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Polarization-Selective Photochromic Reaction of Cyclophane in Glassy Poly(methyl methacrylate) Matrix

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ABSTRACT: Intramolecular photodimerization of the photochromic molecule tetraethyl [3.3](1,4)-naphthalene-(9,10)-anthracenophane-2,2,15,15-tetracarboxylate (abbreviated hereafter as cyclophane) was induced by irradiation with linearly polarized light in the glassy state of poly(methyl methacrylate) (PMMA). Compared to its homolog, 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA), which is known to undergo intramolecular photodimerization via conformational rearrangements, the reaction of cyclophane is more selective. These results were attributed to the specific cagelike structure of the cyclophane. The time evolution of the induction efficiency $\eta(t)$ obtained from the two dichroic absorbance components of cyclophane shows a rise-and-decay behavior, indicating that irradiation interferes with the selectivity of the reaction. In order to separate this effect from the reorientational relaxation process of cyclophane in the polymer matrix, the optical anisotropy created by linear polarized light was allowed to relax to the equilibrium state by annealing the irradiated samples over different time intervals. The decay of $\eta(t)$ can be well expressed by the sum of exponential functions of annealing time. From the curve-fitting process, it was found that the temperature dependence of the reorientational relaxation rates of cyclophane follows the Arrhenius type with the activation energy comparable to the β-process of the PMMA matrix. The activation energy of HNMA obtained under the same conditions is, on the other hand, similar to the γ-relaxation process of PMMA. These results imply that the reorientational relaxation of molecular dopants might be affected by the local relaxation processes of the matrix, and dopants with different sizes reflect the rotational motions of different segments of polymer chains. The experimental method described in this work not only provides an intriguing means to design polymer materials with controllable refractive index distribution but also gives a molecular basis for the understanding of the destabilization mechanism of dyes/polymer systems used in optoelectronic applications.

Introduction

Selection of photochromic reactions induced by polarized light in bulk polymer matrix has two important features. One is the capability of providing materials with controllable refractive index changes which can be used for information storage[1] and also for polarization-switchable devices[2] since the spatial distribution of the refractive index of polymers can be reversibly created and controlled by polarized light. The other feature is that the kinetics of this selection process have the potential of providing information on extremely slow reorientational dynamics in the glassy state of polymer matrix.[3] Such information cannot be easily obtained by conventional measurement techniques such as luminescence depolarization[4] or transient dichroic absorption[5] because the excited lifetimes involved in these photophysical processes are quite limited. Particularly, these slow relaxations of glassy polymers are known to be strongly related to practically important phenomena such as physical aging[6] or the destabilization of the second harmonic generation (SHG) signals in dyes/polymer systems[7] to which so many studies have been devoted in the past decade.[8-13]

In order to understand these relaxation processes in glassy polymers, we have examined the selectivity of photochromic reactions upon irradiation with linearly polarized light.[14] In these works, the photochromic molecule 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA) which consists of an anthracene and a naphthalene ring linked together by a three-atom chain, C−O−C, was excited with linearly polarized light in the glassy region of poly(methyl methacrylate) (PMMA). It was found that the intramolecular photodimerization of the molecule can be selectively induced by exciting the anthracene moieties with linearly polarized light. Furthermore, the induction efficiency of the reaction reflects the local (β) relaxation of the matrix. However, since the photodimerization of HNMA requires the conformational rearrangements via the C−O−C linkage, the induction efficiency obtained so far in the glassy state of the polymer matrix was not high. Also, the analysis of the growing process of the induction efficiency $\eta(t)$ with irradiation time is complicated because both the conformational transition around the C−O−C linkage and the reorientational relaxation of the anthracene moieties simultaneously contribute to this induction process. For all the well-known photochromic molecules such as azobenzene,[15] indigo,[15] fulgide[16] derivatives, and bichromophoric molecules,[17] intramolecular conformational transitions are necessary to induce the reactions. Therefore, the reaction efficiency is largely reduced in the glassy region of polymer matrix because these intramolecular motions become quite limited below the glass transition temperature (T_g). To improve the induction efficiency of the reaction, experiments using photochromic molecules with particular chemical structures are desirable. For this purpose, we have synthesized a photochromic cyclophane containing an anthracene and a naphthalene which are linked together from both sides by two three-

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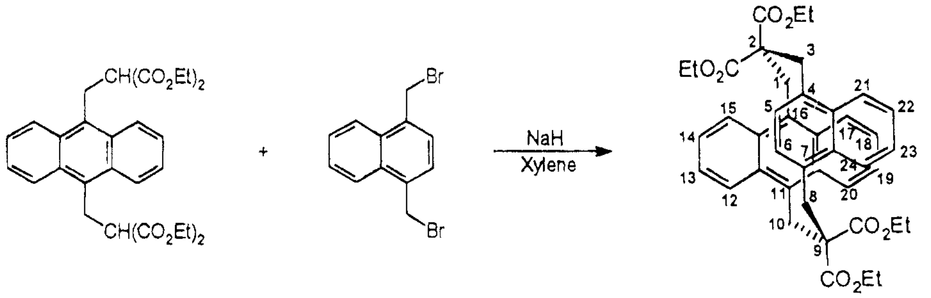
Scheme 1. Synthesis Scheme for Tetraethyl [3.3](1,4)-Naphthaleno-(9,10)-anthracenophane-2,2,15,15-tetracarboxylate (Abbreviated as cyclophane)



(1) (2) (3)

atom chains, C−C−C.[18−19] The advantage of this photochromic cyclophane is that its intramolecular photodimerization does not strongly require conformational rearrangements because the anthracene and naphthalene moieties are initially in the face-to-face position. Particularly, the cyclophane has a chemical structure similar to that of HNMA and thus allows us to compare these experimental results with those already reported.

In this work, we first reported the photoselection of the cyclophane tetraethyl [3,3](1,4)-naphthaleno-(9,10)-anthracenophane-2,2,15,15-tetracarboxylate in glassy PMMA matrix. Subsequently, the kinetics of the intramolecular photodimerization of the molecule under this particular excitation condition were analyzed. In order to directly observe the reorientational process of the cyclophane in PMMA, the optical anisotropy created by irradiation with linearly polarized light was allowed to relax to the equilibrium state by annealing the irradiated samples over different periods of time. The decay with annealing time of $\eta(t)$ was then analyzed and compared to the local relaxation data of PMMA obtained directly by a number of techniques such as dielectric and dynamic mechanical relaxation. Finally, the effects of the local relaxation processes of polymer matrix on the reorientational relaxation of photochromic molecules with different sizes will be discussed together with the principle to design amorphous polymer materials with controllable refractive index distribution using polarization-selective photochromic reactions.

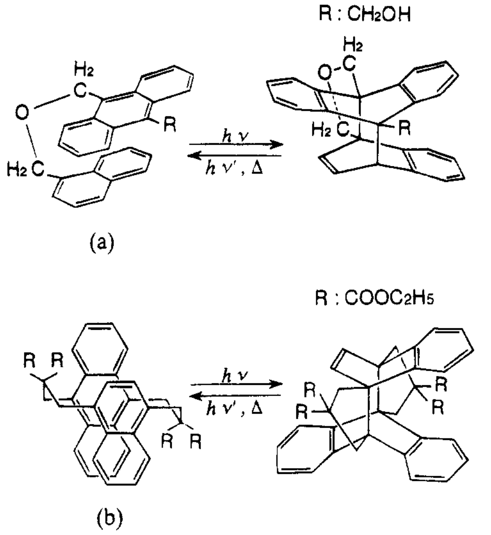


Figure 1. Intramolecular photodimerization of 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA) (a) and cyclophane (b).

Experimental Section

Samples. Two kinds of photochromic molecules were used in this work. One was 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA) which was prepared as described previously.[3] The other was tetraethyl [3.3](1,4)-naphthaleno-(9,10)-anthracenophane-2,2,15,15-tetracarboxylate[19] (**3**) (abbreviated as cyclophane) which was synthesized by reacting 9,10-bis[(2,2-bis(ethoxycarbonyl)ethyl]anthracene (**1**) with 1,4-bis(bromomethyl)naphthalene (**2**) in xylene under dark according to Scheme 1. The details of the synthesis and the structure analysis using NMR and single-crystal X-ray analysis of this cyclophane are reported elsewhere.[19] Figure 1 shows the chemical structures and the intramolecular photodimerization of these two photochromic compounds. The cyclophane was designed to have a basic structure similar to that HNMA, i.e., containing an anthracene and a naphthalene ring which are connected to each other from both sides by the two three-carbon-atom chains C−C−C. The four ethoxycarbonyl groups were introduced in an attempt to increase the solubility of the cyclophane in polymer matrix. The concentrations of HNMA and cyclophane in PMMA were ca. 10^{-3} M which were adjusted by casting benzene solutions of PMMA containing the appropriate quantities of these photochromic molecules. The matrix PMMA ($M_w = 1.44 \times 10^5$, T_g = 110 °C; Wako Pure Chemicals Inc., Japan) was purified by precipitation using tetrahydrofuran as good solvent and methanol as nonsolvent. The microstructures of this PMMA (58.9% syndiotactic, 35.4% heterotactic, and 5.7% isotactic) were identified from ^{1}H NMR spectra of the α-CH_3 groups with dimethyl sulfoxide-d_8 (Aldrich) as solvent. PMMA films with thickness 0.2 mm containing these photochromic molecules were dried at 170 °C in vacuo in the dark over 2 days prior to the experiments.

Instruments and Data Analysis. All the instruments used in this work have been described previously.[3,14] In brief, UV light with the wavelength mainly at 365 nm from a high-pressure mercury lamp was converted into linearly polarized light by using a polarizer (HNP'B, Polaroid) and then impinged on the sample which was placed in a brass holder. The temperature of the samples was thermoregulated with a precision of ±0.5 °C. The change with irradiation time of the two dichroic absorbance components of HNMA and cyclophane at 393.5 and 402 nm, respectively, was monitored at room temperature by using a UV−visible spectrophotometer (Shimadzu, UV-160) after irradiation over different time intervals. The curve-fitting process was performed on a Macintosh computer using the nonlinear least squares method. The time-dependent induction efficiency, $\eta(t)$, is defined as:

$$\eta(t) = 100[\mathrm{OD}_\perp(t) - \mathrm{OD}_\parallel(t)]/\mathrm{OD}_0 \qquad (1)$$

where $\mathrm{OD}_\perp(t)$ and $\mathrm{OD}\|(t)$ are respectively the absorbances measured in the direction perpendicular and parallel to the polarization of the exciting light. OD_0 is the magnitude of the absorbance before irradiation. Since the difference between the two dichroic components is small, experiments under the same conditions were repeated over several times and the average of these values was taken as the data point. The maximum deviation of the data points obtained by this procedure was indicated by the error bar in the figures.

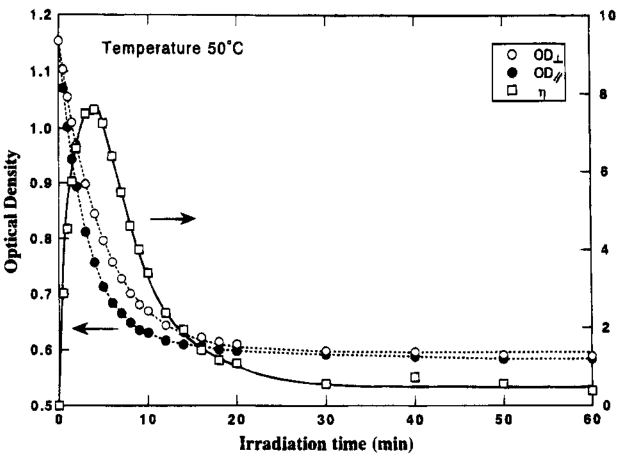


Figure 2. Two dichroic absorbance components and induction efficiency, $\eta(t)$, of cyclophane in PMMA irradiated with linearly polarized light at 50 °C.

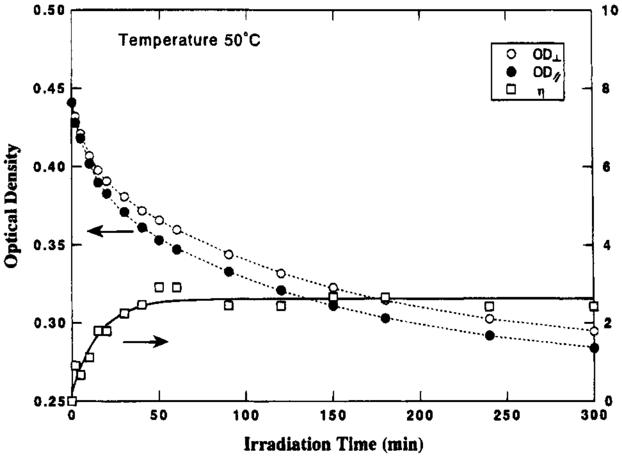


Figure 3. Two dichroic absorbance components and induction efficiency, $\eta(t)$, of HNMA in PMMA irradiated at 50 °C.

Results and Discussion

The induction efficiency, $\eta(t)$, obtained from eq 1 for cyclophane in PMMA matrix exhibits rise-and-decay kinetics. As an example, the irradiation time dependence of $\eta(t)$ obtained by irradiation at 50 °C is shown in Figure 2. $\eta(t)$ rises quickly at the early stage (ca. 4 min) of irradiation and gradually decreases with irradiation time after passing a maximum which is slightly temperature dependent. In the later stage of irradiation (ca. 30 min), $\eta(t)$ almost disappears, indicating that there is no selectivity at long irradiation time. This behavior of cyclophane is strongly in contrast with that observed with HNMA, as shown in Figure 3 as an example. Compared to cyclophane, the reaction of HNMA in the same PMMA matrix was induced more slowly (ca. 60 min), and after reaching a value ca. 2.3%, $\eta(t)$ becomes unchanged within the experimental time scale (300 min). The rise part of $\eta(t)$ for cyclophane in the early stage of irradiation can be attributed to the selectivity of the reaction induced by linearly polarized light.

In order to elucidate the decay process of $\eta(t)$ shown in Figure 2, another sample was prepared under the same conditions and irradiated at 50 °C with polarized light over 4 min, which is the irradiation time necessary for $\eta(t)$ to reach its maximum magnitude. Then irradiation was stopped, and the sample was subsequently annealed at the same temperature in the dark. As shown in Figure 4, $\eta(t)$ decays very slowly over 250 min of annealing, suggesting that the decay process of $\eta(t)$ shown in Figure 2 does not solely originate from the reorientational relaxation of cyclophane in PMMA.

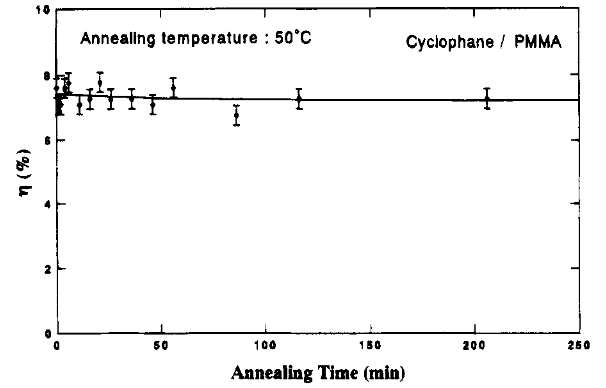


Figure 4. Dependence on the annealing time of the induction efficiency, $\eta(t)$, of cyclophane obtained after 4 min of irradiation with linearly polarized light at 50 °C.

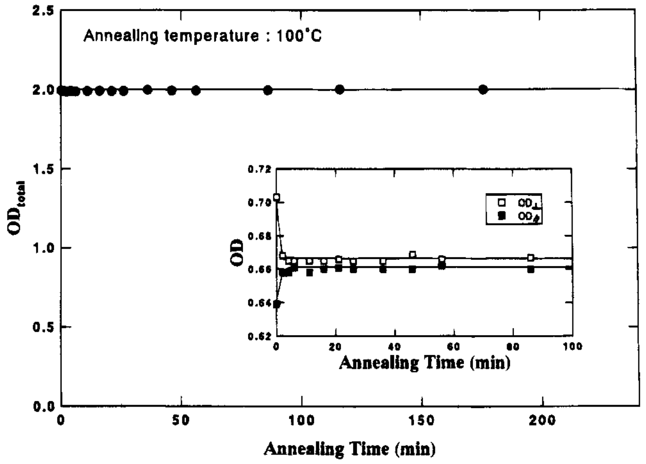


Figure 5. Effects of heating on the two polarized components and the total absorbance of cyclophane in PMMA at 100 °C. The two dichroic components obtained in the early stage of annealing are enlarged and shown in the inset.

To examine the thermal backward reaction of cyclophane photodimers, a PMMA doped with cyclophane was irradiated at 50 °C over 4 min. The light source was then turned off, and the sample was subsequently heated at 100 °C in vacuo in the dark. The two dichroic components, $\mathrm{OD}_\perp(t)$ and $\mathrm{OD}_\parallel(t)$, were monitored over different time intervals during heating. The total absorbance, $\mathrm{OD}_{\mathrm{total}}(t) = \mathrm{OD}_\parallel(t) + 2\mathrm{OD}_\perp(t)$, which is proportional to the absorbance measured under unpolarized light,[5] was also calculated from the corresponding dichroic components. These results are depicted in Figure 5. As seen in the inset of the figure, at the very early stage of annealing, $\mathrm{OD}_\perp(t)$ decreases whereas $\mathrm{OD}_\parallel(t)$ increases. After a short period of ca. 5 min, these two components approach each other and remain unchanged over 200 min of heating. On the other hand, the total absorbance, $\mathrm{OD}_{\mathrm{total}}(t)$, was constant during this period, implying that the cyclophane photodimers are stable at 100 °C. The quick changes in the magnitudes of these two dichroic components within the first 5 min of annealing are due to the reorientational relaxation of cyclophane. As described later, this process becomes clearer when the sample is annealed at lower temperatures. It is worth noting that above 130 °C the thermal dissociation reaction of photodimers takes place and cyclophane is recovered. These experimental results obviously indicate that the thermal backward reaction of cyclophane photodimers does not occur below the T_g of PMMA (110 °C). Consequently, we conclude that the

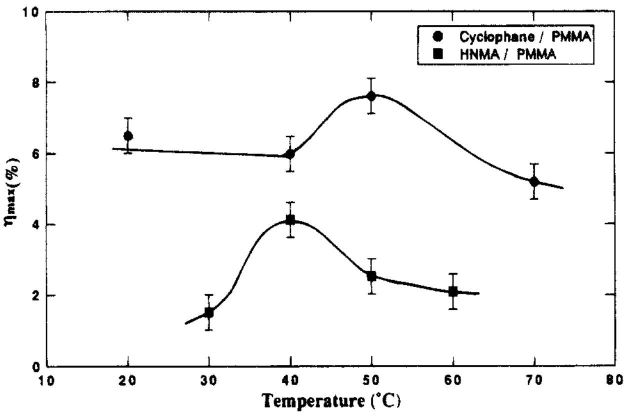


Figure 6. Temperature dependence of the maximum efficiency, η_{max}, of cyclophane and HNMA in PMMA obtained by irradiation with linearly polarized light.

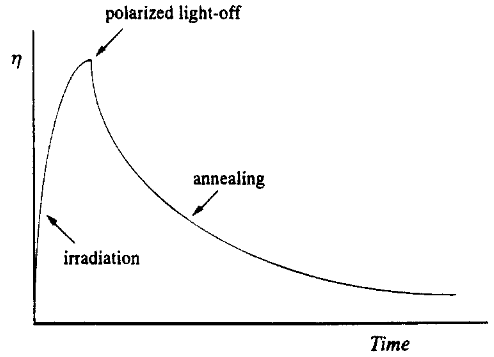


Figure 7. Schematic representation of the annealing-after-irradiation procedure for monitoring the reorientational relaxation of cyclophane in the glassy region of PMMA.

decay of $\eta(t)$ illustrated in Figure 2 is not completely due to the reorientational relaxation of cyclophane in the PMMA matrix but is also related to the photochemical kinetics of cyclophane. Detailed studies on the photochemical reactions of cyclophane in glassy polymer matrices are necessary to elucidate this decay process.

The temperature dependence of the highest induction efficiencies, η_{max}, which both the photochromic molecules can achieve, is shown in Figure 6. Under the same condition, η_{max} of cyclophane is larger than that of HNMA over the whole range of experimental temperatures. This suggests that the high selectivity of the intramolecular photodimerization of cyclophane comes from the specific cagelike structure of the molecule. Furthermore, the temperature at which η_{max} reaches its maximum is higher for cyclophane than for HNMA, implying that the reorientational relaxation of cyclophane reflects the local relaxation process of PMMA involving larger segments. This conclusion will be verified by the direct observation of the orientational relaxation of these two photochromic molecules in PMMA using the annealing-after-irradiation experiments described below.

The results shown in Figure 5 suggest that the information on the reorientation dynamics of cyclophane in PMMA can be observed by following the time evolution of dichroic absorbances upon annealing the irradiated sample in the dark. For this purpose, we performed the annealing-after-irradiation experiments in the range between the ambient temperature and the T_g of the PMMA matrix. The details of the experimental procedure are illustrated in Figure 7. At first, PMMA films doped with cyclophane were irradiated at 50 °C over 4 min, i.e., the experimental condition under which $\eta(t)$ reaches its maximum. Then the light source for irradiation was turned off, and the samples were subsequently annealed at a given temperature over different periods of time. After each annealing time interval, the sample was cooled to room temperature and the two dichroic absorbance components were measured by using a UV–visible spectrometer. This procedure was repeated until the magnitude of the induction efficiency, $\eta(t)$, became unchanged with annealing time. The experimental results obtained in the range between 50 and 100 °C are shown in Figure 8. There exist two extreme cases for the decay processes of $\eta(t)$. Below 50 °C, the efficiency, $\eta(t)$, is almost unchanged with annealing time, whereas it disappears very quickly at 100 °C, which is ca. 10 °C below the T_g of the PMMA matrix. In the intermediate range, $\eta(t)$ decreases with increasing annealing time and obviously is not the exponential function. Particularly, at temperatures far from T_g, $\eta(t)$ does not completely disappear but tends to reach an equilibrium value, η_∞, after 250 min of annealing. Upon approaching T_g, η_∞ decreases and becomes very small at 100 °C. These data indicate that upon annealing the optical anisotropy generated by irradiation with linearly polarized light relaxes toward the isotropic state due to the reorientational relaxation of cyclophane. Furthermore, this relaxation process is restricted at temperatures far from the T_g of PMMA. The fact that the time evolution of $\eta(t)$ dramatically, changes within a narrow range of annealing temperatures implies that the potential barrier which cyclophane is required to overcome for undergoing reorientation in PMMA is quite high and would correlate to some local relaxation processes of the PMMA matrix. To draw a conclusion for this correlation, it is necessary to analyze the decay process of $\eta(t)$. Since these decays are not exponential, at first we fitted them to the Kohlrausch–Williams–Watts (KWW) kinetics, i.e., the so-called stretched exponential function:[20]

$$\eta(t) = A \exp[-(k_r t)^\beta] \qquad (2)$$

where A is the prefactor equal to the induction efficiency before annealing, k_r is the average reorientational relaxation rate of cyclophane, and β is the exponent describing the width of the relaxation distribution of cyclophane.

The curve-fitting processes were very satisfactory, but the exponent β larger than unity was obtained for several temperatures. Therefore, we abandoned the KWW mechanism and fitted $\eta(t)$ to the sum of two exponentials and a base line. The latter was introduced to take into account for the fact that $\eta(t)$ approaches a constant at long times of annealing. The following equation was used,

$$\eta(t) = A(F_1 e^{-k_1 t} + F_2 e^{-k_2 t}) + \eta_\infty \qquad (3)$$

where $A = (\eta(0) - \eta_\infty)$, the pre-exponential factor which was incorporated into eq 3 to express the contribution of the restricted reorientational relaxation process of cyclophane to the decay of $\eta(t)$, k_1 and k_2 are the decay rates of $\eta(t)$ with the corresponding fractions F_1 and F_2, and η_∞ is the limiting effiency obtained at long times of annealing.

Fitting the experimental results to eq 3 yields very satisfactory results as shown by the solid curves in Figure 8. These experimental results probably reflect the existence of a distribution of free volumes in the local environments of cyclophane. The fast decay

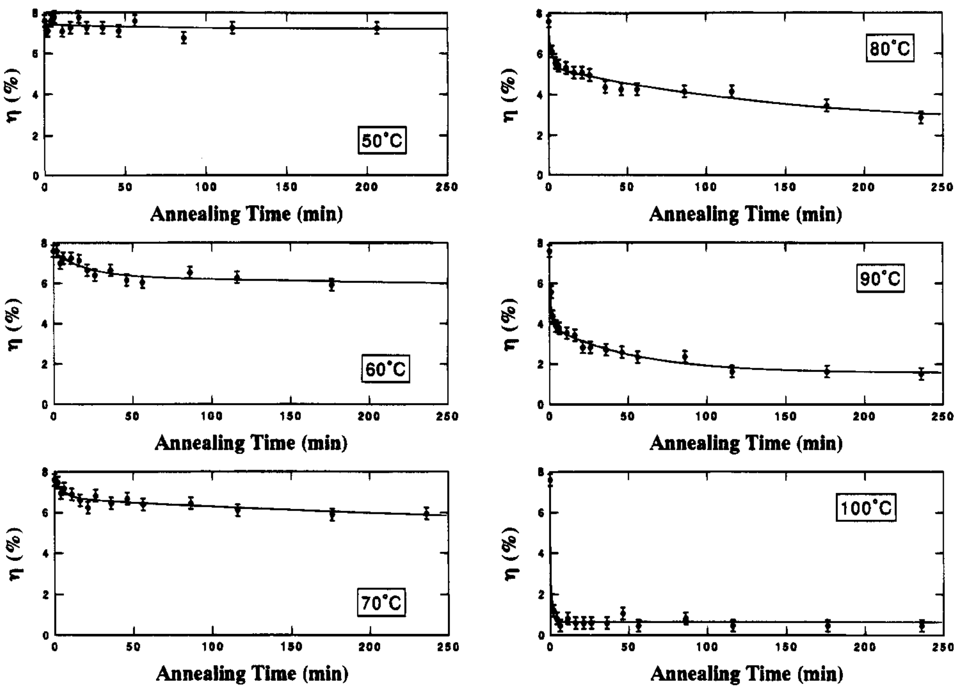


Figure 8. Time evolution of the induction efficiency, $\eta(t)$, upon annealing at different temperatures. The solid curves were obtained by fitting the data to eq 3 using the nonlinear least squares method.

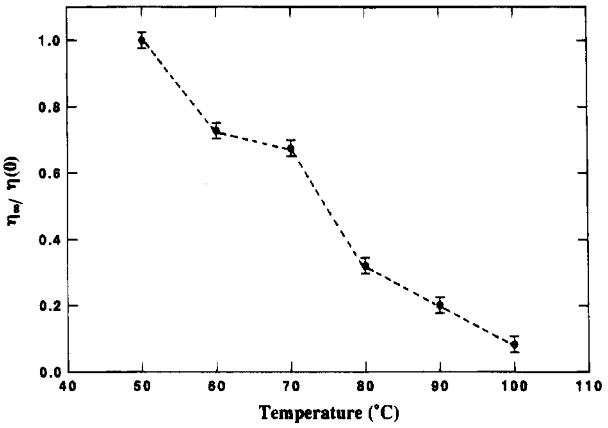


Figure 9. Temperature dependence of the fraction $\eta_\infty/\eta(0)$ for the restricted reorientation of cyclophane in PMMA obtained from eq 3.

process of $\eta(t)$ on the short time scale characterized by the rate constant k_1 and the corresponding fraction F_1 can be explained as the contribution from the reorientational relaxation process of cyclophane in the regions of PMMA with the free volumes much larger than the size of the probe. On the other hand, the rate constant k_2 and the fraction F_2 of the slower decay process came from the rotational relaxation of cyclophane in the regions of PMMA with the free volumes comparable to its size. The base line η_∞ is evidence for the restricted relaxation process of the molecule in the regions of much smaller free volumes. Note that such behavior has already been observed in the fluorescence depolarization experiments for the rotational relaxation of the probe molecules embedded in lipid bilayers and was analyzed using the wobbling-in-cone model.[21] Upon increasing temperature, the fraction of these small free volumes decreases as evidenced by the diminution of η_∞ and almost disappears at 100 °C. Shown in Figure 9 is the temperature dependence of the fraction $\eta_\infty/\eta(0)$ corresponding to this particular relaxation process.

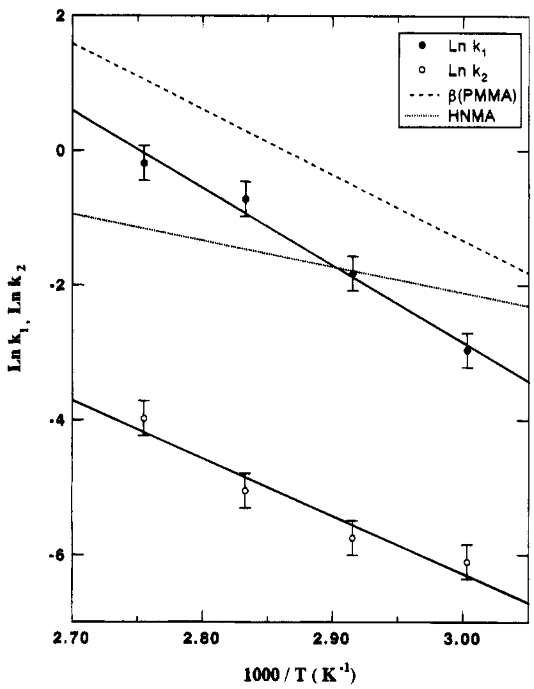


Figure 10. Temperature dependence of the reorientational relaxation of molecular dopants in the glassy state of PMMA obtained by the annealing-after-irradiation method: reorientational rates k_1 (●) and k_2 (○) of cyclophane, reorientational rate k_r (···) of HNMA, and β-relaxation (– – –) of PMMA observed by dielectric relaxation.[22]

As illustrated in Figure 10, the temperature dependence of the two rate constants, k_1 and k_2, follows the Arrhenius type within the temperature range of this experiment. The activation energies corresponding to these two processes are 22.8 and 16.9 kcal/mol, respectively. These two values are close to the activation energy of the β-relaxation process of PMMA obtained previously by dielectric relaxation data.[22] According to these results, the activation energy of the β-relaxation (rotation of the $-COOCH_3$ side groups) of PMMA is in between the range 19–21 kcal/mol. Taking into account that (1) to undergo reorientational relaxation in PMMA matrix, cyclophane is required to overcome certain potential barriers which are given by the temperature

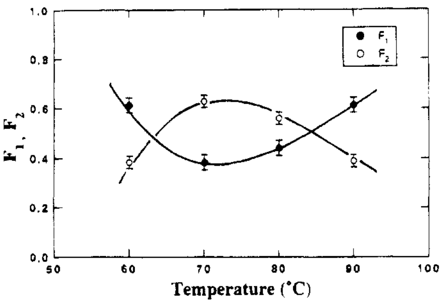


Figure 11. Temperature dependence of the two fractions, F_1 and F_2, of cyclophane in PMMA obtained by fitting the experimental results to eq 3.

dependence of k_1 and k_2, (2) upon annealing, the free-volume rearrangements of PMMA are driven by the relaxation of PMMA segments, and (3) the activation energies of the two rate constants, k_1 and k_2, are close to that of the β-process of PMMA, it can be concluded that the reorientational motions of cyclophane in PMMA are mainly affected by the rotations of the $-COOCH_3$ side groups of the matrix. On the other hand, the annealing time dependence of $\eta(t)$ of HNMA can be well expressed by the sum of an exponential and a base line, i.e., $\eta(t) = [(\eta(0) - \eta_\infty)\exp(-k_r t) + \eta_\infty]$. The dotted line shown in Figure 10 is the temperature dependence of the reorientational relaxation rate, k_r, of the anthracene moieties of HNMA in PMMA obtained under the same conditions by the annealing-after-irradiation method describing above.[23] It was found that this activation energy is ca. 7.8 kcal/mol and much smaller than the β-process but comparable to the γ-relaxation (α-CH_3 rotations) of PMMA observed by quasielastic neutron scattering[24] and cross polarization/magic angle sample spinning (CP/MAS) ^{13}C NMR spectroscopy.[25] These results clearly suggest the effect of polymer local relaxations on the size of molecular dopants.

The temperature dependence of the two fractions, F_1 and F_2, of cyclophane is shown in Figure 11. As temperature increases, F_1, the fraction of cyclophane in the region with larger free volumes, decreases whereas F_2, the fraction of cyclophane in the region with smaller free volumes, increases. Eventually, F_1 and F_2 seemingly approach each other at a temperature close to T_g, except for the data obtained at 90 °C where some uncertainty associated with the very fast decay component in the early stage of annealing might affect the analysis of $\eta(t)$. From the above results, we think that the reorientational relaxation of molecular dopants in glassy PMMA is controlled by the local relaxation processes of the matrix. Furthermore, dopants with different sizes reflect the relaxation of different polymer segments.

The experimental results described above indicate that polymer materials with controllable refractive index distribution can be obtained by taking advantage of the reaction selectivity induced by polarized light. By choosing photochromic molecules with suitable chemical structures such as cyclophane, the high selectivity can be obtained. It should be noted that since the light intensity used in this work is relatively low (ca. 0.5 mJ/cm^2 s), η_{max} of cyclophane is limited at 8%. Much higher induction efficiency is obtainable in principle if laser is used as a light source. In addition, the annealing-after-irradiation method shown in this work can provide useful *informations* on the extremely slow reorientation dynamics of molecular dopants in the glassy state of polymer matrices. This method is complementary with those such as nonlinear optics[7] and modified fluorescence depolarization reported recently.[26]

Summary

Polarization-selective intramolecular photodimerization of the cyclophane tetraethyl [3,3](1,4)-naphthaleno-(9,10)-anthracenophane-2,2,15,15-tetracarboxylate in glassy poly(methyl methacrylate) was investigated and compared to its homolog, 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene. The following results were obtained.

(1) Under the same experimental conditions, the selectivity of the reaction of cyclophane is higher than that of HNMA. These results can be attributed to the specific cagelike structure of the cyclophane.

(2) By using the annealing-after-irradiation techniques, we were able to monitor the reorientation dynamics of cyclophane in the glassy state of PMMA. It seems that the relaxation of cyclophane reflects the free-volume distribution of glassy PMMA, and the β-process of PMMA could be one of the main driving forces for these reorientation dynamics.

(3) By combining the above results with those obtained from the reorientation dynamics of HNMA in the same matrix, we conclude that the reorientational relaxation of molecular dopants with different sizes is affected by different segmental motions of the matrix.

Further correlations between the reorientation dynamics of these photochromic molecules and the local relaxation of polymers are currently under investigation by using polymers with similar T_g and side groups of different chemical structures. These experimental results will be reported in the near future.

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