Polarization-Selective Photochromic Reaction in Glassy Polymers: Effects of Local Relaxation Processes of Polymer Matrix

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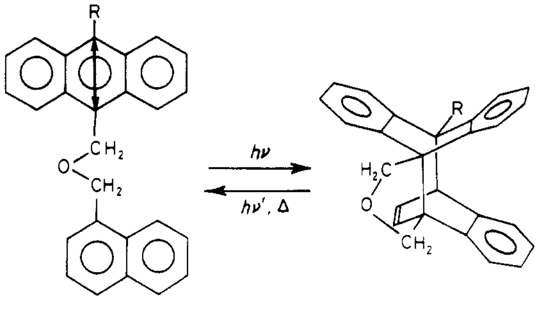
ABSTRACT: The extent to which the intramolecular heterophotodimerization of the photochromic molecule 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA), incorporated into a poly(methyl methacrylate) (PMMA) matrix, is induced by irradiation with linearly polarized light was investigated. The degree of photodimerization was evaluated by using the polarization-induced efficiency parameter, η, which is defined as the normalized difference between the two components of dichroic absorbance. It was found that η is affected by both the β-relaxation process and the glass transition temperature, T_g (T_g = 103 °C) of the PMMA matrix. As irradiation time increases, η increases and reaches a limiting value, η_{max}, of ca. 6% at temperatures of around 40 °C. These results indicate that, by utilizing the selective induction of the intramolecular heterophotodimerization of HNMA, which occurs upon excitation with polarized light, it is possible to generate and control the spatial distribution of the refractive index of glassy polymer films, thereby making them potentially useful as optoelectronic materials for wave guiding or light modulation.

I. Introduction

The phenomenon of photochromism has been investigated extensively by a large number of researchers over several decades.[1] Due to both the reversibility and the large changes in refractive index which accompany this particular type of photochemical reaction, much effort has been devoted to the development of photochromic materials for optical imaging.[2,3] In most cases, the photochromic molecules are incorporated into polymer matrices. A change in refractive index may then be achieved either by photodimerization[4,5] or photopolymerization of vinyl monomers in the presence of photosensitizers.[6] The kinetics of photochromic reactions occurring in polymers is completely different from that in organic liquids, and this has given rise to a number of reports on the reaction kinetics of photochromic molecules in the bulk state of polymers.[7] Recently, the concept of free volume distribution, which was originally suggested by the experiments of Paik and Morawetz,[8] has been used to interpret experimental data on the trans-cis photoisomerization of a number of azo and stilbene derivatives[9-12] in polymer matrices. Other alternative approaches to the variation of the refractive index of polymer matrices have also been proposed. These include the variation of the compositions of compatible blends of two polymers that have markedly different refractive indices[13] or the adjustment of the concentration of low molecular weight dopants possessing high polarizabilities.[14]

Photochemical reactions between anthracene and naphthalene, which result in the formation of photochromic compounds, have been the subject of several recent reports.[15,16] The photoaddition reaction between anthracene and naphthalene does not occur in bimolecular cases, but it has been found to occur efficiently when anthracene and naphthalene are linked together by a three-atom chain.[17,18] We have reported previously the results of a detailed study of the kinetics of the intramolecular homophotodimerization of bis(9-anthrylmethyl) ether (BAME), a photochromic molecule containing only anthracene moieties, in polystyrene and poly(vinyl acetate) (PVAc).[19] The change in the refractive index that accompanies this reaction in the bulk state of PVAc was found to be sufficiently large for being used as optical recording materials.[20] The polarization of the transition moments of the electronic ground state and the excited singlet state of anthracene has been studied[21] and has also been used in fluorescence depolarization experiments to probe the local segmental motions of polymer chains.[22]

Scheme I
Intramolecular Heterophotodimerization of 9-(Hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA; R = $-CH_2OH$)



The aim of this work was to generate an arbitrary spatial distribution of refractive index in glassy polymer materials by using a method based on the selective intramolecular heterophotodimerization of a bichromophoric molecule containing anthracene and naphthalene moieties, which results from excitation with linearly polarized light. For this purpose, 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA) (see Scheme I), a homologue of bis(9-anthrylmethyl) ether, was synthesized and incorporated into a PMMA matrix.

When HNMA is excited with wavelengths longer than 365 nm, only the anthracene moiety in HNMA is excited. Since naphthalene does not absorb significantly in the spectral region of anthracene emission, there is no transfer of electronic excitation energy from anthracene to naphthalene chromophores. As a consequence, the polarization of the excited singlet state of anthracene will be localized during its excited lifetime. It is therefore expected that the intramolecular heterophotodimerization of HNMA, incorporated in glassy polymers, can be induced

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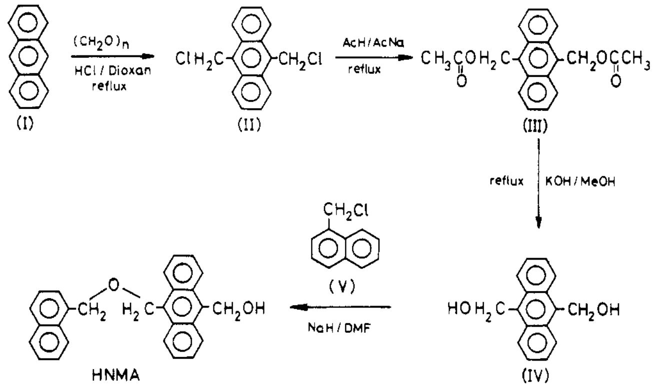
Scheme II
Procedure for the Synthesis of HNMA



selectively by the excitation of anthracene moieties in HNMA with linearly polarized light.

This paper reports the effects of linearly polarized light on the intramolecular heterophotodimerization of HNMA. The influence of local relaxation processes of polymer matrices on the orientational distribution of HNMA molecules that have been excited by using linearly polarized light is also examined. The extent to which the intramolecular heterophotodimerization of HNMA, incorporated into a glassy PMMA matrix, is induced was measured over the temperature range 20–100 °C by monitoring the temporal behavior of dichroic absorbances of anthracene moieties after various irradiation times. The temperature dependence of the induction efficiency of this reaction due to linearly polarized light is discussed in terms of the local relaxation processes of the polymer matrix.

II. Experimental Section

(A) Materials. Poly(methyl methacrylate) (PMMA) (Wako Pure Chemicals Industries, Japan) was used as a polymer matrix. The molecular weight of this polymer obtained by intrinsic viscosity measurements was 1.33 × 10^6. PMMA was precipitated using tetrahydrofuran (THF)/methanol mixtures and dried under vacuum prior to the experiments. 9-(Hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA) was synthesized according to the similar procedure described previously.[23] The synthesis procedure is given in Scheme II.

Briefly, 9,10-bis(chloromethyl)anthracene (II) is obtained by refluxing a dioxane solution of anthracene (I) with paraformaldehyde and hydrochloric acid under a fine dispersion of HCl gas for 5 h. Reflux of II with sodium acetate in acetic acid gives 9,10-bis(methylacetyl)anthracene (III). Reflux of III in methanol with potassium hydroxide gives 9,10-bis(hydroxymethyl)anthracene (IV). Crude HNMA is obtained by coupling the compound IV with 1-(chloromethyl)naphthalene (V) (Aldrich, recrystallized in benzene) in DMF at room temperature. The crude product is purified by gel filtration using a Sephadex column and dimethylformamide (DMF) as an eluent. Finally, pure HNMA is obtained by recrystallizing the desired fraction in benzene. Since HNMA and anthracene derivatives are sensitive to light, the synthesis as well as the purification were carried out in the dark. ^{1}H NMR data taken by a Varian XL-200 NMR spectrometer with tetramethylsilane (TMS) as an internal standard are as follows (DMSO-d_6): δ 5.2 (s, 2 H), 5.3–5.4 (t, 1 H), 5.4–5.5 (d, 2 H), 5.6 (s, 2 H), 7.4–8.5 (m, 15 H).

(B) Film Preparation. After purification, HNMA was incorporated in a PMMA matrix at the concentration of ca. 10^{-3} mol/L by casting benzene solutions of HNMA and PMMA. The cast films were dried under vacuum at 170 °C in the dark for several days to remove solvent as well as air dissolved in these samples. The thickness of HNMA-doped PMMA films used in this experiment was about 0.3 mm determined by a spacer sandwiched between two glass plates. The samples were placed in a copper heating block linked to a temperature controller. The temperatures in this experiment were controlled with an accuracy of ±0.5 °C.

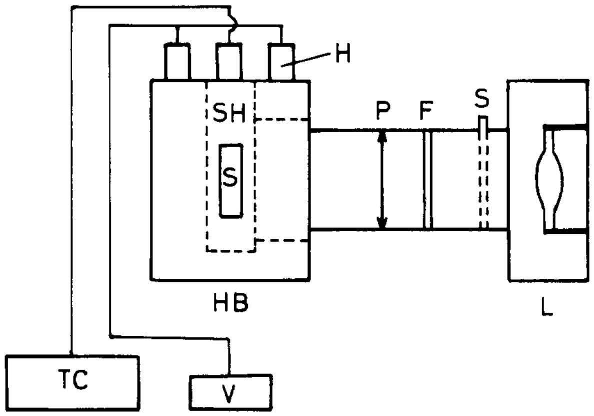


Figure 1. Block diagram of the apparatus for irradiation with linearly polarized light: L, Hg lamp; S, shutter; F, filter; P, polarizer; H, heater; SH, sample holder, S, sample; HB, heating block; TC, temperature controller; V, variac.

(C) Irradiation Procedure. HNMA incorporated in PMMA films was irradiated with UV light mainly at 365 nm by using an apparatus with the block diagram shown in Figure 1.

UV light from a high-pressure mercury lamp (250 W, Model USH-35, Ushio Co., Japan) was passed through a SC-052 Corning filter in order to obtain mainly the 365-nm component. Linearly polarized light was obtained by a UV polarizer (Polaroid, HNP'B) placed in front of a heating block containing films of PMMA doped with HNMA. The variation with time of the absorbance of HNMA after various irrradiation times was monitored by a UV–visible spectrophotometer (Shimadzu Model UV-160, Japan). The dichroic absorption at the first peak (393.5 nm) in the long-wavelength side of HNMA-doped PMMA films was measured using the same instrument equipped with a rotating polarizer placed between the light source and the sample. The dichroic absorption was measured parallel and perpendicular to the direction of the polarization of the exciting light.

(D) Data Analysis. The induction efficiency, η, of the intramolecular heterophotodimerization of HNMA upon excitation with linearly polarized light is defined by

$$\eta(t) = 100\{OD_{\perp}(t) - OD_{\parallel}(t)\}/OD_0 \qquad (1)$$

where $OD_{\perp}(t)$ and $OD_{\parallel}(t)$ are the absorbances of HNMA at 393.5 nm in the direction perpendicular and parallel to that of the polarization of the exciting light and OD_0 is the initial absorbance of the sample at the same wavelength.

The parameter η depends on the orientational distribution of anthracene rings in PMMA reacted upon irradiation with polarized light and is independent of HNMA concentrations. Note that since HNMA is randomly dispersed in PMMA, $\eta(t)$ is equal to zero before irradiation (t = 0) and for all values of t if the reaction is not inducible by polarized light. Furthermore, the time dependence of η depends on the orientational relaxation of reacted HNMA in the PMMA matrix. Its physical meaning will be discussed later in more detail.

III. Results and Discussion

The time dependence of the two dichroic absorbance components of HNMA incorporated in the PMMA matrix at 50 °C is shown in Figure 2. There is a distinct difference between these two components. The fact that the dichroic absorbance components measured in the direction perpendicular to the polarization of exciting light are larger than those obtained in the parallel direction indicates that the intramolecular photodimerization of HNMA is selectively induced by linearly polarized light. Also, as shown in the same figure, the induction efficiency, $\eta(t)$, of the reaction exhibits the particular dependence on irradiation time: η starts increasing from zero with increasing irradiation time and approaches a limit-

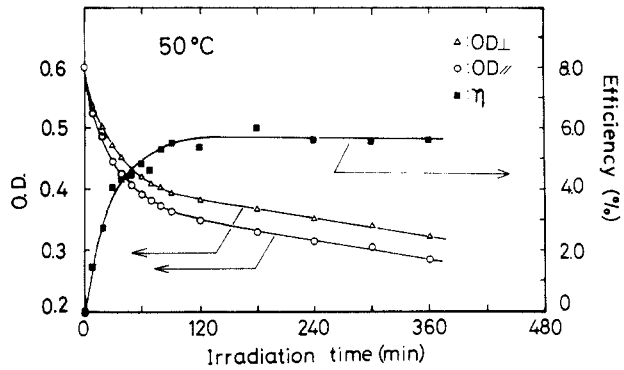


Figure 2. Time dependence of the two components of dichroic absorbance and the induction efficiency, η, of HNMA incorporated in PMMA irradiated by linearly polarized light at 50 °C.

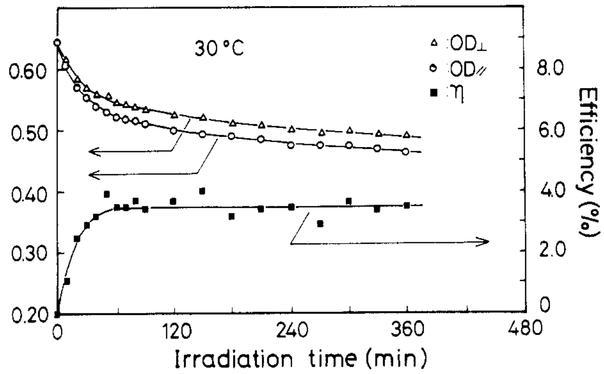


Figure 3. Time dependence of the two components of dichroic absorbance and the induction efficiency, η, of HNMA incorporated in PMMA irradiated by linearly polarized light at 30 °C.

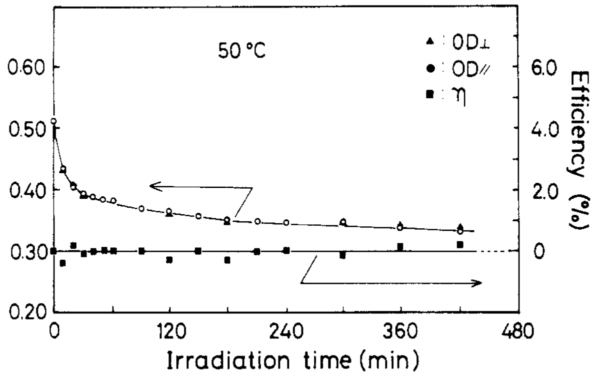


Figure 4. Time dependence of the two components of dichroic absorbance and the induction efficiency, η, of HNMA incorporated in PMMA irradiated by unpolarized light at 50 °C.

ing value η_{max} after a finite irradiation time. It was found that the temporal behavior of $\eta(t)$ and the magnitude of η_{max} depend on the temperature. For comparison, the time dependence of the induction efficiency $\eta(t)$ obtained at 30 °C is shown in Figure 3.

The induction efficiency $\eta(t)$ at this temperature reaches a limiting value of ca. 3.5% which is much smaller than that obtained at 50 °C. To ensure that the induction of the intramolecular heterophotodimerization of HNMA originated from the irradiation with linearly polarized light, experiments were repeated at 50 °C using the same apparatus shown in Figure 1 without a polarizer. The result is shown in Figure 4. The fact that the difference between the two dichroic components disappears upon excitation with unpolarized light at 365 nm implies that the values of $\eta(t)$ observed in this study, though small at certain temperatures, originated from the induction by linearly polarized light. The temperature dependence of η_{max} of HNMA incorporated in a PMMA matrix is shown in Figure 5. Close to room temperature, η_{max} is extremely small. Above 20 °C, η_{max} starts increasing quickly with temperature and reaches a maximum value of 6% at ca. 40 °C. However, above 50 °C η_{max} starts decreasing and finally almost disappears at 100 °C. Note that the glass transition temperature of the PMMA matrix used in this experiment is 103 °C as measured by DSC with the heating rate of 10 °C/min.

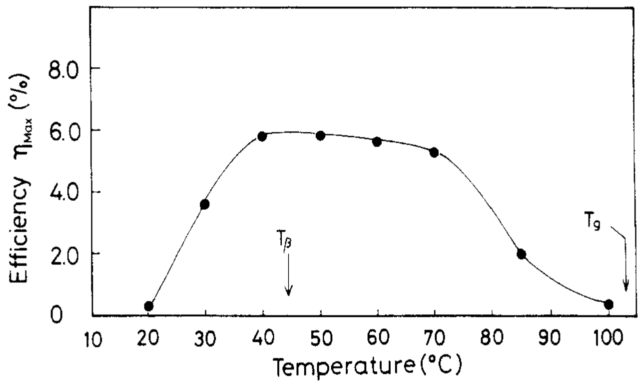


Figure 5. Temperature dependence of the induction efficiency, η_{max}, of HNMA incorporated in PMMA. The arrow indicates the temperature for the β-relaxation process of a PMMA matrix measured at 100 Hz.[24]

The experimental results described above indicate that the intramolecular heterophotodimerization of HNMA incorporated in a polymer matrix can be selectively induced by linearly polarized light. The magnitude of the induction is a function of both time and temperature. Upon irradiation with polarized light at a given temperature, the magnitude of η is limited by the orientational relaxation of excited HNMA in the polymer matrix. These relaxation processes are governed by local segmental motions of PMMA. On the other hand, the temperature for the β-relaxation of PMMA measured by the dielectric relaxation at 100 Hz is around 44 °C,[24] which is close to the temperature where η_{max} reaches a highest value of 6%. As reported previously,[20] for bis(9-anthrylmethyl) ether (BAME), a homologue of HNMA, incorporated in polystyrene, the abrupt increase in the yield of the intramolecular photodimerization was observed at a temperature close to the T_β of the polymer matrix measured at 100 Hz.[25] From these results, it seems that the kinetics of the intramolecular photodimerization, i.e. a diffusion-controlled reaction, of bichromophoric molecules linked by a three-atom chain reflect the onset of the β-relaxation processes of the polymer matrix below T_g.

In general, upon excitation with linearly polarized light, the rate of the intramolecular heterophotodimerization of HNMA is determined by the local relaxation processes of the matrix, which activate the conformational transitions of HNMA favoring the intramolecular reaction. At the temperature for the onset of the β-relaxation, the magnitudes of segmental motions become larger and therefore result in an abrupt change in the induction efficiency, η. On the other hand, the long-range relaxation due to the onset of the glass transition of the polymer matrix allows not only intramolecular conformational transitions of HNMA but also rotational relaxation of HNMA selectively excited by linearly polarized light. As the T_g of the matrix is approached, the orientation of the excited HNMA becomes random. Thus the rise of $\eta(t)$ with time is determined by the balance between the orientational relaxation process of excited HNMA and the intramolecular conformational transitions of

HNMA in the polymer matrix. Under the experimental conditions of this study, the induction efficiency, $\eta(t)$, starts leveling off and reaches the limiting value η_{max} within 6 h. Furthermore, a small decrement of the maximum induction efficiency, η_{max}, of an irradiated sample was found after several weeks at room temperature. This result implies that the thermal history of the sample could affect the value of the induction efficiency, η.

IV. Conclusion

It has been demonstrated in this work that by utilizing the selective excitation of anthracene moieties of HNMA by linearly polarized light, it is possible to induce an arbitrary spatial distribution of reacted photochromic molecules incorporated into a polymer matrix at temperatures below the glass transition temperature, T_g. The following results were obtained:

(1) Upon irradiation with linearly polarized light, the intramolecular heterophotodimerization of 9-hydroxy-10-[(naphthylmethoxy)methyl]anthracene (HNMA), incorporated in a PMMA matrix, can be induced selectively.

(2) The maximum induction efficiency, η_{max}, depends on temperature. At both room temperature and temperatures close to T_g, the induction efficiency is negligible. The highest value of η_{max} (ca. 6%) is obtained at ca. 40 °C, which corresponds to the temperature for the onset of the β-relaxation process of the PMMA matrix.

Since the maximum induction efficiency is fairly small under the experimental conditions used in this work, we could not observe any birefringence of the HNMA-doped PMMA films after irradiation by using a polarized light microscope. However, by increasing the light intensity and the concentration of HNMA dopant in the PMMA matrix and/or applying uniaxial elongation to the films containing HNMA-labeled PMMA chains, the birefringence induced by the irradiation with polarized light should be detectable. Such polymer films may then be potentially useful to the fabrication of optoelectronic materials (optical wave guide, light modulation, etc.) due to the light-induced spatial distribution of the refractive index. The time dependence of the induction efficiency, $\eta(t)$, of HNMA chemically attached to polymer chains may also provide useful information on the orientational relaxation of polymer segments in the glassy state. This information should complement the data obtained from depolarized Rayleigh light-scattering measurement.[26] These experiments are currently in progress and will be reported in the near future.

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