as cyclophane have been utilized[18].

In this communication, we propose an alternative approach which enables us to directly observe the reorientational relaxation process of HNMA in bulk PMMA matrix. For this purpose, PMMA matrices doped with HNMA were irradiated with linearly polarized light under various temperatures below T_g of the matrix. As the induction efficiency reaches its maximum, irradiation is stopped and the samples are subsequently annealed at different temperatures in the glassy region of the matrix. The reorientational relaxation process of HNMA was then monitored by observing the temporal decay of $\eta(t)$. The effects of the local relaxation process of HNMA are elucidated and discussed by comparing the temperature dependence of the reorientational relaxation times of HNMA with the existing data of local relaxations of PMMA obtained previously by dielectric relaxation, cross-polarization/magic angle spinning (CP/MAS) ^{13}C n.m.r. spectroscopy and quasi-elastic neutron scattering (QENS).

Experimental

Materials. HNMA (*Figure 1*) was synthesized and purified according to the procedure described previously[15]. PMMA (Wako Chemicals, Japan, $M_w = 1.4 \times 10^5$, $M_w/M_n = 2.1$) was precipitated twice using tetrahydrofuran/methanol mixtures. The microstructure of the PMMA (58.9% syndiotactic, 35.4% heterotactic and 5.7% isotactic) was determined from ^1H n.m.r. spectra of the γ CH_3 groups with dimethylsulfoxide-d_8 as solvent. The samples, sandwiched between two glass plates with a 0.2 mm spacer, were prepared by casting benzene solutions containing appropriate amounts of HNMA and PMMA. The concentrations of HNMA in these films were adjusted to 2×10^{-3} mol l^{-1}. All the samples were dried under vacuum at 170°C over 3 days prior to the experiments.

Instruments. PMMA doped with HNMA was irradiated using a high pressure mercury lamp (250 W, Ushio Electrics Co.). Linearly polarized light with the wavelength mainly at 365 nm was selected from a mercury light source (250 W, Ushio Electrics Co.) by using a sharp-cut filter (Corning SC-052) combined with a polarizer (Polaroid, HNP'B). The two components of the polarized absorbances at 393.5 nm of the anthracene moieties of HNMA in the directions parallel and perpendicular to the polarization of the exciting light were measured using a double-beam u.v.-visible spectrophotometer (UV-160, Shimadzu). The temperature was thermostatically controlled to within ±0.5°C. Decay analysis was performed by using a non-linear least-squares regression program.

Results and discussion

In order to obtain the reorientational relaxation of HNMA in the glassy PMMA matrix, a PMMA film doped with HNMA was irradiated at 40°C, i.e. the temperature which is known to exhibit the highest induction efficiency for this particular concentration of HNMA[15]. The irradiation time dependence of $\eta(t)$ at 40°C obtained from the two components of the dichroic absorbances $OD_{\parallel}(t)$ and $OD_{\perp}(t)$ [equation (1)] is shown as an example in *Figure 2.* At first, $\eta(t)$ increases with irradiation time and eventually reaches the equilibrium value $\eta_{max} = 6.3\%$ after 50 min of irradiation. This magnitude is in agreement with that reported previously under the same experimental conditions[15]. To estimate the reorientational relaxation times of HNMA in PMMA, several samples prepared under the same conditions were irradiated with linearly polarized light at 40°C over 50 min and subsequently annealed at different temperatures in the dark. The temporal decays of $\eta(t)$ monitored upon annealing are shown in *Figure 3.* As annealing time increases, the induction efficiency $\eta(t)$ decreases and reaches an equilibrium value which strongly depends on the experimental temperature. These results indicate that the optical anisotropy created by irradiation with linearly polarized light relaxes upon heating. However, the fact that $\eta(t)$ remains constant after annealing for >3 h implies that HNMA was not completely randomized in the PMMA matrix. Close to room temperature, $\eta(t)$ is almost unchanged with annealing time whereas $\eta(t)$ relaxes very fast upon approaching T_g of the matrix and eventually falls out of the time-scale of observation at 110°C. On the other hand, the equilibrium value η_∞ decreases with increasing temperature and almost disappears at 90°C which is located ~17°C below T_g of PMMA. With respect to the reorientational relaxation mechanism of small molecules in glassy polymer matrices, the so-called Kohlrausch–Willams–Watt (KWW) kinetics has been used, in some cases, particularly to analyse the decay of the second harmonic generation (SHG) signals[14]. However, as shown in *Figure 3*, the decays of $\eta(t)$ obtained by annealing the irradiated samples under several temperatures clearly

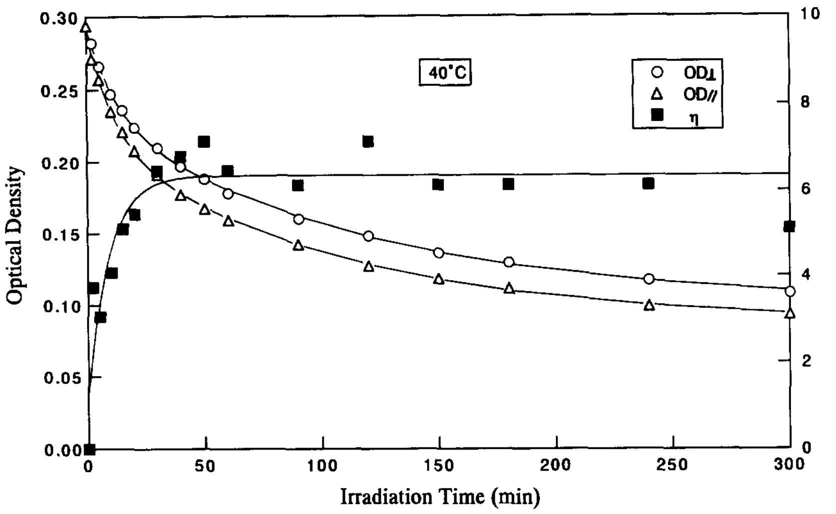

Figure 2 Irradiation time dependence of the two dichroic absorbance components and the induction efficiency $\eta(t)$ of HNMA in PMMA at 40°C

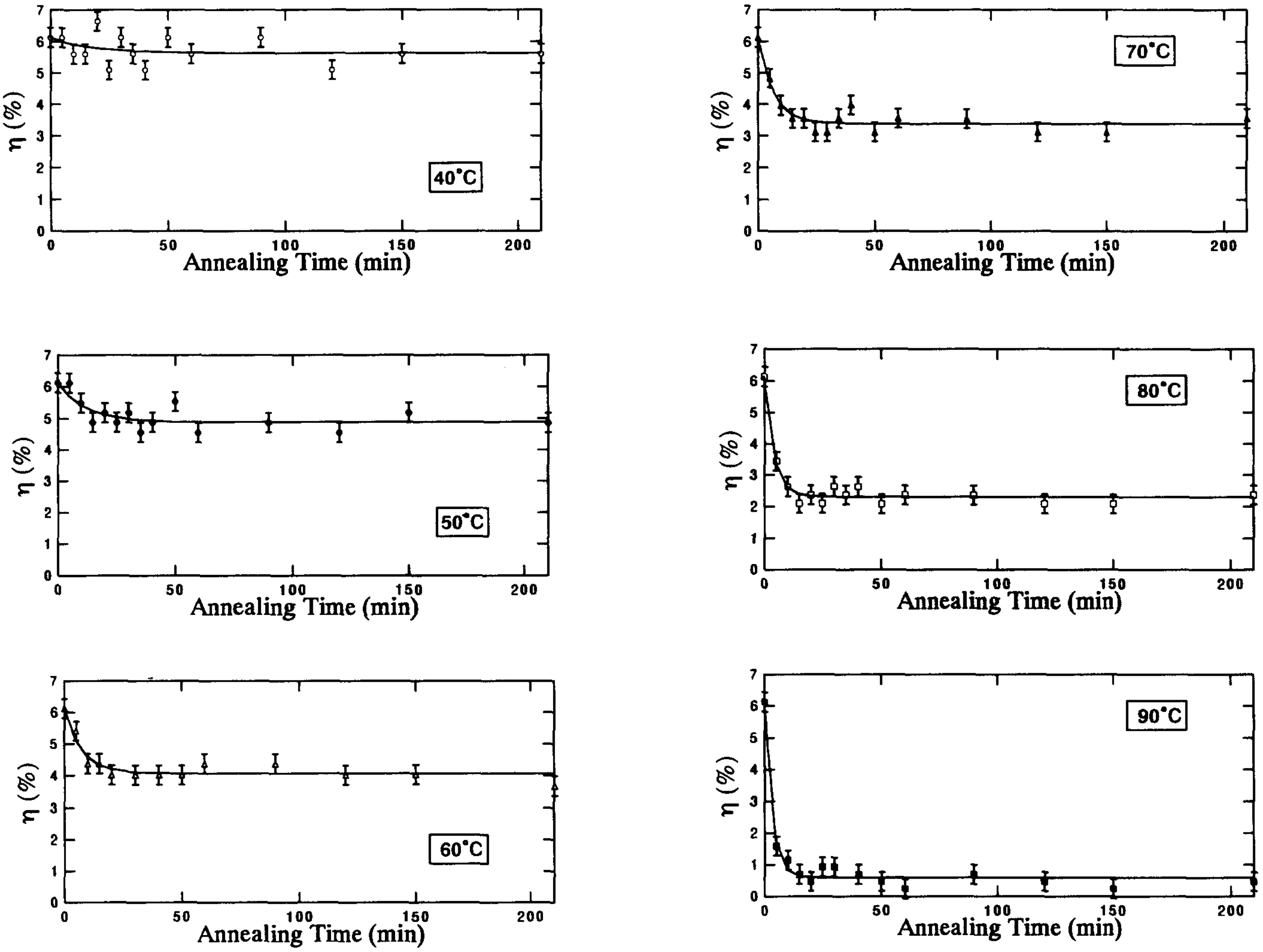

Figure 3 Annealing time dependence of the induction efficiency $\eta(t)$ at different temperatures

show the unrelaxed component. Therefore we fitted the experimental data to the following equation:

$$\eta(t)=\{[\eta(0)-\eta_\infty]\exp(-k_r t)\}+\eta_\infty \quad (2)$$

where $\eta(0)$ is the induction efficiency before annealing, η_∞ is the equilibrium value of $\eta(t)$ and k_r is the reorientational relaxation of HNMA.

The results obtained by the curve fitting process are illustrated by solid lines in *Figure 3*. It was found that equation (2) gives satisfactory fitting. These results imply that upon annealing, HNMA undergoes reorientational relaxation in PMMA with the characteristic constant k_r. Due to the inhomogeneity of the glassy state, there are some regions with large free volumes where HNMA can

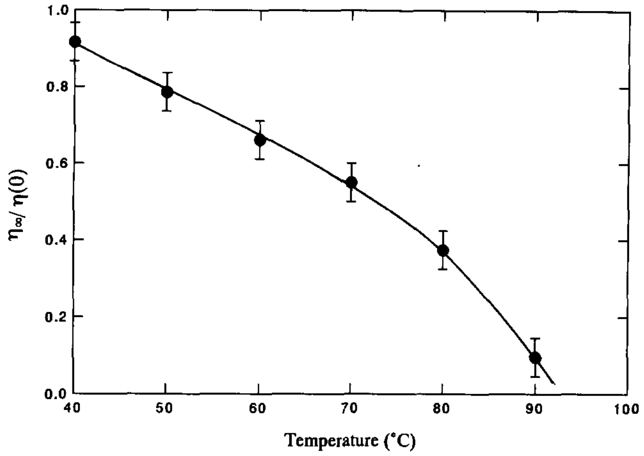

Figure 4 Temperature dependence of the normalized induction efficiency $\eta_{\infty}/\eta(0)$ of HNMA in PMMA

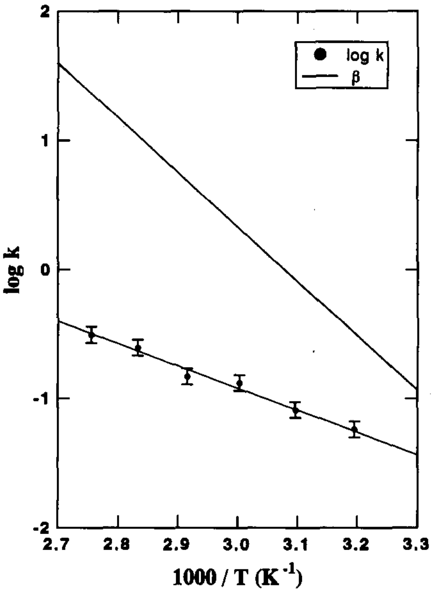

Figure 5 Arrhenius plot of the reorientational rate constant k_r of HNMA in PMMA. (——) Dielectric relaxation data for the β-relaxation process[21]. For comparison, the relaxation frequencies of these data have been shifted by an appropriate amount along the ordinate

relax and there are other regions with small free volumes where the reorientational relaxation process of HNMA is restricted. As a result, HNMA in the former affects the decay of $\eta(t)$ whereas HNMA in the latter affects the equilibrium value η_{∞}. The decrease of η_{∞} with increasing temperature supports this speculation. As shown in *Figure 4*, the fraction of the unrelaxed part of the decay, which is defined as $\eta_{\infty}/\eta(0)$, almost disappears at 90°C. By applying an appropriate model for restricted rotational relaxation such as the 'wobbling-in-cone' model[19], the free volumes associated with this relaxation mode can be estimated and provide, in principle, the information complementary to that already reported by positron annihilation spectroscopy[20]. On the other hand, as shown in *Figure 5*, the temperature dependence of k_r follows the Arrhenius behaviour within the temperature range of this work. The apparent activation energy is 32.7 kJ mol^{-1}. This value corresponds to the potential barrier which HNMA is required to overcome for undergoing reorientational relaxation in the glassy matrix. In terms of free volume distribution, it can be interpreted as the activation energy necessary for the rearrangement processes of free volumes with sizes comparable to HNMA. These rearrangement processes are in turn controlled by the local motions of PMMA chains. One way to gain an insight into the correlations between the local motions of PMMA chains and the reorientational relaxation of HNMA is to compare the activation energy of HNMA with those already obtained for PMMA by other measurement techniques. For PMMA, the local relaxation processes β, γ and δ have been identified with the rotational relaxation of $-COOCH_3$, α-CH_3 and the ester methyl groups. It was found that the activation energy ΔE of HNMA obtained in this work is much smaller than that of the β-process of PMMA (80–88 kJ mol^{-1}) as observed by dielectric relaxation[21]. For comparison, these dielectric data are shown by the solid lines in *Figure 5*. This might imply that the reorientation of HNMA in the regions of larger free volumes is driven by the mobilities of chain segments smaller than the $-COOCH_3$ side groups. On the other hand, the temperature dependence of the γ-process of PMMA has been measured by QENS[22,23], ^{1}H n.m.r.[24] and more recently by CP/MAS ^{13}C n.m.r. over a wide range of temperature (-100 to 100°C)[25]. The activation energies of the γ process obtained in these studies are in the range $\Delta E = 17$–34 kJ mol^{-1}. The variation arises from the different fractions of tacticity in the PMMA samples. The general tendency is that ΔE increases with the syndiotacticity content. The fact that the value $\Delta E = 32.7$ kJ mol^{-1} of HNMA falls in this range and is, in addition, much smaller than ΔE of the β process, suggests that HNMA is required to overcome a potential barrier comparable to the activation energy of the α-CH_3 groups. This speculation is also supported by the high syndiotacticity content (58.9%) of the PMMA used in this work. In other words, the γ-process of PMMA affects the reorientational relaxation of HNMA existing in the regions of larger free volumes with the fraction given by $[1-\eta_{\infty}/\eta(0)]$. It is worth noting that the activation energy for the reorientation of naphthaleno-anthracenophane, a closed form of HNMA, in the same PMMA matrix is close to that of the β process within the same temperature range[18]. These results imply that in the bulk state of PMMA, the reorientational motions of dopants with different sizes are affected by the local motions of different chain segments.

Conclusions

The reorientational relaxation process of the photochromic molecule HNMA incorporated in glassy PMMA was observed from the decay with annealing time of the reaction efficiency induced by linearly polarized light. The following results were obtained.

1. The reorientational relaxation of the dopant can be well described by an exponential function of time and a temperature-dependent baseline, indicating that the local environments around the dopants are inhomogeneous.
2. The temperature dependence of the reorientational rate constants of HNMA suggests that in the regions with free volumes comparable to its size, the reorientations of HNMA are affected by the γ-relaxation of the PMMA matrix.

3. The restricted part of the relaxation process decreases with increasing temperature and completely disappears at temperatures close to the T_g of PMMA.

The correlations between the dopant sizes and the local relaxation processes of PMMA derivatives are currently under investigation in order to establish the matrix–dopant relationships. These details will be reported later.

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