Polarization-Selective Photochromic Reaction in Uniaxially Oriented Polymer Matrix

Q. Tran-Cong,* N. Togoh, A. Miyake, and T. Soen

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received April 24, 1992; Revised Manuscript Received August 5, 1992

ABSTRACT: Selectivity of the intramolecular photodimerization of a bichromophoric molecule, 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA), in the glassy state of poly(methyl methacrylate) (PMMA) was examined upon irradiation with linearly polarized light. Effects of temperature, dopant (HNMA) concentration, and uniaxial elongation of polymer matrix on the induction efficiency η (*Macromolecules* 1990, *23*, 3002) of HNMA were investigated. It was found that upon increasing dopant concentration, the maximum induction efficiency shifts toward the lower temperature side. The same behavior was also observed as the elongational ratio of the PMMA matrix increases. Uniaxial elongation also results in an increase of η. On the other hand, the induction efficiency grows exponentially with irradiation time and is characterized by the growth rate K. The temperature dependence of K indicates that the polarization selectivity of HNMA in PMMA matrix is determined by both orientational relaxation and the conformational transitions of the molecule. Finally, the spatial distribution of reacted HNMA in PMMA induced by polarized light was found to be quite stable. In PMMA, η is reduced to half of its initial value after 10 months at room temperature.

I. Introduction

Polymer materials with controllable refractive index not only are important for optical recording materials[1] but also can provide useful polymer-based materials for optical communication.[2] For these purposes, photochromic molecules have been incorporated into polymer matrices and the reversible changes in the refractive index of the material have been extensively investigated upon irradiation with light of appropriate wavelengths. Due to the pronounced effects of local structures of polymers on the reaction kinetics, there have been a number of works devoted to the understanding of the local inhomogeneity of bulk polymer matrix, especially in the region below the glass transition temperature.[3] So far the change in refractive index of polymers doped with photochromic molecules resulting from irradiation with unpolarized light is an all-or-none transition phenomena. From the viewpoint of wave guiding at the microscopic level for purposes such as optical signal processing, materials with controllable refractive index distribution are expected. Therefore it is of great interest to design such polymers by taking advantage of the selection of photochromic reaction upon irradiation with polarized light.

In the previous work,[4] we found that the intramolecular photodimerization of 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA) in poly(methyl methacrylate) (PMMA) can be selectively induced by irradiation with linearly polarized light. However the maximum induction efficiency η_{max} which can be achieved under these experimental conditions is fairly small. The temperature where η reaches its maximum magnitude, η_{max}, is close to that for the onset of the β-relaxation process of the PMMA matrix. There are several reasons which are responsible for the low value of η. First of all, the fraction of HNMA which is selectively excited by linealry polarized light is small since HNMA is randomly dispersed in the matrix. Secondly, the dopant at high concentration might act as a plasticizer and accelerate the orientational relaxation of itself. As a consequence, the spatial distribution of the anthracene moieties which are selectively excited by linearly polarized light, might be wiped our during the excited lifetime of the molecule. In order to elucidate the induction mechanism as well as to improve the induction efficiency of the reaction, it is necessary to examine these effects more in detail.

In this work, the effects of dopant concentration on the induction efficiency of this photochromic reaction are examined at first. The experimental results observed under these conditions are compared to the local relaxation data obtained by mechanical measurements. Subsequently, the induction process of the reaction in uniaxially oriented matrix is described. The kinetics of the induction process is discussed on the basis of the analysis of the time evolution process of the induction efficiency. Finally, the stability of the spatial distribution of reacted HNMA molecules in polymer matrix is also examined and discussed with respect to the segmental orientational relaxation of polymer segments.

II. Experimental Section

1. **Samples.** The photochromic molecule 9-(hydroxymethyl)-10-[(naphthylmethoxy)methyl]anthracene (HNMA, Scheme I) was synthesized and purified according to the procedure described previously.[4] Poly(methyl methacrylate) (PMMA, $M_w = 1.4 \times 10^5$, $M_w/M_n = 2.1$) was purified by precipitation using tetrahydrofuran and methanol mixtures. Samples are obtained by casting PMMA benzene solutions containing HNMA at appropriate concentrations. PMMA films doped with HNMA are sandwiched between two glass plates with a spacer of 0.2-mm thickness. All samples are dried under vacuum in the dark at 150 °C over several nights prior to the experiment.

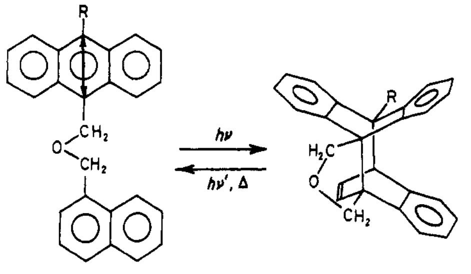
2. **Procedure of Uniaxial Elongation.** Samples are uniaxially elongated by the following procedure. At first, PMMA films doped with HNMA (3 cm × 1 cm side by side) are dipped into a silicon oil bath at 120 °C which is ca. 10 °C above the glass trnsition of the PMMA matrix. As the thermal equilibrium is achieved, the specimen was uniaxially elongated with a speed of 2 mm/s. After being drawn to the desired elongation ratio, the specimen is quenched to room temperature and its surfaces are wiped with n-hexane to remove a trace of silicon oil. Subsequently, the sample is mounted into a sample holder with both ends fixed by epoxy adhesives and is kept at room temperature over one night prior to the irradiation experiment. The elongation ratio α is defined as $\alpha = L/L_0$ where L_0 and L are the lengths of the specimen before and after elongation, respectively. Since

---

* To whom correspondence should be addressed.

0024-9297/92/2225-6568$03.00/0

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



the thickness of the sample is eventually changed after elongation and subsequently results in an alteration of the initial absorbance, samples with appropriate thickness are prepared so that after the elongation process, all the samples have the same thickness prior to irradiation experiments.

3. **Apparatus.** A Mercury lamp (250 W, Ushio Electric Co., Japan) was used as the light source for irradiation. Exciting light with the wavelength 365 nm is converted to linearly polarized light by using a setup described previously.[4] The irradiation time dependence of the absorbance at 393.5 nm of the anthracene moieties was followed by using a UV photometer (UV-160, Shimadzu, Japan). In order to elucidate the correlation between the reaction kinetics and the local relaxation process of polymer matrix, the mechanical relaxation of PMMA and PMMA doped with HNMA is measured in the frequency range 1–900 Hz from −50 to +110 °C by using a rheometer (Model UVH-4, Rheology Co., Japan). The temperature dependence of the frequency dispersion curve was obtained by a single temperature scan of 5 °C/min. On the other hand, the glass transition temperatures (T_g) of these samples are measured by using a differential scanning calorimetry (DSC, Max Science 3100) with a heating rate of 5 °C/min. T_g's are determined from the midpoint of the transition.

4. **Data Analysis.** Selectivity of the intramolecular photodimerization of HNMA upon irradiation with linearly polarized light is analyzed by using the induction efficiency η which is defined as follows:[4]

$$\eta(t) = \frac{OD_{\perp}(t) - OD_{\parallel}(t)}{OD_0} \tag{1}$$

where $OD_{\perp}(t)$ and $OD_{\parallel}(t)$ are the absorbance of HNMA at 393.5 nm in the direction perpendicular and parallel to that of the polarization of the exciting light. OD_0 is the initial absorbance of the sample at the same wavelength. For the samples with a low concentration of HNMA, the two dichroic absorbance components become fairly small as irradiation time increases. Therefore, the averages of the induction efficiency η obtained after repeating the experiments over two or three time were taken as data points. In this case, the maximum deviation of η is ca. ±10% and is indicated in the corresponding figures.

III. Results and Discussion

1. **Dopant Concentration.** The concentration of HNMA in PMMA is varied from 10^{-3} to 10^{-2} M. The typical time dependence of the two components of dichroic absorbance and the corresponding induction efficiency η calculated from eq 1 are shown in Figure 1. As irradiation time increases, the absorbance measured in the perpendicular direction is always larger than that observed in the direction parallel to the polarization of the exciting light. This fact indicates that HNMA selectively undergoes intramolecular photodimerization upon irradiation with linearly polarized light. On the other hand, the induction efficiency η exhibits a peculiar time dependence. At first, η increases with increasing irradiation time. As the irradiation time exceeds some critical value, η reaches an equilibrium value, η_{max}, and does not show any further changes with irradiation time within the experiment time scale. This critical irradiation time changes with temperature and concentration of HNMA. The temperature dependence of η_{max} for the two concentrations 1×10^{-3} and 1×10^{-2} M of HNMA is shown in Figure 2. At certain specific temperatures, the equilibrium value η_{max} exhibits a maximum. As reported previously,[4] this maximum is determined by the competition between the conformational transitions around the –C–O–C– linkage and the reorientational relaxation of anthracene moieties during excitation. As seen in Figure 2, upon increasing the dopant concentrations, the entire curve shifts toward the lower temperature side whereas its maximum magnitude is almost unchanged with the concentration of HNMA. In the previous study, it was found that for HNMA with the concentration 2×10^{-3} M, the maximum of η_{max} appears at the temperature which is close to that for the onset of the β-relaxation of PMMA. In order to examine more clearly the correlation between the local relaxation of polymer matrix and the selectivity of the reaction, we measure directly the glass transition temperatures (T_g) and the mechanical relaxation of PMMA doped with HNMA at several concentrations and compare these results with those obtained for pure PMMA. As shown in Figure 3, the glass transition temperature of pure PMMA is slightly higher than that of PMMA doped with HNMA at 1×10^{-2} M (equivalent to ca. 0.3 wt %) HNMA. The difference in T_g between these two samples indicates that HNMA in PMMA has acted as a plasticizer and modifies the glass transition temperature of the matrix. On the other hand, the temperature dependence of the mechanical tan δ's of PMMA doped with 1×10^{-3} and 1×10^{-2} M HNMA measured at 4 Hz is shown in Figure 4a,b. The broad peaks at temperatures below T_g which are assigned

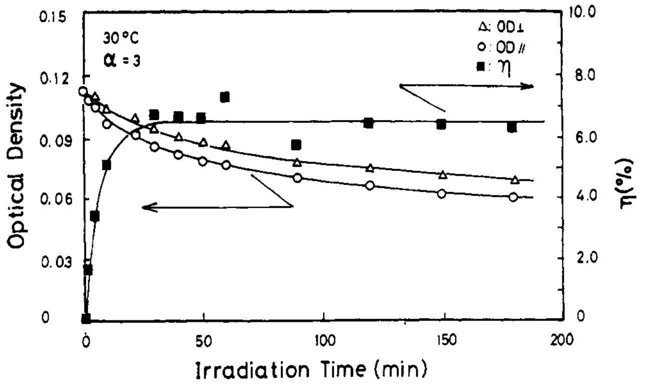


Figure 1. Time dependence of the two dichroic absorbance components and the induction efficiency η of HNMA in PMMA with $\alpha = 3$ at 30 °C for $C_{HNMA} = 1.0 \times 10^{-3}$ M.

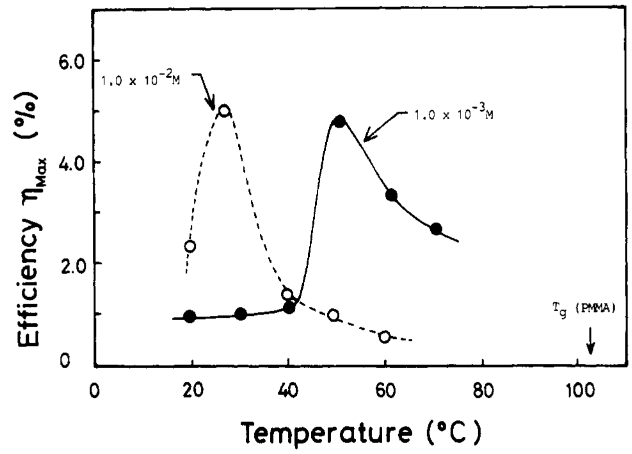


Figure 2. Effects of HNMA concentration on the temperature dependence of the equilibrium induction efficiency η_{max} for the case $\alpha = 1$.

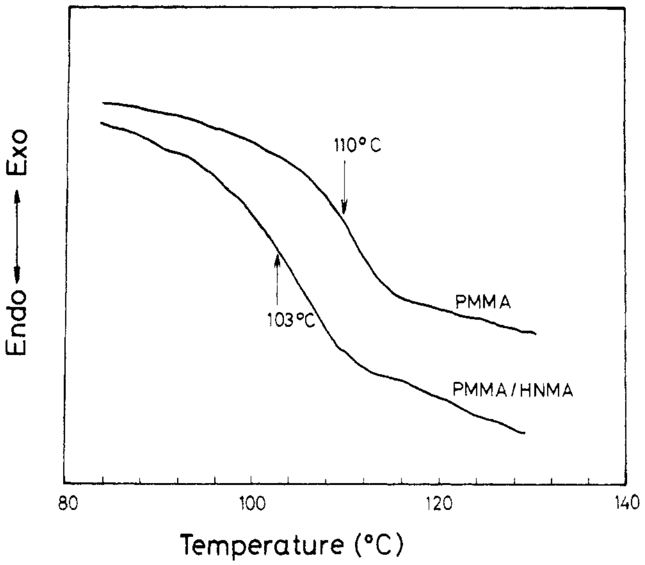


Figure 3. Effects of HNMA concentration on the glass transition temperature of the PMMA matrix: (upper part) pure PMMA; (lower part) with 0.3 wt % HNMA. The heating rate is 5 °C/min.

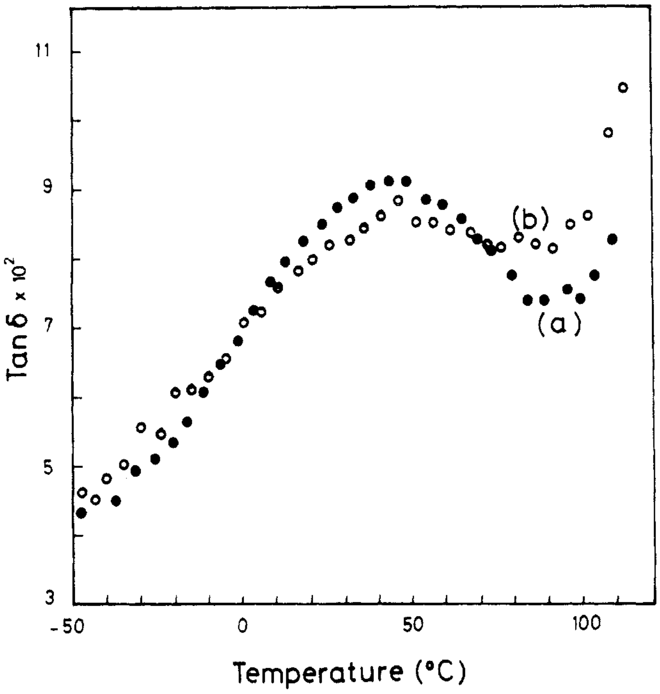


Figure 4. Mechanical tan δ of PMMA doped with HNMA at 4 Hz: $C_{\mathrm{HNMA}} = 1.0 \times 10^{-3}$ M (a, ●) and 1.0×10^{-2} M (b, ○).

to the secondary relaxation (β) process of these samples, are almost unchanged with the dopant concentrations. However the relaxation width increases with increasing HNMA concentration, implying that the relaxation time distribution becomes broadened upon increasing HNMA concentration. Note that, in the range of concentrations studied in this work, no evidence was found for the aggregation of HNMA as examined by differential scanning calorimetry as well as by optical microscopy. The experimental results shown in Figure 2 indicate that as the concentration of HNMA increases, the mobility of HNMA increases. This result is consistent with the effects of dopant concentration on the T_g of PMMA shown in Figure 3. On the other hand, the dipole–dipole interaction between excited anthracene moieties at this concentration can also result in a decrease of the induction efficiency η due to the broadening of the absorption transition dipole moment of anthracenes. The explanation for the decrease in the induction efficiency η_{max} based on the energy transfer of the Förster type[5] between anthracene moieties is also supported by the mean distance of ca. 50 Å between HNMA at the concentration 10^{-2} M. This distance was roughly estimated by assuming that HNMA is a sphere and homogeneously dispersed in the PMMA matrix. Note that the active sphere, i.e. the distance for excited energy transfer (R_0), of anthracene is ca. 25 Å[6] and is supposed to be larger than this value due to the additional diffusion in the matrix.

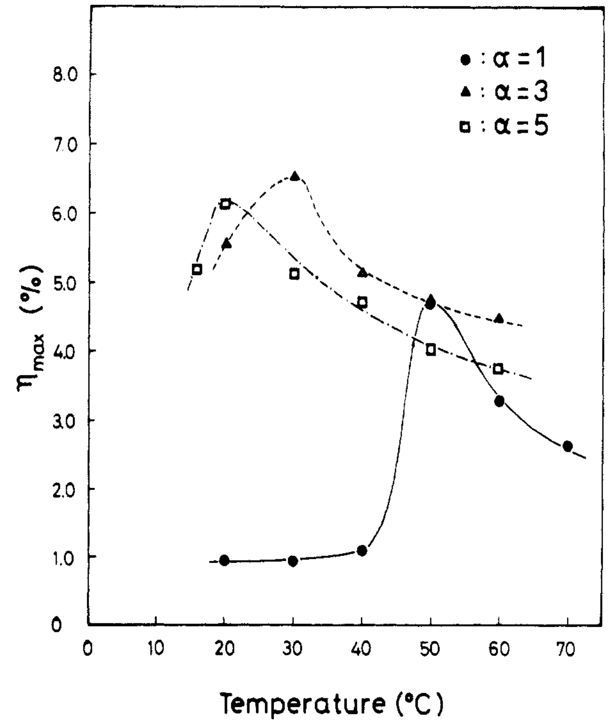


Figure 5. Temperature dependence of the equilibrium induction efficiency η_{max} of HNMA in uniaxially oriented PMMA matrix: (●) $\alpha = 1$; (▲) $\alpha = 3$; (□) $\alpha = 5$.

2. Effects of Elongation. In general, the magnitude of the induction efficiency η is determined by two competitive processes. One is the relative orientation between the absorption transition moment of anthracene and the direction of linearly polarized light. The other is the probability of the conformational transition around the ether linkage –C–O–C– between the anthracene and naphthalene moieties of HNMA. Experimentally varying either one of these two processes is expected to modify the induction efficiency. For this purpose, similar experiments were carried out with uniaxially elongated PMMA doped with HNMA. The temperature dependence of the equilibrium induction efficiency η_{max} for three samples with different elongation ratios α is shown in Figure 5. As α increases, the maximum of the equilibrium induction efficiency η_{max} shifts toward the lower temperature side and the magnitude also increases. This shift indicates that the induction efficiency η_{max} reflects the local relaxation mechanism of the uniaxially oriented polymer matrix. Namely, the more the polymer chains in the matrix are elongated, the more the orientational relaxation of polymer segments takes place at lower temperatures. The increment of η_{max} with increasing elongational ratio implies that the orientational process of PMMA segments has improved the selectivity of the reaction upon irradiation with linearly polarized light. However, the maximum magnitude of the equilibrium induction efficiency η_{max} for the case $\alpha = 5$ is somewhat smaller than that of $\alpha = 3$. This behavior is probably due to the orientational relaxation process of the PMMA matrix which takes place during the stretching process. Such relaxation processes have been observed by fluorescence depolarization experiments for polystyrene matrices.[7] Upon approaching the glass transition temperature of PMMA, η gradually decreases and tends to reach a negligibly small value as already seen in the case of samples without elongation. In a word, these experimental results show that the induction efficiency of the intramolecular photodimerization of HNMA can be improved by elongating the polymer matrix. However, since HNMA is dispersed in PMMA, the initial distribution of anthracene is not strongly affected by the elongation process. It is worth noting that the two components of dichroic absorbance of anthracene moieties measured at 393.5 nm remain almost unchanged with elongation ratio α before irradiation. These results suggest that the initial distribution of the anthracene moieties of HNMA is almost unaffected under the drawing conditions described in this work. One of the reasons responsible for this result is that the anthracene moieties of HNMA might undergo reorientational relaxation during the stretching process of the matrix. Such reorientation dynamics of small aromatic dopants in PMMA matrix has been observed recently under various aging conditions by measuring the second harmonic generation (SHG) signals from poled films.[8] According to these results, the local free volumes of larger sizes are created at high temperatures and allow the greater mobility of the dopant when the samples are aged at high temperatures. Therefore, selectivity of the intramolecular photodimerization of HNMA in uniaxially oriented PMMA may be much more improved by varying the experimental conditions such as temperature and drawing speed or by covalently attaching HNMA to a PMMA chain in order to decrease the mobility of the molecule.

3. Time Evolution Process of the Induction Efficiency. Since the growth with time of the induction efficiency $\eta(t)$ strongly depends on both temperature and elongation ratio, the time dependence process of $\eta(t)$ is analyzed in order to understand the growth kinetics of the optical anisotropy induced by polarized light. As shown in Figure 1, $\eta(t)$ increases with time in the early stage of irradiation and eventually approaches the equilibrium value as irradiation time reaches a certain critical value. The plot of $\ln\,[\eta_{max} - \eta(t)]$ versus irradiation time exhibits a linear relationship for uniaxially elongated samples as well as the sample without elongation. These results suggest the following kinetics:

$$[\eta_{max} - \eta(t)] = A\exp(-Kt) \tag{2}$$

where A is a prefactor equivalent to the equilibrium value which the induction efficiency can reach and K is a constant expressing the growth rate of the optical anisotropy generated in the sample by irradiation.

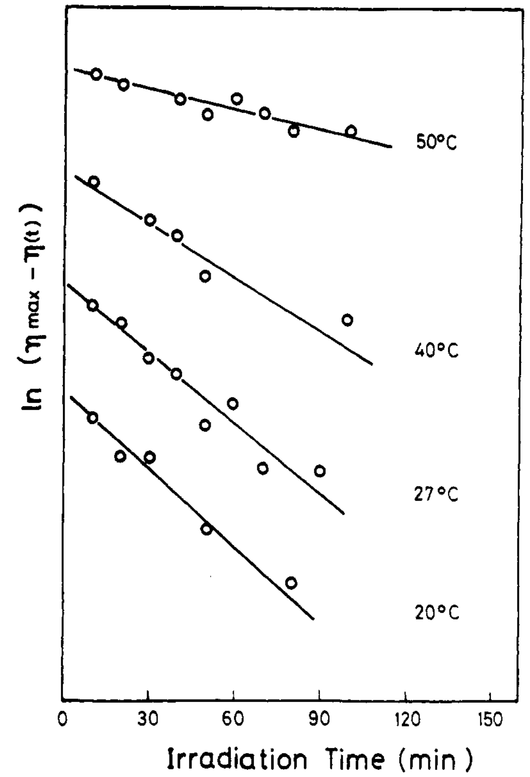


Figure 6. Kinetics of the growing process of the optical anisotropy in PMMA generated by irradiation with linearly polarized light for $C_{HNMA} = 1.0 \times 10^{-2}$ M in PMMA matrix with $\alpha = 1$.

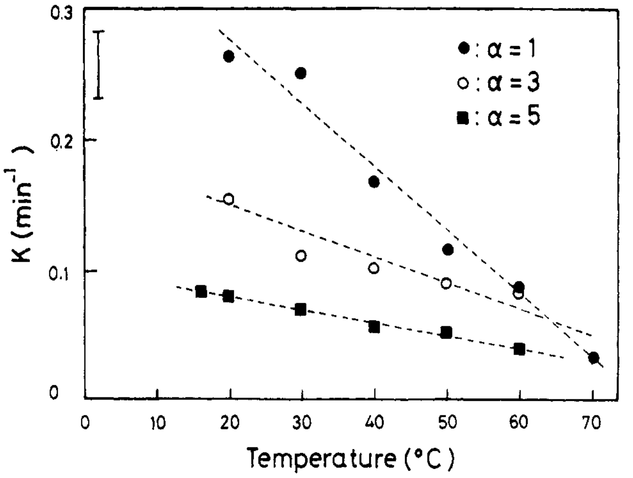


Figure 7. Temperature dependence of the growth rate K in uniaxially oriented PMMA: (●) $\alpha = 1$; (○) $\alpha = 3$; (■) $\alpha = 5$. $C_{HNMA} = 1.0 \times 10^{-3}$ M. The bar indicates the maximum deviation from the average value.

As an example, the temperature dependence of $\ln\,[\eta_{max} - \eta(t)]$ versus irradiation time for a PMMA sample with $\alpha = 1$ containing 10^{-2} M of HNMA is depicted in Figure 6. The growth rate K exhibits peculiar temperature dependence, as shown in Figure 7. K decreases with increasing temperature. Furthermore close to the T_g of the matrix, K tends to approach a negligibly small value. This specific feature is probably coming from the competition between the two processes: the increase in the probability of the conformational transitions around the -C-O-C ether linkage and the randomization of the absorption transition moment of anthracene moieties which are selectively excited along the direction of linearly polarized light. Namely, upon approaching the glass transition temperature T_g of the matrix, the probability for the rotation around the -C-O-C bond becomes higher and at the same time the reorientational process of excited anthracenes becomes faster. During the excited lifetime of anthracene, the former process tends to increase the selectivity of the reaction whereas the later tends to minimize this process. Since the reorientation relaxation of anthracene is much faster than the conformational transition process, the growth rate K becomes smaller as temperature increases. As mentioned above, since the initial orientational distribution of anthracenes is almost unaffected by the drawing process before irradiation, only the conformational transitions of HNMA which are driven by the orientational relaxation of PMMA segments, contribute to the dependence of K on temperature. The dependence of K upon the elongation ratio α obtained at different temperatures is shown in Figure 8. At constant

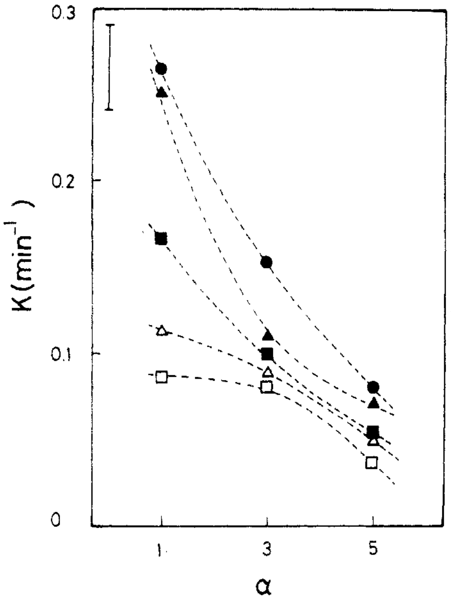


Figure 8. Dependence of the growth rate K on elongation ratio α: (●) 20 °C; (▲) 30 °C; (■) 40 °C; (△) 50 °C; (□) 60 °C. $C_{\mathrm{HNMA}} = 1.0 \times 10^{-3}$ M. The bar indicates the maximum deviation from the average value.

temperature, K decreases with increasing α. On the other hand, for a constant elongation ratio, the variation of K with temperature becomes smaller for samples with larger elongation ratio. These results suggest that the orientational relaxation of polymer segments probably takes place during the experiments, especially at temperatures close to the T_g of the matrix.

From these experimental results, the growth rate K obtained from the time-dependent induction efficiency η is probably the difference between two distinct rate constants K_c and K_r. Here K_c is the rate constant of the conformational transitions of HNMA and K_r is the rotational relaxation rate of excited anthracene moieties. However, a theoretical model including the reaction kinetics of HNMA as well as the reorientational relaxation of anthracene moieties is necessary to support these explanations. Experimentally, the rate constants K_c and K_r can be obtained by independent measurements. Monitoring the reaction kinetics of HNMA upon irradiation with unpolarized light[9] can provide information on the temperature dependence of K_c. On the other hand, the rotational relaxation rate K_r of the anthracene moieties can be independently measured, in principle, by phosphorescence depolarization,[10] time-resolved delay luminescence anisotropy[11] or by the time dependence of the second harmonic generation (SHG) signals which has been shown to be a useful technique for monitoring the orientation dynamics of dopants in polymer matrices.[8] From the viewpoint of photodimerization, an alternative approach from the experimental side is also possible. That is to carry out the experiments described in this work with some homolog of HNMA which is chemically designed such that the intramolecular conformational transitions via the ether linkage is forbidden. Therefore the rate constant K in this particular case reflects only the reorientational relaxation of the dopant. One of the suitable candidates for this purpose is the naphthalenoanthracene cyclophane derivative[12] where the anthracene and naphthalene moieties are initially linked together from both sides in the conformation parallel to each other. These experiments are currently under progress and will be reported later.

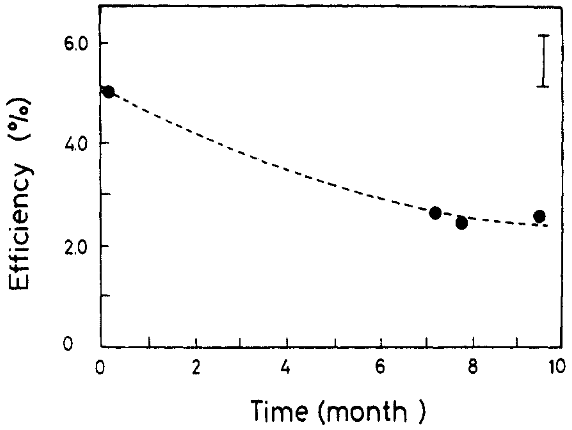


Figure 9. Stability of the induction efficiency $\eta_{\max}$ in PMMA with $\alpha = 1$ at room temperature. The bar indicates the maximum deviation from the average value.

4. Stability of the Distribution of Selectively Reacted HNMA Induced by Polarized Light in a PMMA Matrix. From the experimental results described above, it is obvious that the spatial distribution of photochromic reaction in bulk polymer matrix can be created and controlled by taking advantage of polarized light. Though the refractive index change accompanying irradiation by linearly polarized light under the conditions of this work is not measured yet, it is known that for bis(9-anthrylmethyl) ether (BAME), a homolog of HNMA, the change in refractive index accompanying its intramolecular photodimerization is quite large.[13] Therefore the refractive index distribution of amorphous polymers can be controlled by the method described in this work.

The temperature dependence of the equilibrium induction efficiency $\eta_{\max}$ depicted in Figure 2 as well as of the growth rate K (eq 2) shown in Figures 7 and 8 indicates that the achievable induction efficiency η depends strongly on the orientational relaxation of anthracene moieties. Since HNMA can undergo very slow reorientational relaxation in the glassy state of the PMMA matrix due to the physical aging process,[14] it is of great interest to examine the stability of $\eta_{\max}$ obtained after irradiation with polarized light. The time dependence of the equilibrium induction efficiency $\eta_{\max}$ of the as-cast PMMA film containing 1×10^{-2} M HNMA which was obtained after irradiation over 2 h with linearly polarized light at 27 °C and kept in the dark at room temperature, is illustrated in Figure 9. $\eta_{\max}$ decreases to half of its initial value over the period of 10 months in the dark. These results suggest that anthracene moieties can relax even in the glassy state of PMMA. However this process is extremely slow and, as a consequence, the refractive index distribution in PMMA by linearly polarized light is stable and can be maintained over a reasonably long period of time.

IV. Conclusion

The effects of dopant concentration as well as elongation on the induction efficiency of photochromic reaction in glassy polymer matrix were demonstrated upon irradiation with linearly polarized light. The following results were obtained.

(1) The induction efficiency can be improved by uniaxial elongation of polymer matrix. The shift of $\eta_{\max}$ toward the low-temperature side indicates that η indeed reflects the segmental relaxation of polymer segments.

(2) The growing process of the optical anisotropy generated in the sample varies exponentially with time. The growth rate was obtained and found to be strongly

affected by both reorientational relaxation of anthracene and the intramolecular conformational transition of the photochromic molecule.

(3) The optical anisotropy created by polarized light is quite stable and can be maintained over a reasonably long period of time at room temperature.

Since the selectivity of the intramolecular photodimerization of HNMA is sensitive to the local environments of polymer matrix, the induction efficiency as well as its time dependence can provide useful information on anisotropy of free volumes in an elongated polymer matrix.[15,16] These works are currently in progress to elucidate these possibilities.

Acknowledgment. The technical assistance of Y. Ishida in gel filtration is gratefully acknowledged.

References and Notes

(1) Tomlinson, W. J.; Chandross, E. A. In *Advances in Photochemistry*; Pitts, J. N., Jr., Hammond, G. S., Gollnick, K., Eds.; John-Wiley: New York, 1980; Vol. 12, p 201.

(2) Schriever, R.; Franke, H.; Festl, H. G.; Kratzig, E. *Polymer* **1985**, *26*, 1423.

(3) Horie, K.; Mita, I. *Adv. Polym. Sci.* **1989**, *88*, 77.

(4) Tran-Cong, Q.; Kumazawa, T.; Yano, O.; Soen, T. *Macromolecules* **1990**, *23*, 3002.

(5) Forster, T. *Ann. Phys.* (*Leipzig*) **1948**, *2*, 55.

(6) (a) Pesce, A. J.; Rosen, C.-G.; Pasby, T. L. *Fluorescence Spectroscopy*; Marcel Dekker: New York, 1971. (b) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973.

(7) Fajolle, R.; Tassin, J. F.; Sergo, P.; Pambrun, C.; Monnerie, L. *Polymer* **1983**, *24*, 379.

(8) (a) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3640. (b) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3648.

(9) Tran-Cong, Q.; Meisyo, K.; Ishida, Y.; Yano, O.; Soen, T.; Shibayama, M. *Macromolecules* **1992**, *25*, 3305.

(10) For example, see: Miller, L. J.; North, A. M. *J. Chem. Soc., Faraday Trans. 2* **1976**, *71*, 1233.

(11) Jovin, T. M.; Bartholdi, M.; Vaz, W. L. C.; Austin, R. H. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 176.

(12) Kim, H.; Waldow, D. A.; Han, C. C.; Tran-Cong, Q.; Yamamoto, M.; *Polym. Commun.* **1991**, *32*, 108.

(13) Yoshizawa, H.; Ashikaga, K.; Yamamoto, M.; Tran-Cong, Q. *Polymer* **1989**, *30*, 534.

(14) (a) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241. (b) Yu, W.-C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355. (c) Meyer, E. F.; Jamieson, A. M.; Simha, R.; Palmen, J. H. M.; Booji, H. C.; Maurer, F. H. *Polymer* **1990**, *31*, 243.

(15) Jean, Y. C.; Nakanishi, H.; Hao, L. Y.; Sandreczki, T. C. *Phys. Rev. B* **1990**, *42*, 9705.

(16) Tran-Cong, Q.; Tanaka, H. To be submitted for publication.