Photocontrol of the Refractive Index of Poly(methyl methacrylate) with a Nitrone Additive

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ABSTRACT: Hydroxy-substituted aromatic nitrone derivatives were used for the photochemical control of the refractive index of poly(methyl methacrylate) (PMMA) films. Upon irradiation with 366-nm light in solution, these derivatives underwent rearrangement reactions, which eventually produced *N,N*-diarylformamide derivatives in quantitative yields. Similar photoreactions of the aromatic nitrones in the PMMA films lowered the refractive index of the films by as much as 0.014. The magnitude of the observed refractive-index change was enough for hydroxy-substituted nitrones to be used as additives for the fabrication of graded-index-type polymer optical fibers. In addition, the refractive index of the PMMA films remained almost constant at any conversion of the starting nitrone derivatives for at least 70 days at room temperature. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2517–2520, 2004

Key words: additives; isomer/isomerization; photochemistry; refractive index; thin films

INTRODUCTION

Polymer optical devices have frequently been used instead of SiO_2 glass devices because the former materials have the advantages of easy casting, shock resistance, and low specific gravity. Polymer optical fibers (POFs) are among the most important devices for optical communications.[1,2] Although organic polymer materials with lower transparency than that of SiO_2 optical fibers are not suitable for long-range optical communications, the aforementioned advantages and fast transmission abilities of POFs make possible their use for short-range communications.

Recently, much attention has been paid to graded-index (GI) POFs, which allow us to expect high-speed optical communications. The refractive-index-profile characteristics of this POF material are mostly produced through the interfacial polymerization of methyl methacrylate (MMA) in the presence of an additive possessing a higher refractive index than that of MMA.[3] However, GI-type POFs are much more expensive than electrical wire. Therefore, establishing an economical and simple method of preparing this type of POF material would be significant.

The photochemical control of the polymer refractive index has been the subject of extensive research because of its potential application to the development of GI-type POF materials.[4–6] Horie and coworkers showed that photochemical transformations of norbornadienyl[4] and cinnamoyl[5] chromophores incorporated into transparent polymers were effective for changing polymer refractive indices. In their studies, the refractive index was reduced because of π conjugation greatly weakened by photoisomerization. The modulation of the polymer refractive index was also achieved through the photoisomerization of α-(4-*N,N*-dimethylaminophenyl)-*N'*-phenylnitrone as an additive to the corresponding oxaziridine derivative.[6] Kada et al.[6] concluded that a refractive-index profile could be generated for GI-type POF materials through the control of the irradiation intensity and time.

The high stability of the GI profile and the facile fabrication of GI POFs are required from a practical point of view. Extremely high photoreactivities of additives may destroy the GI profile during storage. Very recently, Ritter et al.[7] reported that the introduction of a hydroxy group at the *ortho*-position of the benzene ring in α-phenyl-*N*-isopropylnitrone lowered the excited-state reactivity of this nitrone derivative through intramolecular hydrogen bonding. Considering this finding as well as the stability of the GI profile, we designed *ortho*-hydroxy-substituted α-aryl-*N*-phenylnitrone derivatives (**1a–1d**) as additives and inves-
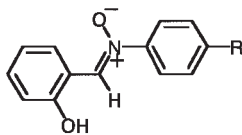
tigated the substituent effects on the photoreactivity of **1a–1d** and the extent of the refractive-index change in poly(methyl methacrylate) (PMMA) films containing **1a–1d**:
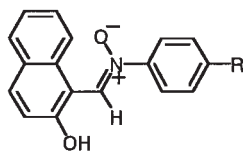
1a (R= H); **1b** (R= Me)   **1c** (R= H); **1d** (R= Me)

EXPERIMENTAL

Materials and solvents

N-Arylhydroxylamines were prepared through the treatment of nitrobenzene or 4-nitrotoluene with NaBH$_4$ in the presence of catalytic amounts of Te in methanol. *N*-Arylhydroxylamine (48 mmol) and 2-hydroxy-1-naphthaldehyde or 2-hydroxybenzaldehyde (48 mmol) were dissolved in ethanol (40 mL) and stirred for 3 h at room temperature. Pale-yellow crystals separated out and were collected and recrystallized from ethanol. The physical and spectroscopic properties of **1a–1d** were as follows:

1a. mp: 147.0–148.0°C. ν (KBr, cm^{-1}): 3450 (O—H), 3056 (C—H), 1620 (C=N), 1564 (C=C). δ_H [500 MHz, CDCl$_3$, tetramethylsilane (TMS) as an internal standard, ppm]: 12.52 (1H, s, OH), 8.88 (1H, s, CH=N), 7.93 (1H, d, J = 8.8 Hz), 7.87 (2H, d, J = 8.3 Hz), 7.81 (1H, d, J = 8.5 Hz), 7.76 (1H, d, J = 8.3 Hz), 7.56–7.54 (3H, m), 7.53 (1H, dd, J = 7.5, 8.8 Hz), 7.40 (1H, dd, J = 7.5, 8.3 Hz), 7.21 (1H, d, J = 8.5 Hz). δ_C (125 MHz, CDCl$_3$, ppm): 162.3, 146.2, 139.1, 135.7, 133.0, 130.4, 129.4 (2C), 129.2, 128.2, 128.0, 124.0, 122.5, 121.9 (2C), 121.0, 108.9. ANAL Calcd for C$_{17}$H$_{13}$NO$_2$: C, 77.25%; H, 5.34%; N, 5.30%. Found: C, 77.24%; H, 5.53%; N, 5.09%.

1b. mp: 149.0–149.5°C. ν (KBr, cm^{-1}): 3420 (O—H), 3064 (C—H), 1623 (C=N), 1572 (C=C). δ_H (500 MHz, CDCl$_3$, TMS as an internal standard, ppm): 12.54 (1H, s, OH), 8.85 (1H, s, CH=N), 7.92 (1H, d, J = 8.5 Hz), 7.81 (1H, d, J = 7.3 Hz), 7.76 (1H, d, J = 8.6 Hz), 7.75 (2H, d, J = 6.8 Hz), 7.54 (1H, dd, J = 7.0, 8.5 Hz), 7.40 (1H, dd, J = 7.0, 7.3 Hz), 7.33 (2H, d, J = 6.8 Hz), 7.21 (1H, d, J = 8.6 Hz), 2.45 (3H, s, CH$_3$). δ_C (125 MHz, CDCl$_3$, ppm): 162.1, 143.9, 140.8, 138.5, 135.5, 133.0, 129.9 (2C), 129.1, 128.2, 127.9, 123.9, 122.4, 121.7 (2C), 121.0, 108.9, 21.2. ANAL. Calcd for C$_{18}$H$_{15}$NO$_2$: C, 77.96%; H, 5.45%; N, 5.05%. Found: C, 77.95%; H, 5.45%; N, 5.05%.

1c. mp: 116.5–117.0°C. ν (KBr, cm^{-1}): 3250 (OH), 2956 (CH), 1657 (C=N). δ_H (500 MHz, CDCl$_3$,

TMS as an internal standard, ppm): 12.51 (1H, s, OH), 8.06 (1H, s, CH=N), 7.81 (2H, d, J = 6.3 Hz), 7.51–7.50 (3H, m), 7.45 (1H, dd, J = 7.6, 8.4 Hz), 7.19 (1H, d, J = 8.4 Hz), 7.03 (1H, d, J = 8.4 Hz), 6.90 (1H, dd, J = 7.6, 8.4 Hz). δ_C (125 MHz, CDCl$_3$, ppm): 159.9, 146.0, 141.0, 134.6, 132.8, 130.4, 129.3 (2C), 121.8, 120.3 (2C), 119.2, 116.8. ANAL. Calcd for C$_{13}$H$_{11}$NO$_2$: C, 72.45%; H, 5.26%; N, 6.55%. Found: C, 72.47%; H, 5.13%; N, 6.55%.

1d. mp: 116.0–117.0°C. ν (KBr, cm^{-1}): 3358 (OH), 3012 (CH), 2920 (CH), 1608 (C=N). δ_H (500 MHz, CDCl$_3$, TMS as an internal standard, ppm): 12.53 (1H, s, OH), 8.03 (1H, s, CH=N), 7.66 (2H, d, J = 8.5 Hz), 7.44 (1H, dd, J = 7.4, 8.0 Hz), 7.28 (2H, d, J = 8.5 Hz), 7.17 (1H, d, J = 7.4 Hz), 7.02 (1H, d, J = 7.4 Hz), 6.88 (1H, dd, J = 7.4, 8.0 Hz), 2.43 (3H, s, CH$_3$). δ_C (125 MHz, CDCl$_3$, ppm): 159.8, 143.8, 140.8, 140.5, 134.4, 132.7, 129.8 (2C), 121.5 (2C), 120.3, 119.1, 116.9, 21.1. ANAL. Calcd for C$_{14}$H$_{13}$NO$_2$: C, 73.99%; H, 5.77%; N, 6.16%. Found: C, 73.75%; H, 5.74%; N, 6.30%.

PMMA (Wako; polymerization degree = 1000–1500) was used as a host polymer without further purification. Acetonitrile as a solvent was purified according to the standard method. All the other chemicals were obtained from commercial sources and were of the highest grade. PMMA films containing 20 wt % **1a–1d** were prepared through the spin coating of a 2-methoxyethyl acetate solution onto silica glass (for UV spectral measurements) and onto silicon wafers (for refractive-index measurements), followed by vacuum drying at 40°C.

Measurements

UV absorption spectra were recorded on a Shimadzu UV-2200 spectrophotometer (Kyoto, Japan) and a Hitachi UV-3300 spectrophotometer (Tokyo, Japan). ^{1}H- and ^{13}C-NMR spectra were taken with a JEOL JNM-A500 spectrometer (Tokyo, Japan) with TMS as an internal standard. Infrared spectra were taken with a Shimadzu Prestige-21 infrared spectrometer.

Solutions or films containing **1a–1d** were irradiated with 366-nm light from a 450-W high-pressure mercury lamp. This monochromatic light was selected with Corning 0-52 (Corning, NY), Corning 7-60, and Toshiba IRA-25S glass filters (Tokyo, Japan).

The refractive indices of the films were measured before and after irradiation with a Gaertner L115B ellipsometer (Stamford, CT). The light source for the index measurements was a 632.8-nm He–Ne laser.

The quantum yields were determined at low conversions (10–15%) of the starting nitrone derivatives according to the method of Hatchard and Parker,[8] which uses a potassium trioxalatoferrate(III) actinom-
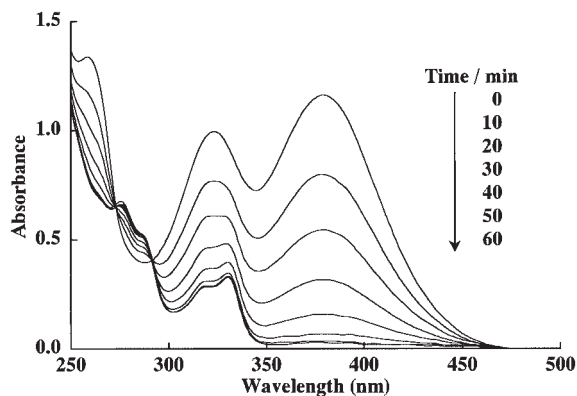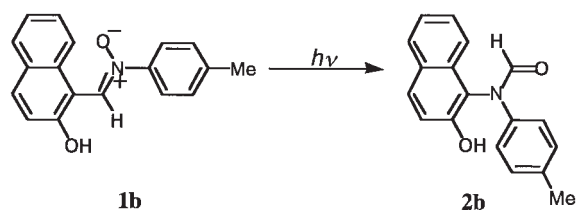
Figure 1 UV absorption spectral changes caused by the 366-nm irradiation of a nitrogen-purged acetonitrile solution of **1a** (1.0×10^{-4} mol dm^{-3}) at room temperature.
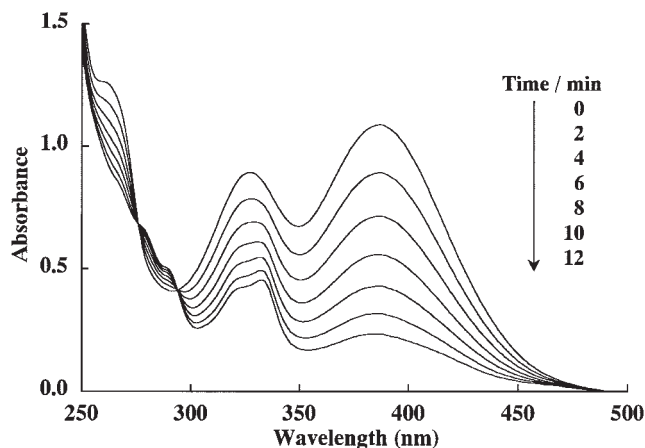

Figure 2 UV absorption spectral changes caused by the 366-nm irradiation of a PMMA film containing **1a** (20 wt %) and prepared on silica glass at room temperature.

eter. All the quantum yields were averages of more than five determinations. To quantify the disappearance of **1a–1d** spectrophotometrically, we used their molar absorption coefficients at given wavelengths.

RESULTS AND DISCUSSIONS

Photoreactivity in solution

Figure 1 presents the typical absorption spectral changes caused by the irradiation of a nitrogen-purged acetonitrile solution of **1a** with 366-nm light. The absorption detected around 320 and 380 nm decreased with irradiation, whereas isosbestic points were observed at 270 and 290 nm. Similar absorption spectral changes were observed for the other nitrone derivatives (**1b–1d**), demonstrating that the observed photochemical reaction greatly weakens π conjugation in a given molecule. On the basis of the spectroscopic and physical data of the **1b**-derived product isolated in a quantitative yield, we could determine this structure to be N,N-diarylformamide derivative **2b** (Scheme 1).[9] Because the irradiation of an acetonitrile solution of α-(1-naphthyl)-N-(1-naphthylmethyl)nitrone quantitatively affords the corresponding oxaziridine derivative,[10] this finding strongly suggests that the observed photorearrangement proceeds via an oxaziridine intermediate. Clearly, π conjugation in **1** is substantially weakened upon the formation of **2**, and this leads us to predict that photoisomerization

and subsequent photorearrangement are accompanied by a decrease in linear polarizability (α).

To compare the photoreactivity of **1a–1d**, we determined the quantum yields for the disappearance of these nitrone derivatives (Φ_{-1}) spectrophotometrically: $\Phi_{-1a} = 0.036 \pm 0.001$, $\Phi_{-1b} = 0.039 \pm 0.001$, $\Phi_{-1c} = 0.045 \pm 0.002$, and $\Phi_{-1d} = 0.045 \pm 0.001$. These results confirm that the α-hydroxynaphthyl group lowers the reactivity to some extent. Interestingly, the replacement of the hydroxy group in **1b** by the methoxy group (**1e**) increases the photoreactivity of **1b** by a factor of 15 ($\Phi_{-1e} = 0.59 \pm 0.03$),[7] and so the existence of intramolecular hydrogen bonding is very likely to make the modulation of the GI profile much easier.

Photoreactions and changes in the refractive index in polymer films

PMMA films containing 20 wt % **1a–1d** were prepared on both silica glass and Si wafers. The thickness of the transparent films was about 1 μm. The starting nitrone derivative **1a** in the films exhibited UV absorption spectral changes, very similar to those observed in solution, upon irradiation at 366 nm (Fig. 2). Therefore, it is very likely that the same photoreaction took place also in the films. A comparison of the rates (at which the UV absorption spectra of **1a** in solution and in PMMA film are changed) reveals the occurrence of much more rapid photochemical transformation in the latter state than in the former (Figs. 1 and 2). The same results were obtained for the other nitrone derivatives and were consistent with the weakened intramolecular hydrogen bonding in the polymer films. Intermolecular hydrogen-bonding interactions between the *ortho*-hydroxy group in **1** and the ester carbonyl oxygen in the polymer may be responsible for the increased rate of the reaction.
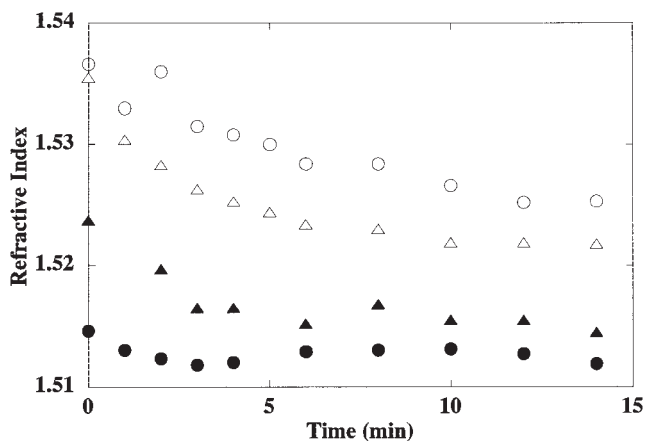

Scheme 1

Figure 3　Refractive index of PMMA films, containing (○) **1a**, (△) **1b**, (●) **1c**, and (▲) **1d** (20 wt %) and prepared on Si wafers, as a function of the irradiation time.

Figure 3 presents refractive indices for polymer films containing **1** as a function of the irradiation time. The plots show that the indices for the films prepared with **1a** and **1b** gradually decreased with the irradiation time and then became constant after 14 min of irradiation. The observed decrease in the refractive index corresponds well to that in the first absorption band of the corresponding nitrone derivative. On the contrary, the refractive index for the **1c**–PMMA-derived film was reduced only slightly even after 14 min of irradiation, despite the photochemical reaction in this polymer film. An ellipsometer analysis of the film carried out before and after irradiation showed that its thickness decreased by about 2–10% as the photoreaction proceeded (Fig. 4). This finding suggests that the shrinkage of films containing **1c** and **1d**, which is responsible for an increase in the number density of the molecules in these films (N), suppresses a reduction in the refractive index (n), as shown by the Lorentz–Lorenz equation:
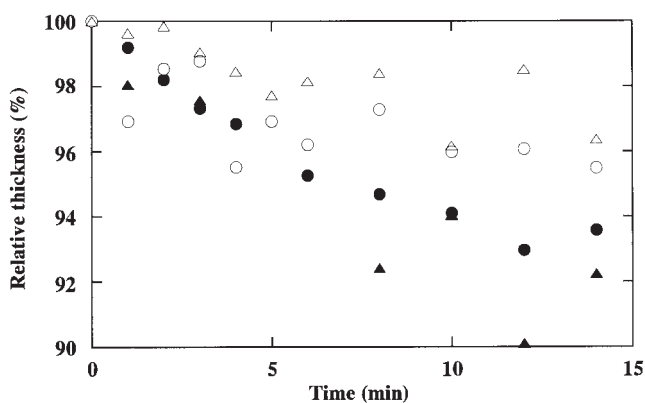

Figure 4　Relative thickness of PMMA films, containing (○) **1a**, (△) **1b**, (●) **1c**, and (▲) **1d** (20 wt %) and prepared on Si wafers, as a function of the irradiation time.
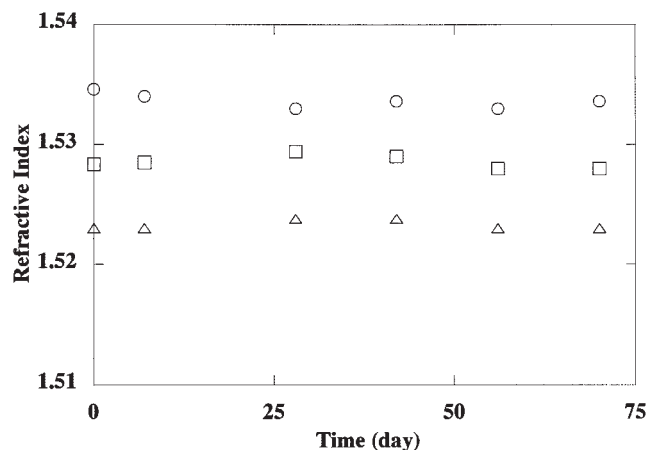

Figure 5　Stability of the refractive index of PMMA films, containing **1b** (20 wt %) and prepared on Si wafers, left in a dark place. The irradiation time was (○) 0, (□) 2, or (△) 14 min.

$$(n^2 - 1)/(n^2 + 2) = (4/3)\pi N\alpha \qquad (1)$$

These considerations reveal the hydroxynaphthyl-substituted nitrone derivatives **1a** and **1b** to be much better additives for controlling the refractive index of a PMMA film. As demonstrated in Figure 5, the index values of the PMMA–**1b**-derived films remained almost unchanged at photochemical conversions of 0, 50, and 100% when the films were allowed to stand at least 70 days in a dark place at room temperature. In addition, the large refractive-index change of 0.014 observed for additive **1b** has led us to conclude that the photochemical reaction of this additive in a PMMA film can be used to generate a refractive-index profile for GI-type POF materials.

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