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Photoreactivity of diarylnitrone additive/pendant in poly(methyl methacrylate) film and photocontrol of refractive index for this polymer film

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Abstract

Photoreactivities of hydroxy-substituted diarylnitrones (**1a–f**) in solution and methyl methacrylate(MMA)-derived polymer film were studied. The methyl group introduced at the *ortho*-position on the *N*-aryl benzene ring of **1** (**1c–e**) was found to exert a great steric effect on the photoreaction pathway to eventually give a different photoproduct distribution. This steric effect also contributed to suppressing a decrease in the refractive index of PMMA polymer film. The irradiation at 366 nm of MMA-derived copolymer film (bearing the diarylnitrone pendants) lowered the refractive index of this film by $-\Delta n = 0.0152$, which was much larger than the refractive-index decrease of PMMA polymer film containing **1c–e** as additives ($-\Delta n = 0.0017$–0.0044).

Keywords: Diarylnitrone; Photoreactivity; Polymer film; Refractive index; Photocontrol

1. Introduction

The photocontrol of the refractive index of polymer film is still drawing much attention for its application to optical communication devices such as a plastic optical fiber [1,2]. A large number of photoreactive compounds have been used as additives for a given polymer component [3–9]. Kudo et al. have synthesized calixarene derivatives containing various norbornadienyl groups and found that the refractive index of these derivatives is decreased to a great extent (e.g., $-\Delta n = 0.061$) on irradiation [10]. This large refractive-index change may be due to the high density of photoreactive functional group in a given calixarene derivative.

In our previous paper, photocontrol of the refractive index of PMMA film was investigated with hydroxy-substituted diarylnitrone additives and the maximal refractive-index change of −0.014 was attained with α-(2-hydroxy-1-naphthyl)-*N*-(4-tolyl)nitrone [11]. In order to obtain a much greater change in the refractive index of the polymer film, we also attempted to introduce this type of diarylnitrone pendant into PMMA by the radical copolymerization of MMA with methacryloyloxy-substituted diarylnitrone [12]. Although the radical copolymerization was suppressed by the addition of propagating radical to the diarylnitrone moiety [12–14], the use of steric hindrance to the addition of propagating radical allowed us to quantitatively prepare the desired copolymer, for the first time. For example, the radical copolymerization of MMA with α-(2-hydroxy-4-methacryloyloxyphenyl)-*N*-(2,6-dimethylphenyl)nitrone (HMDN) afforded the HMDN-MMA copolymer having [nitrone pendant]:[MMA unit] = 17.3:82.7 [12].

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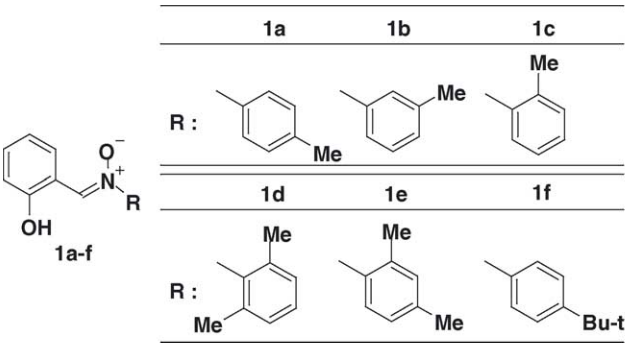
It is of great significance to elucidate factors that control the refractive index of a given polymer film from a practical point of view. For this purpose we synthesized α-(2-hydroxyphenyl)-*N*-(alkyl-substituted phenyl)nitrone derivatives (**1a–f**) in addition to the HMDN-MMA copolymer and investigated steric and electronic effects of alkyl group(s) on the photoreactivity of hydroxy-substituted diarylnitrones as well as the photocontrol of the refractive index for MMA-derived polymer film containing diarylnitrone as an additive or a pendant.



2. Experimental

2.1. Materials

According to the previously described procedures [11], **1a–f** were prepared by the reactions of 2-hydroxybenzaldehyde with 4-tolylhydroxylamine (**1a**), 3-tolylhydroxylamine (**1b**), 2-tolylhydroxylamine (**1c**), 2,6-dimethylphenylhydroxylamine (**1d**), 2,4-dimethylphenylhydroxylamine (**1e**), and 4-*tert*-butylphenylhydroxylamine (**1f**) in ethanol, respectively. The crude hydroxylamines were purified by column chromatography over silica gel, followed by recrystallization from ethanol to give analytical-grade **1a–f** in 34–91% yields. The ^{1}H NMR spectrum of α-(2-hydroxyphenyl)-*N*-(4-tolyl)nitrone (**1a**) was consistent with that of previously prepared sample [11]. The physical and spectroscopic data of **1b-f** are as follows.

2.1.1. *α-(2-Hydroxyphenyl)-N-(3-tolyl)nitrone (**1b**)*

mp 53.5–54.0 °C. IR (KBr, cm^{-1}) ν 3422 (O–H), 3047 (C–H), 2920 (C–H), 1608 (C=N). ^{1}H NMR (500 MHz, $CDCl_3$). δ (ppm) = 12.55(1H, s), 8.03(1H, s), 7.59(1H, s), 7.53(1H, d, J = 7.4 Hz), 7.43(1H, dd, J = 6.9, 8.6 Hz), 7.36(1H, dd, J = 8.0, 7.4 Hz), 7.29(1H, d, J = 8.0 Hz), 7.17(1H, d, J = 8.0 Hz), 7.01(1H, d, J = 8.6 Hz), 6.88(1H, dd, J = 6.9, 8.0 Hz), 2.44(3H, s). ^{13}C NMR (125 MHz, $CDCl_3$). δ (ppm) = 159.9, 146.1, 141.0, 139.7, 134.5, 132.8, 131.2, 129.1, 122.4, 120.3, 119.2, 118.8, 116.9, 21.3. Analysis: calculated for $C_{14}H_{13}NO_2$: C, 73.99%; H, 5.77%; N, 6.16%; found: C, 73.92%; H, 5.58%; N, 5.96%.

2.1.2. *α-(2-Hydroxyphenyl)-N-(2-tolyl)nitrone (**1c**)*

mp 102.0–102.5 °C. IR (KBr, cm^{-1}) ν 3421 (O–H), 3030 (C–H), 2966 (C–H), 1602 (C=N). ^{1}H NMR(500 MHz, $CDCl_3$). δ (ppm) = 12.50(1H, s), 7.73(1H, s), 7.45(1H, dd, J = 8.6, 10.3 Hz), 7.43(1H, d, J = 10.3 Hz), 7.39(1H, dd, J = 7.4, 6.9 Hz), 7.33(1H, d, J = 8.0 Hz), 7.31(1H, dd, J = 8.6, 8.0 Hz), 7.13(1H, d, J = 8.0 Hz), 7.04(1H, d, J = 7.4 Hz), 6.89(1H, dd, J = 6.9, 8.0 Hz), 2.48(3H, s). ^{13}C NMR (125 MHz, $CDCl_3$). δ (ppm) = 159.9, 146.1, 144.3, 134.6, 132.5, 132.3, 131.6, 130.1, 126.8, 123.8, 120.4, 119.2, 116.6, 17.2. Analysis: calculated for $C_{14}H_{13}NO_2$: C, 73.99%; H, 5.77%; N, 6.16%; found: C, 74.11%; H, 5.58%; N, 6.08%.

2.1.3. *α-(2-Hydroxyphenyl)-N-(2,6-dimethylphenyl)nitrone (**1d**)*

mp 138.5–139.0 °C. IR (KBr, cm^{-1}) ν 3425 (O–H), 3032 (C–H), 2926 (C–H), 1601 (C=N). ^{1}H NMR(500 MHz, $CDCl_3$). δ (ppm) = 12.51(1H, s), 7.63(1H, s), 7.46(1H, t, J = 8.6 Hz), 7.26(1H, dd, J = 6.9, 8.0 Hz), 7.15(2H, d, J = 8.6 Hz), 7.12(1H, d, J = 8.0 Hz), 7.04(1H, d, J = 8.0 Hz), 6.90(1H, dd, J = 6.9, 8.0 Hz), 2.42(6H, s). ^{13}C NMR (125 MHz, $CDCl_3$). δ (ppm) = 160.0, 145.7, 144.8, 134.5, 132.3, 132.0(2C), 129.5, 128.7(2C), 120.4. 119.1, 116.6, 16.9(2C). Analysis: calculated for $C_{15}H_{15}NO_2$: C, 74.67%; H, 6.27%; N, 5.81%; found: C, 74.98%; H, 6.44%; N, 5.84%.

2.1.4. *α-(2-Hydroxyphenyl)-N-(2,4-dimethylphenyl)nitrone (**1e**)*

Mp 118.5–119.0 °C. IR(KBr, cm^{-1}) ν 3420 (O–H), 3032 (C–H), 2943 (C–H), 1605 (C=N). ^{1}H NMR(500 MHz, $CDCl_3$). δ (ppm) = 12.54(1H, s), 7.70(1H, s), 7.44(1H, dd, J = 6.9, 8.6 Hz), 7.43(1H, d, J = *5.7* Hz), 7.31(1H, d, J = 8.0 Hz), 7.12(1H, s), 7.10(1H, d, J = 5.7 Hz), 7.02(1H, d, J = 8.6 Hz), 6.88(1H, dd, J = 6.9, 8.0 Hz), 2.42(3H, s), 2.37(3H, s). ^{13}C NMR (125 MHz, $CDCl_3$). δ (ppm) = 159.9, 144.2, 143.9, 140.2, 134.4, 132.5, 132.2, 131.9, 127.3, 123.6, 120.3, 119.1, 116.7,21.1, 17.2. Analysis: calculated for $C_{15}H_{15}NO_2$: C, 74.67%; H, 6.27%; N, 5.81%; found: C, 74.33%; H, 6.06%; N, 5.53%.

2.1.5. *α-(2-Hydroxyphenyl)-N-(4-tert-butylphenyl)nitrone (**1f**)*

mp 144.0–145.0 °C. IR (KBr, cm^{-1}) ν 3426 (O–H), 3063 (C–H), 2949 (C–H), 1607 (C=N). ^{1}H NMR (500 MHz, $CDCl_3$). δ (ppm) = 12.54(1H, s), 8.04(1H, s), 7.70(2H, d, J = 8.6 Hz), 7.51(2H, d, J = 8.6 Hz), 7.44(1H, dd, J = 6.9, 8.0 Hz), 7.17(1H, d, J = 8.0 Hz), 7.03(1H, d, J = 8.0 Hz), 6.90(1H, dd, J = 6.9, 8.0 Hz), 1.36(9H, s). ^{13}CNMR(125 MHz, $CDCl_3$). δ (ppm) = 159.9, 154.1, 143.6, 140.6, 134.4, 132.8, 126.2(2C), 121.4(2C), 120.4, 119.1, 117.0, 34.9, 31.2(3C). Analysis: calculated for $C_{17}H_{19}NO_2$: C, 75.81%; H, 7.11%; N, 5.20%; found: C, 75.65%; H, 7.17%; N, 5.12%.

The mixture of 2,6-dimethylaniline (4.1 mmol) and salicylaldehyde (4.1 mmol) was heated for 1 h at 60 °C with stirring. The crude product was purified by column chromatography over silica gel (eluent, toluene). NMR spectral data of *N-(2*-hydroxybenzylidene-2,6-dimethylaniline (**2d**) as an authentic sample are as follows.

2.1.6. **2d**

^{1}H NMR (500 MHz, $CDCl_3$). δ (ppm) = 13.08(1H, s), 8.34(1H, s), 7.40(1H, t, J = 8.0 Hz), 7.34(1H, d, J = 8.0 Hz), 7.10(2H, d, J = 8.0 Hz), 7.05(1H, d, J = 8.0 Hz), 7.02(1H, dd, J = 7.4, 8.0 Hz), 6.95(1H, dd, J = 7.4, 8.0 Hz), 2.20(6H, s). ^{13}C NMR (125 MHz, $CDCl_3$). δ (ppm) = 166.7, 161.2, 148.2, 133.2(2C), 132.2, 128.3(2C), 128.2, 124.9, 119.0, 118.8, 117.3, 18.5(2C).

4-Formyl-3-hydroxyphenyl methacylate (FHM) was prepared according to the usual procedure. Methacryloyl chloride (5.0 g: 0.048 mol) in 10 mL of chloroform was added dropwise to a mixture of 2,4-dihydroxybenzaldehyde (8.0 g: 0.058 mol) and triethylamine (TEA: 4.9 g, 0.048 mol) in 40 mL of chloroform over a 30 min-interval in an ice-water bath. After 1 h stirring, the mixture was washed with water and then concentrated to dryness under reduced pressure. Colorless crystalline solid obtained was purified by column chromatography over silica gel (eluent, ethyl acetate: *n*-hexane = 1: 1 v/v), followed by recrystallization from ethanol to give FHM (7.8 g: 0.038 mol, 79%) having the following NMR spectral data.

2.1.7. FHM

^{1}H NMR (500 MHz, $CDCl_3$). δ (ppm) = 11.23 (1H, s), 9.87 (1H, s), 7.59 (1H, d, J = 8.3 Hz), 6.83 (1H, d, J = 8.3 Hz), 6.79 (1H, s), 6.36 (1H, s), 5.81 (1H, s), 2.06 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$). δ (ppm) = 195.8, 165.1, 163.5, 158.0, 135.7, 135.2, 128.5, 119.0, 114.3, 111.1, 18.6.

α-(2-Hydroxy-4-methacryloyloxyphenyl)-*N*-(2,6-dimethylphenyl)nitrone (HMDN) was prepared as follows. 2,6-dimethylphenylhydroxylamine [15] (2.39 g: 0.0116 mol) and FHM (1.59 g: 0.0116 mol) were stirred in 20 mL of ethanol for 2 days at r.t. The mixture was concentrated in vacuo and pale yellow crystalline solid separated out was filtered with suction and recrystallized from ethanol to afford HMDN (2.03 g: 0.0062 mol, 53%) having the following physical and spectroscopic data.

2.1.8. HMDN

^{1}H NMR (500 MHz, $CDCl_3$). δ (ppm) = 13.06 (1H, s), 7.59 (1H, s), 7.26 (1H, overlap with solvent signal), 7.15 (1H, d, J = 7.3 Hz), 7.12 (1H, d, J = 8.3 Hz), 6.80 (1H, s), 6.72 (1H, d, J = 8.3 Hz), 6.36 (1H, s), 5.79 (1H, s), 2.40 (6H, s), 2.07 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$). δ (ppm) = 165.1, 161.7, 156.4, 145.5, 144.2, 135.6, 133.2, 132.1 (2C), 129.6, 128.7 (2C), 127.8, 114.4, 113.2, 113.1, 18.3 and 16.9 (2C). Analysis: calculated for $C_{19}H_{19}NO_4$: C, 70.14%; H, 5.89%; N, 4.31%; found: C, 69.84%; H, 5.82%; N, 4.46%.

Poly(methyl methacrylate) (PMMA) (Wako, n = 1000–1500) as a host polymer was used without further purification. MMA-derived copolymer bearing the nitrone pendants was prepared by the bulk copolymerization of MMA with HMDN in the presence of 2,2′-azobis(isobutyronitrile) [12]. PMMA films containing 20 wt.% **1a–f** were prepared by spin coating of a 2-methoxyethyl acetate solution on a silica glass (for UV spectral measurements) or on a silicon wafer (for refractive index measurements), followed by vacuum drying at 40 °C.

2.2. Measurements and calculations

UV absorption spectra were recorded on a Hitachi UV-3300 spectrophotometer. ^{1}H and ^{13}C NMR spectra were taken with a JEOL JNM-A500 spectrometer using tetramethylsilane as an internal standard. IR spectra were taken with a Shimadzu Prestige-21 infrared spectrophotometer. Acetonitrile solutions or PMMA films containing **1a–f** were irradiated with 366 nm light from a 450 W high-pressure Hg lamp. This monochromatic light was selected by employing Corning 0–52, Corning 7–60, and Toshiba IRA-25S glass filters. Refractive indices of the films were measured before and after irradiation with a Gaertner L115B elipsometer. The light source for the index measurements was a 632.8 nm He–Ne laser. MOPAC calculations were accomplished by using CAChe 5.0 for Windows available from Fujitsu Ltd, 2002.

3. Results and discussion

3.1. Substituent effects on photoreactivity of **1** and photoproduct distribution in acetonitrile

Fig. 1 shows UV absorption spectral changes of **1a–f** caused by the irradiation of their nitrogen-saturated acetonitrile solutions with 366 nm light. The absorption of **1a** detected around 300 nm and 360 nm was decreased with irradiation, while isosbestic points were observed at 275 nm. These spectral changes are very similar to those observed for **1b** and **1f**, indicating that the alkyl group attached to the *meta*- or *para*-position on the *N*-aryl benzene ring exerts a negligible effect on the photoreactivity. This is consistent with the previous results [16]. It is, thus, very likely that the nitrone derivatives **1a**, **1b**, and **1f** undergo photoisomerization and photorearrangement to afford the corresponding *N*,*N*-diarylformamides [16].

In the cases of **1c** and **1e**, the reactions apparently seem to stop at about 50% conversion, as seen from their absorption spectral changes having isosbestic point at 270 nm. Interestingly, much less marked spectral changes were observed on the irradiation of **1d**, whereas the absorption detected around 260 nm was remarkably increased with this irradiation. These findings suggest that the *ortho*-methyl group affects the reaction pathway of hydroxy-substituted diarylnitrones to result

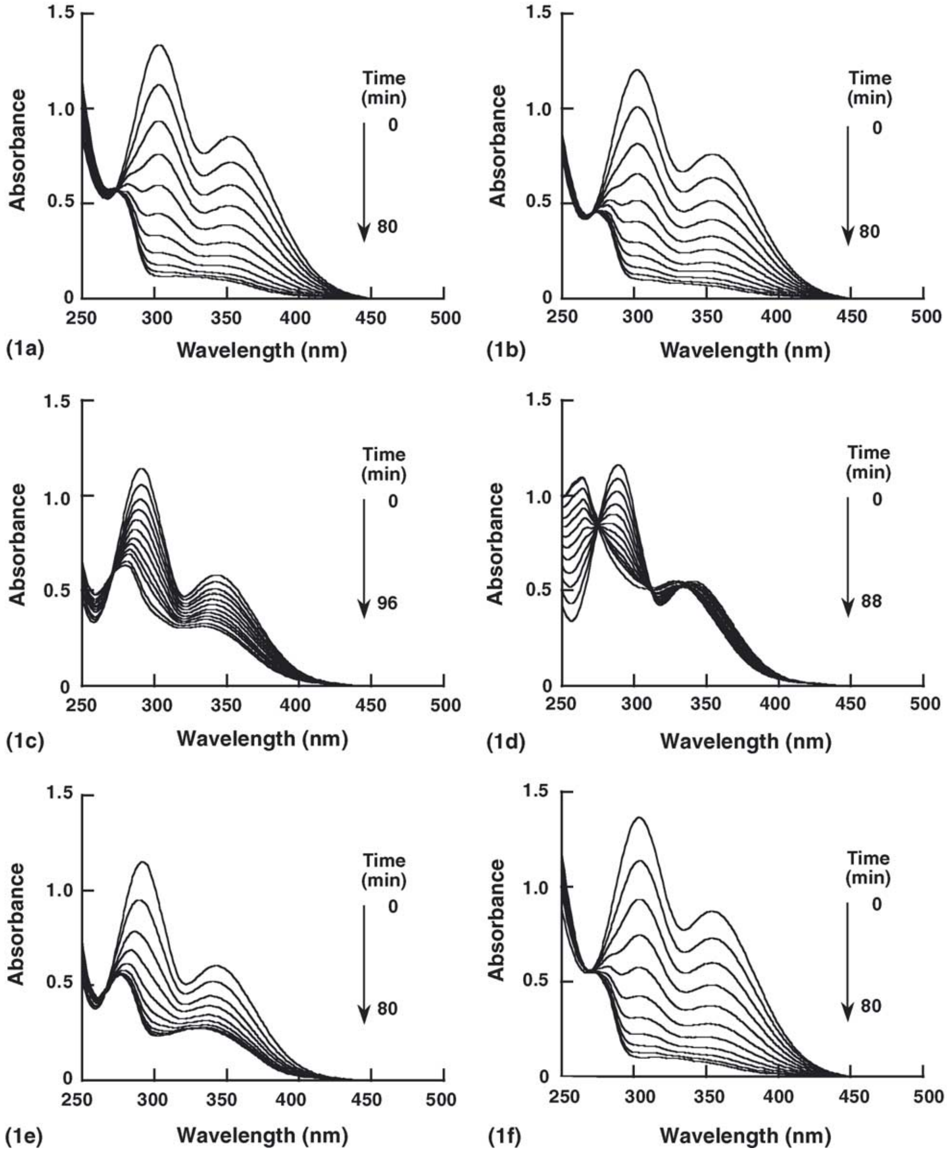


Fig. 1. UV spectral changes of **1a–f** (l.0 × l0^{4} mol dm^{-3}) in acetonitrile with irradiation at room temperature. Time intervals are 8 min.

in a product distribution different from that for **1a**, **1b**, and **1f**.

Taking into account the possibility that steric hindrance of this methyl group weakens π-conjugation between the $-CH{=}N^{+}(-O^{-})-$ moiety and the *N*-aryl benzene ring, we performed MOPAC calculations with **1a** and **1d** in order to estimate the rotational barriers of the *N*–Ar and *C*–Ar bonds (Fig. 2). Clearly, lowest-energy conformations in any cases have two aryl planes which are both perpendicular to the $-CH{=}N^{+}$-plane. In addition, rotational barriers for the *C*–Ar bond in **1a** and **1d** are fairly low, whereas the *N*–Ar bond in the latter nitrone possesses a much larger energy barrier for this bond rotation (16–26 kcal mol^{-1}) as compared to the *N*–Ar bond in the former nitrone (2–3 kcal mol^{-1}). Therefore, the $-CH{=}N^{+}$- and *N*-aryl planes in **1d** should be perpendicular to one another, allowing us to expect the strongly weakened π-conjugation between these two planes. This expectation is substantiated by the finding that on itroducing the *ortho*-methyl groups the absorption maxima of **1a** are blue-shifted by 10–20 nm. Because **1c** and **1e** show UV absorption spectra similar to that of **1d**, it can be concluded that the presence of the *ortho*-methyl group lowers coplanarity between the chromophores in **1** and then exerts a great effect on the reaction pathways.

The irradiation of an acetonitrile solution of **1d** gave *N*-(2-hydroxybenzylidene)-2,6-dimethylaniline (**2d**), the ^{1}H NMR spectrum of which agreed with that of independently prepared authentic sample, as one of major products. The direct photolysis of diarylnitrones that gives the deoxygenation product in a good yield is an attractive photoreaction and has

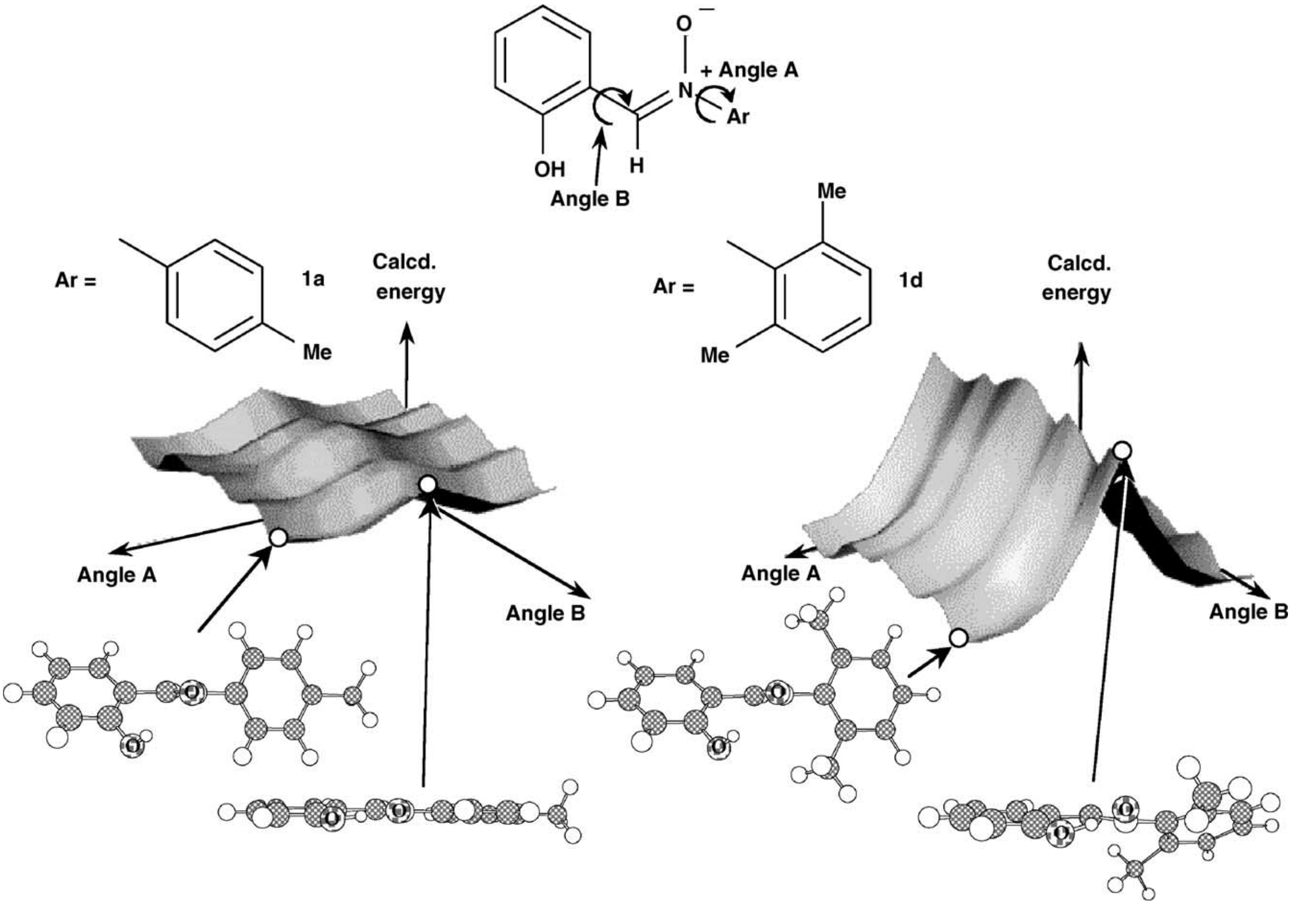


Fig. 2. The potential energy map of conformations determined by varying the two angles A and B. The energy of each conformation is estimated by MM2 and PM5 calculations.

no precedent. In our previous study it was demonstrated that **1a** undergoes at first photoisomerization into an oxaziridine intermediate and the subsequent photorearrangement of this intermediate eventually affords *N*-(2-hydroxyphenyl)-*N*-(4-tolyl)formamide quantitatively, which exists as two stable conformers in solution [16]. A comparison of the ^{1}H NMR spectrum of this formamide with that of the product mixture obtained in this study confirms that proton signals at 8.24 and 8.30 ppm are safely assigned to the formyl protons of two conformers for the **1d**-derived rearrangement product (**3d**) (Fig. 3). The area ratio of given ^{1}H NMR signals for **1d**, **2d**, and **3d** allowd us to calculate their compositions as shown in Table 1. The higher composition of **2d** than that of **3d** indicates the deoxygenation of **1d** to be a major reaction pathway. The UV absorption spectrum of **2d** given in Fig. 4 is similar to that (having maxima at 257 and 323 nm) recorded after the irradiation of **1d**. It is likely that the perpendicular orientation of the *N*-aryl benzene ring described above exerts a great effect on the ring-opening mode of an oxaziridine intermediate which plays a central role in the photochemistry of diarylnitrone derivatives.

Table 1
Composition of each compound obtained by the 5 h irradiation of **1d** (2.1 mmol dm^{-3}) in chloroform at room temperature

Conversion (%)[a]	Composition (%)		
	1d	**2d**	**3d**
72	28	38	34

[a] Estimated by the sum of composition for **2d** and **3d**.

3.2. Photoreactivity of **1a–f** in PMMA film and photocontrol of refractive index for this polymer film

As shown in Fig. 5, on irradiation at 366 nm hydroxy-substituted diarylnitrones (**1a–f**) doped in PMMA film underwent efficient photoreactions giving similar UV spectral changes to those observed in solution. The great difference in photoreactivity between the film and solution states is that any **1** in the former state shows a much higher reactivity than the latter-state **1**. In a previous study it was found that the replacement of the *ortho*-hydroxy group in **1** by the methoxy enhances the excited-state reactivity by

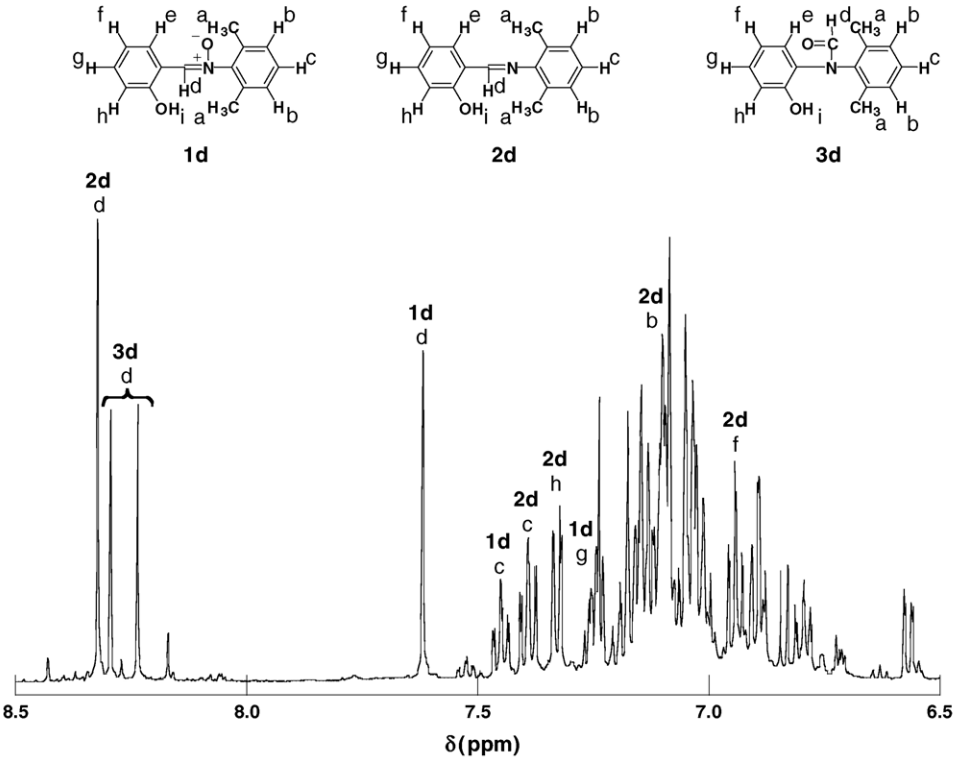


Fig. 3. ^{1}H NMR spectrum of the reaction mixture obtained by the 5 h irradiation of **1d** (2.1 mmol dm^{-3}) in chloroform at room temperature. Only unambiguously assignable ^{1}H NMR signals were indicated in this figure.

about an order of magnitude [16]. It is, thus, reasonable to interpret the reactivity enhanced in the film state in terms of a weakened intramolecular hydrogen bond. Interestingly, UV spectral changes caused by the irradiation of **1** possessing the *ortho*-methyl group on the *N*-aryl benzene ring in the film and solution states are very similar to each other, whereas the other derivatives, **1a**, **1b**, and **1f**, in the film state exhibit spectral changes being analogous to those for **1c–e**. These findings reveal that the *N*–Ar bond in **1** experiences a large rotational barrier in the PMMA polymer matrix. As already discussed, photodeoxygenation and photorearrangement are considered to be major reaction pathways in this polymer matrix.

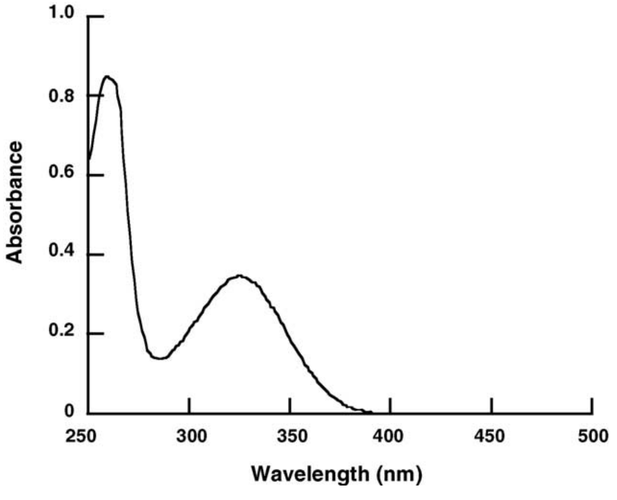


Fig. 4. UV spectrum of **2d** (1.0×10^{-4} mol dm^{-3}) in acetonitrile.

In Fig. 6 are shown refractive index changes (Δn) caused by the irradiation of PMMA films (in which **1a–f** are doped) on silicon wafers. As seen from this figure, the refractive indices of PMMA films were decreased in the presence of **1a**, **1b**, and **1f** as additives by $-\Delta n = 0.0061$–0.0082. In contrast, a slight decrease in refractive index was only observed when the **1c–e**-doped PMMA films were irradiated. Particularly, the refractive-index decrease of the **1d**-doped film was $-\Delta n = 0.0017$. Because the n values of irradiated PMMA films are almost the same for **1a–e** ($n = 1.515$–1.516), the magnitude of Δn should be determined mainly by the n values of non-irradiated films. As already described, the $-CH{=}N^{+}$-plane in **1d** is perpendicular to the plane of the *N*-aryl benzene ring in its thermodynamically most stable conformation. It is, thus, very likely that the great energy barrier for rotation about the *N*–Ar bond renders the difference in polarizability volume between **1d** and **1d**-derived photoproducts very small.

3.3. *Photoreactivity of the MMA-HMDN copolymer and photocontrol of its refractive index*

MMA-derived copolymer bearing the nitrone pendants (the structure of which is very similar to that of

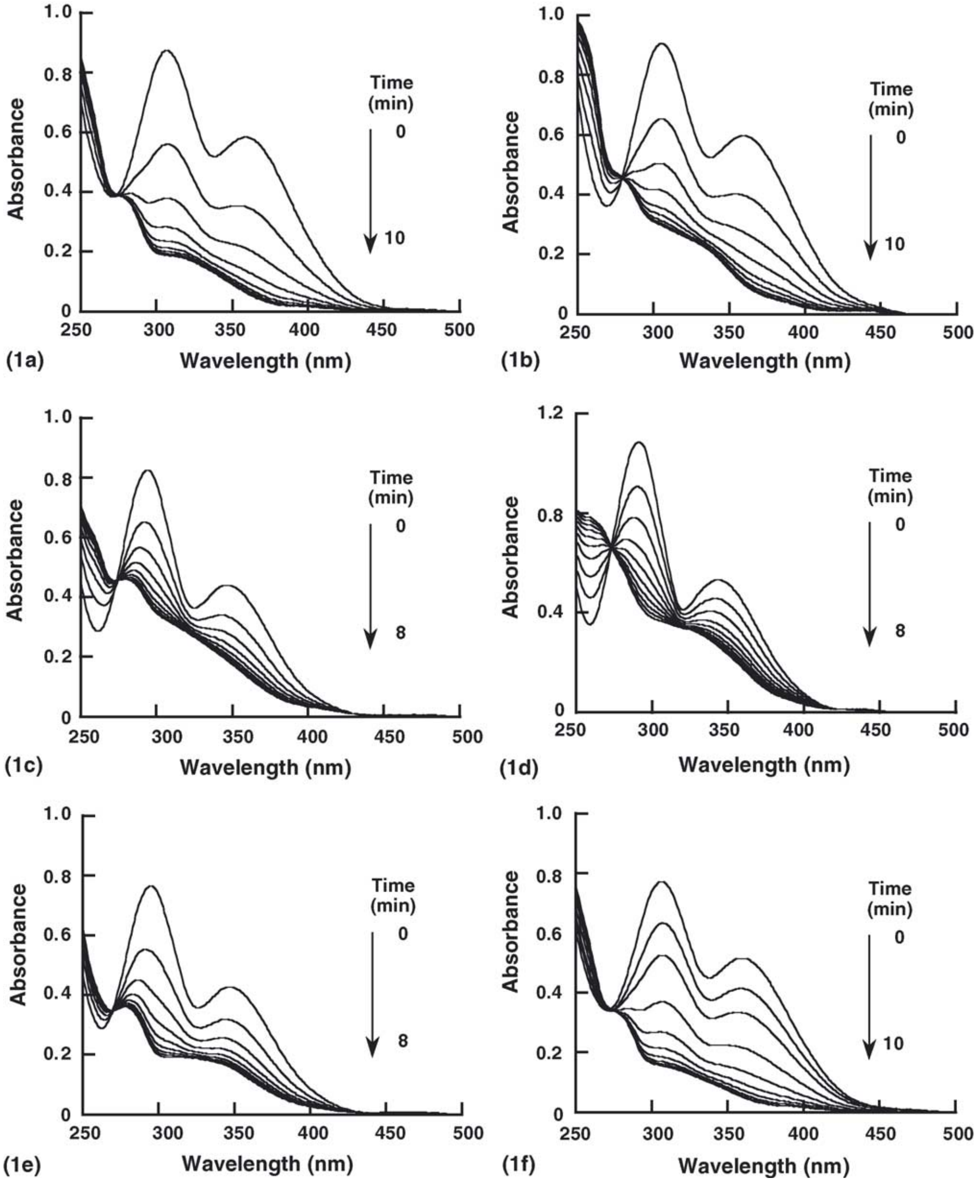


Fig. 5. UV spectral changes of **1a–f** (20 wt.%) in PMMA films with irradiation at room temperature. Time intervals are 1 min.

1d) was prepared by the radical copolymerization of MM A with hydroxy-substituted diarylnitrone having a polymerizable C═C bond (HMDN), as reported in a previous paper [12]. The composition of this copolymer was [MMA]:[HMDN] = 83:17 and the following equation allowed us to estimate the nitrone content as 42 wt.%.

$$\frac{0.17w_{\mathrm{N}}}{0.83m_{\mathrm{M}}+0.17\times(m_{\mathrm{H}}-w_{\mathrm{N}})}=0.42 \qquad (1)$$

where, w_{N} is the formula weight of nitrone pendant (240.3) and m_{M} and m_{H} are molecular weights of MMA (100.1) and HMDN (325.4), respectively. It is, thus, possible to prepare the MMA-HMDN copolymer containing a high concentration of the nitrone pendant by means of the radical copolymerization of the *ortho*-methyl- and hydroxy-substituted diarylnitrone monomer. The transparent copolymer film could be readily made by spin coating on a silica glass or a silicon wafer. The film was irradiated with 366 nm light in order to record UV absorption spectral and refractive index changes. The former changes given in Fig. 7 confirm that they are very similar to those obtained by the irradiation of **1d** in the PMMA film, indicating almost the same photoreaction to proceed also in the MMA-HMDN copolymer film. As demonstrated in Fig. 8, its refractive index was decreased ($-\Delta n = 0.0152$), while the irradiation of the MMA-HMDN copolymer containing 17 wt.% of the nitrone pendant lowered its refractive index

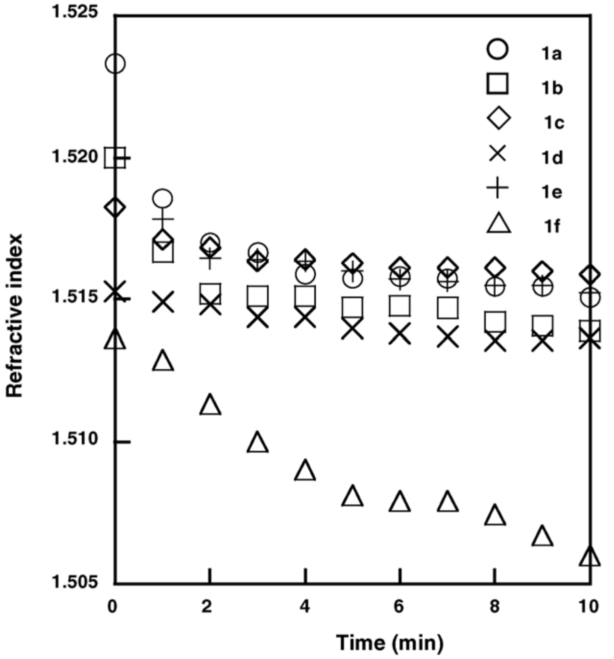


Fig. 6. Refractive-index changes of PMMA films containing **1a–f** (20 wt.%) with irradiation at room temperature.

by $-\Delta n = 0.0024$. These findings confirm that the increased nitrone content in this copolymer film is reflected in a much larger decrease in refractive index and also the magnitude of $-\Delta n = 0.0024$ is comparable to that ($-\Delta n = 0.0017$) for the PMMA film containing 20 wt.% **1d** as an additive.

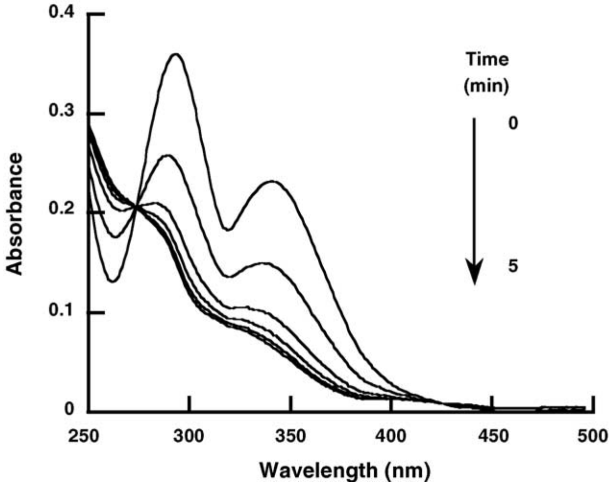


Fig. 7. UV spectral changes of the MMA-HMDN copolymer film with irradiation at room temperature. Time intervals are 1 min.

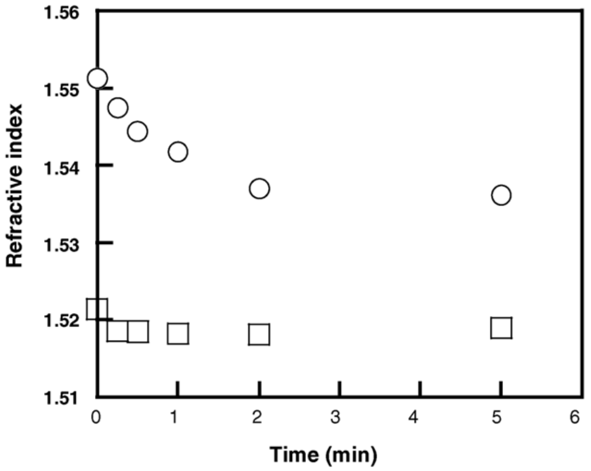


Fig. 8. Refractive-index changes of the MMA-HMDN copolymer films with irradiation at room temperature. The nitrone contents in these copolymers are 42 (◯) and 17 wt.% (☐).

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