Macromolecules **2005,** *38,* 7207−7208

A Photoinduced Refractive Index Increase in Poly(methyl methacrylate) Film Doped with *N*-Acetyl-α-dehydroarylalanine Naphthyl Esters

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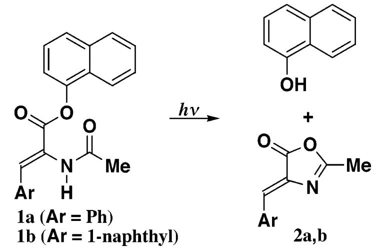
Received May 31, 2005
Revised Manuscript Received July 14, 2005

As a result of great demand for advanced optical materials such as plastic optical fiber,[1] the photochemical decrease in refractive index for polymer films has attracted considerable attention for the past decade.[2−4] We succeeded in lowering the refractive index of poly(methyl methacrylate) (PMMA) film (doped with hydroxy-substituted diarylnitrones) by as much as 0.014 ($-\Delta n$) by their quantitative photochemical conversions into diarylformamides showing a much weaker π-conjugation.[3] On the other hand, there are only a few studies directed toward the photochemical increase in refractive index for a given polymer film.[6−10] Langer et al.[6] reported that the photoirradiation of polymers bearing thiocyanate pendants enhances the polymer refractive index by 0.031; an additional increase in refractive index is observed upon treating the polymer with hydrazine ($\Delta n = +0.035$). Murase et al.[7] also showed that the 3 h photochemical and 3 h thermal treatments of PMMA film doped with 30 wt % of phenyl azide raise the index of this film by 0.0161. While the refractive index changes described above seem to be sufficient magnitude for utilizing these polymers as optical materials, it is necessary to increase the stability of polymer refractive index and also to speed up the photochemical transformation being responsible for the refractive index change of a given polymer film.

In the course of our systematic study regarding the excited-state reactivities of *N*-acyl-α-dehydroarylalanines, it was found that (*Z*)-*N*-acetyl-α-dehydrophenylalanine aryl ester derivatives in the singlet excited state undergo the heterolytic cleavage of the ester C(=O)−O bond to eventually form the corresponding oxazolones and aryl alcohols by way of the cyclization of acylinium intermediates (Scheme 1).[11] In contrast to the photoisomerization of diarylnitrone derivatives, the photoheterolysis of dehydrophenylalanine aryl esters gave oxazolones as one of the major products, the absorption of which appeared on the much longer wavelength side than that of the aryl esters. Thus, the novel photochemical transformation of these esters into oxazolones results in an enhancement in the π-conjugation, namely, the linear polarizability of given molecules, which allows us to propose that this photoreaction is accompanied by an increase in refractive index. In this Communication we present the results which demonstrate that the short period of time irradiation of PMMA film doped with *N*-acetyl-α-dehydrophenylalanine 1-naphthyl ester (**1a**) or *N*-acetyl-α-dehydro(1-naphthyl)alanine 1-naphthyl ester (**1b**) increases the refractive index of this polymer film greatly, and then our refractive index photocontrol system enables application to new optical materials.

Scheme 1



1a (**Ar = Ph**)
1b (**Ar = 1-naphthyl**)
2a,b

The starting (*Z*)-isomers of **1a** and **1b** were prepared by the ring-opening reactions of (*Z*)-2-methyl-4-(benzylidene)-5(4*H*)-oxazolone (**2a**) and (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (**2b**) with 1-naphthol in dry chloroform containing triethylamine, respectively.[12,13] In Figure 1 are typically shown UV absorption spectral changes caused by the irradiation ($\lambda > 280$ nm, 450 W high-pressure Hg lamp) of a nitrogen-saturated acetonitrile solution of **1a** at room temperature. In both cases when the photoreaction proceeds to a certain extent, the strong UV absorptions of the starting **1a** (290 nm) and **1b** (314 nm) were decreased with appearance of the 328 nm (**1a**) and 367 nm (**1b**) absorptions, while there were isosbestic points at 300 nm (**1a**) and 280 and 325 nm (**1b**). Because the absorption band appeared on the long wavelength side is very similar to that of the oxazolone derivative **2**, we were led to conclude that **1a** and **1b** undergo the almost exclusive heterolysis of the ester C(=O)−O bond to afford **2a** and **2b**, respectively, as already demonstrated in the previous study.[11] If we consider the irradiation time at which the UV absorption spectrum of **1** stops to change, the photoheterolysis of (*Z*)-**1b** in solution turns out to be apparently slower than that of (*Z*)-**1a** by about 1 order of magnitude. This may be due to either a decrease in rate for the heterolytic cleavage of the ester bond in the singlet excited-state **1b** or an increase in rate for the recombination of a **1b**-derived ion pair intermediate.

Our attention is now directed to the UV absorption spectral and refractive index changes of the PMMA film containing the arylalanine naphthyl ester **1**, caused by irradiation. PMMA films doped with **1a** and **1b** were made on silica glasses (for UV spectral measurements) and on silicon wafers (for refractive index measurements) by spin-coating of 2-methoxyethyl acetate solutions followed by vacuum-drying at 40 °C. A comparison of UV absorption spectral changes in solution (Figure 1) and in polymer film (Figure 2) revealed that the photoheterolysis of (*Z*)-**1** in the latter state proceeds more rapidly as compared to that in the former state to give **2**, possibly, along with 1-naphthol (irradiation conditions: $\lambda > 280$ nm, 450 W high-pressure Hg lamp). It is very likely that the heterolytic ester bond cleavage is a unimolecular process, and hence, its rate in solution and film states is not much different from each other. Thus, we were led to propose that the PMMA polymer medium greatly suppresses the recombination of an

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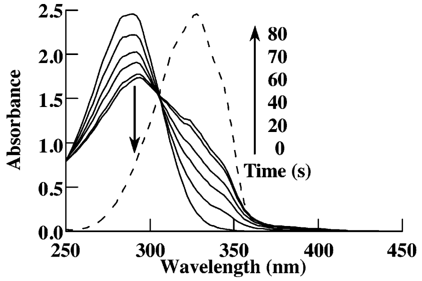

Figure 1. UV absorption spectral changes (solid lines) observed during the irradiation of **1a** (1.0×10^{-4} mol dm^{-3}) in nitrogen-saturated acetonitrile and UV absorption spectrum of the oxazolone **2a** (dashed line, 1.0×10^{-4} mol dm^{-3}) in acetonitrile. These spectra were recorded on a Shimadzu UV-3150 spectrophotometer.

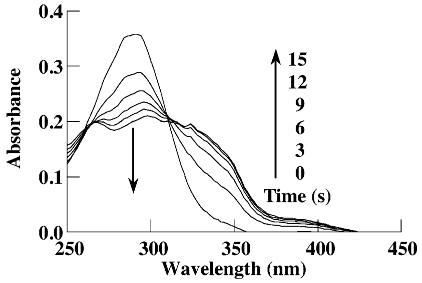

Figure 2. UV absorption spectral change observed during the irradiation of poly(methyl methacrylate) film doped with 6.7 wt % of **1a**. These spectra were recorded on a Shimadzu UV-3150 spectrophotometer.

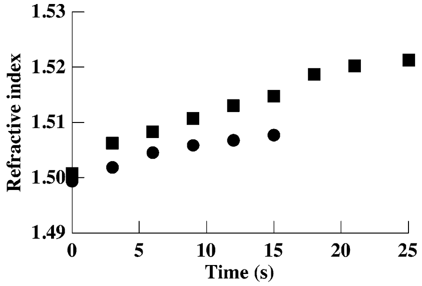

Figure 3. Refractive index of poly(methyl methacrylate) film doped with 6.7 wt % of **1a** (●) or **1b** (■) as a function of irradiation time.

initially formed ion pair intermediate to result in an increase in the total reaction rate. As we expected, the refractive index change of PMMA film containing **1** was observed at 632.8 nm (He−Ne laser) when its index was measured with a Gaertner L115B ellipsometer before and after the irradiation. The plots of refractive index vs irradiation time depicted in Figure 3 confirmed that the refractive index is increased with irradiation time, and then the large refractive index change of $\Delta n = +0.020$ is achieved by only the 25 s irradiation of PMMA film doped with 6.7 wt % of **1b**. The increased concentration of (Z)-**1** in PMMA film is predicted to give higher Δn value, but the relatively low solubility of this type of the arylalanine derivative in PMMA made it very difficult to increase its concentration up to, say, 20 wt %. From an analysis of molecular size effects of diarylnitrone additive on the refractive index change in PMMA film, it was found that the magnitude of Δn has a tendency to increase as the maximum wavelength of the first absorption band in a given additive is shifted to longer wavelengths.[14] It is anticipated on the basis of this finding that the oxazolone **2b** exhibits its absorption at longer wavelengths than does **2a**, and hence, the photochemical transformation of (Z)-**1b** gives the larger Δn value. The results obtained are compatible with this anticipation and may shed much light on application to new optical materials.

Acknowledgment. This research was partially supported by a “High-Tech Research Project” from the Ministry of Education, Sports, Culture, Science and Technology, Japan.

Supporting Information Available: Selected data for **1a** and **1b** as well as figures showing UV absorption spectral change observed during the irradiation of **1b** in acetonitrile and that in poly(methyl methacrylate) film. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Daum, W.; Krauser, J.; Zamzow, P. E.; Ziemann, O. *POF—Polymer Optical Fibers for Data Communication*; Springer-Verlag: Berlin, 2002.
(2) Murase, S.; Kinoshita, K.; Horie, K.; Morino, S. *Macromolecules* **1997**, *30*, 8088−8090.
(3) Tanaka, K.; Shima, K.; Kondoh, H.; Igarashi, T.; Sakurai, T. *J. Appl. Polym. Sci.* **2004**, *93*, 2517−2520.
(4) Kudo, H.; Ueda, W.; Sejimo, K.; Mitani, K.; Nishikubo, T.; Anada, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1415−1422.
(5) Meeten, G. H. *Optical Properties of Polymers*; Elsevier Applied Science: London, 1989.
(6) Langer, G.; Kavc, T.; Kern, W.; Kranzelbinder, G.; Toussaere, E. *Macromol. Chem. Phys.* **2001**, *202*, 3459−3467.
(7) Murase, S.; Shibata, K.; Furukawa, H.; Miyashita, Y.; Horie, K. *Polym. J.* **2003**, *35*, 203−207.
(8) Kim, E.; Choi, Y.-K.; Lee, M.-H. *Macromolecules* **1999**, *32*, 4855−4860.
(9) Schofberger, W.; Zaami, N.; Mahler, K. A.; Langer, G.; Jakopic, G.; Pogantsch, A.; Kern, W.; Stelzer, F. *Macromol. Chem. Phys.* **2003**, *204*, 779−786.
(10) Kashiyama, Y.; He, J.; Machida, S.; Horie, K. *Macromol. Rapid Commun.* **2001**, *22*, 185−188.
(11) Hoshina, H.; Nakayama, K.; Igarashi, T.; Sakurai, T. *Heterocycles* **2002**, *57*, 1239−1245.
(12) Rao, Y. S.; Filler, R. *Synthesis* **1975**, 749−764.
(13) Rzeszotarska, B.; Karolak-Wojciechowska, J.; Broda, M. A.; Galdecki, Z.; Trzezwinska, B.; Koziol, A. E. *Int. J. Peptide Protein Res.* **1994**, *44*, 313−319.
(14) Tanaka, K.; Fukuda, M.; Igarashi, T.; Sakurai, T. *Polymer*, in press.

MA051116O