Radical Copolymerization of Diarylnitrone Derivatives Having a Polymerizable Group with Methyl Methacrylate

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Recently, much attention has been devoted to plastic optical materials, especially to plastic optical fiber (POF), because of many advances in optical network technology.[1,2] Instead of step index-type POF, graded index-type POF with high information transmission ability is drawing great attention from a technological point of view.[1,2] For fabricating such a POF material, the precise control of refractive index of the polymer is required.

Linear polarizability (α) is related to refractive index (*n*) by the Lorentz−Lorenz equation

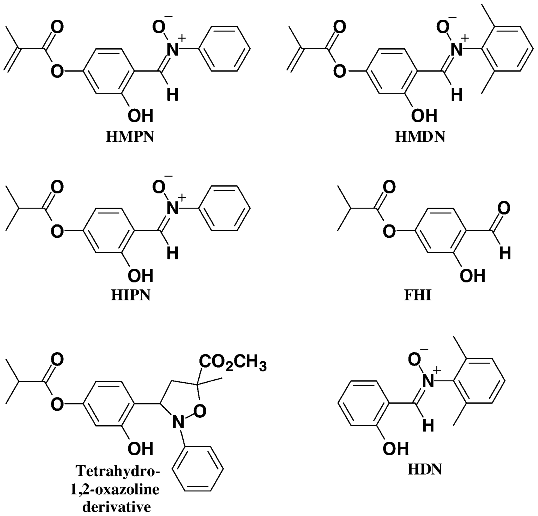
$$\frac{n^2-1}{n^2+2}=\frac{4}{3}\pi N\alpha \tag{1}$$

where *N* is the number density of molecules. This equation suggests that one of the best methods for controlling refractive index is to utilize the photoisomerization of a given molecule, which affects the magnitude of π-conjugation between two chromophores in its molecule, i.e., the linear polarizability. There have been many studies regarding the photocontrol of refractive index of a polymer film, in which photoreaction weakens π-conjugation between chromophores to result in a decrease in the refractive index of the film.[3−6]

Very recently, we reported that on irradiation in polar solvents hydroxy-substituted diarylnitrones undergo photorearrangement to quantitatively afford *N*,*N*-diarylformamides via an oxaziridine intermediate;[7] this rearrangement brings about a considerable reduction in π-conjugation between the two aryl chromophores. On the basis of the above information, our research group investigated the photocontrol of refractive index of poly(methyl methacrylate) (PMMA) containing a diarylnitrone derivative as an additive and found that the polymer matrix accelerates the photorearrangement of this additive and greatly enhances the stability of refractive index of the PMMA film irradiated for a given period of time.[8]

Considering that an additive may be able to migrate in a polymer film, it is preferable to fix the chromophore for refractive index control on a given polymer chain. Heinenberg and co-workers have succeeded in preparing a polymer having a nitrone chromophore by the reaction of poly(formylphenyl methacrylate) with phenylhydroxylamine.[9,10] They also attempted the radical copolymerization of α-(4-methacryloyloxyphenyl)-*N*-phenylnitrone with MMA but failed to obtain the corresponding copolymer, owing to the preferential 1,3-dipolar cycloaddition of the methacryloyl group to the nitrone moiety [−CH=N$^+$(−O$^-$)−].[9] Nitrone derivatives undergo radical addition to form stable nitroxides and, hence, can be used as radical trapping agents.[11,12] It is very likely that the high ability of nitrones to capture propagating radicals is one of the reasons for their failure in the radical copolymerization with MMA. If 1,3-dipolar addition to and radical trapping by the nitrone pendant could be suppressed, the radical copolymerization of diarylnitrones carrying a polymerizable group with MMA should proceed efficiently to give diarylnitrone-substituted PMMA directly.

Chart 1



Our attention is directed to steric hindrance by the substituents introduced into diarylnitrone derivative to the addition reactions described above. One substituent is hydroxy at the 2-position of α-phenyl group; this substituent also plays an important role in inducing quantitative photorearrangement reaction.[7] The other substituent is methyl at the 2- and 6-positions of the *N*-phenyl group. To elucidate the role of steric hindrance in the radical polymerization process, we prepared α-(2-hydroxy-4-methacryloyloxyphenyl)-*N*-phenylnitrone (HMPN) and α-(2-hydroxy-4-methacryloyloxyphenyl)-*N*-(2,6-dimethylphenyl)nitrone (HMDN) (Chart 1).

As already described, nitrone derivative has the great ability to capture propagating radicals and inhibit radical polymerization because the propagating radical adds to the nitrone moiety to yield a stable nitroxide.[11,12] This nitroxide couples with another propagating radical to inhibit the radical polymerization. The results in Table 1 show that the polymer yield decreases with an increase in HMPN concentration, but prolonged polymerization results in an increase in polymer yield even at [HMPN] = 0.30 mol/L. This reveals that neither the 1,3-dipolar cycloaddition of MMA nor the addition of propagating radical to the nitrone moiety takes place to a substantial extent. In the ^{1}H NMR spectrum of the copolymer ($CDCl_3$, TMS standard), there are signals which can be assigned to the diarylnitrone chromophore based on comparison with the spectrum of HIPN. Especially, the CH=N$^+$(−O$^-$) proton and hydroxy proton signals (the area ratio of which is 1.0) are detected at 8.1 and 13.1 ppm, respectively. This spectral analysis

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Table 1. Bulk Copolymerization of HMDN and HMDN with MMA at 60 °C[a]

comonomer					copolymer		
M_1	$[M_1]/[MMA]$	[AIBN] (mmol/L)	time (h)	yield (%)	$M_n \times 10^{-4}$ (GPC)[b]	M_w/M_n (GPC)[b]	$[CH{=}N^+{-}O^-]/[MMA]$[c]
HMPN	0.1/99.9	5	5	16.4	16.4	1.7	0.0/100.0
	0.5/99.5	5	7	5.0	7.1	2.2	0.2/99.8
	3.4/96.6	5	24	9.5	5.1	2.4	1.4/98.6
	3.4/96.6	5	50	17.0	8.9	2.0	6.6/93.4
HMDN	3.5/96.5	5	6	3.3	7.7	4.8	6.3/93.7
	3.5/96.5	5	24	71.7	>36.8	2.2	4.2/95.8
	13.1/86.9	5	6	0.0			
	3.5/96.5	10	6	31.0	>23.8	2.0	5.7/94.3
	13.1/86.9	10	24	64.9	21.1	2.2	17.3/82.7

[a] Polymerization mixture in a glass tube sealed under vacuum was heated at 60 °C with stirring. After a prescribed time, the mixture was poured into aqueous methanol, and then precipitated polymer was filtered and dried in vacuo at 40 °C. The filtrate was evaporated in vacuo to give negligible amounts of methanol-soluble oligomers. HMDN was not dissolved completely at room temperature but dissolved at 60 °C. [b] Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were measured at 40 °C by the use of tetrahydrofuran and polystyrene ($500-1.11 \times 10^6$) as an eluent and a molecular weight standard, respectively. [c] Estimated from the area ratio of given ^{1}H NMR signals.

shows that the side chain carrying the nitrone chromophore exists in the same proportion in the copolymer. In contrast, the NMR signals at 9.6, 4.8, 3.2, and 2.5 ppm cannot be assigned to the MMA unit or the nitrone chromophore.

These signals are very likely to attributable to the 1,3-dipolar cycloaddition product. We therefore attempted to prepare this addition product by treating the model diarylnitrone HIPN with excess MMA for 50 h at 60 °C. We isolated 4-formyl-3-hydroxyphenyl isobutylate (FHI; yield 5%) and the tetrahydro-1,2-oxazoline derivative (yield 82%), which corresponds well to the desired addition product. No polymeric materials were obtained. Ali and co-workers reported that highly regio- and stereoselective 1,3-dipolar cycloaddition between cyclic nitrone and MMA proceeds to yield the endo adduct.[13] The stereoisomer (yield 5%) of tetrahydro-1,2-oxazoline derivative was also obtained. The fact that the adduct is obtained in high yield indicates that steric hindrance of the hydroxy group does not suppress the 1,3-dipolar addition. The unknown signals in the ^{1}H NMR spectrum of the MMA−HMPN copolymer are therefore safely assigned to the protons of the oxazoline residue. Additionally, weak signals detected at 11.3 and 9.9 ppm are attributable to the hydroxy and formyl protons of the 4-formyl-2-hydroxyphenyl pendant in the copolymer, respectively. The area ratio of signals for each hydroxy proton and methoxy proton in the MMA−HMPN copolymer gave the following polymer composition ratio: [MMA unit]:[nitrone unit]:[oxazoline unit]:[4-formyl-2-hydroxyphenyl unit] = 95.1:1.3:3.5:0.1.

To exert a large steric effect on the 1,3-dipolar cycloaddition, two methyl groups were introduced into the ortho positions on the *N*-arylbenzene ring in HMPN (HMDN). The radical copolymerization of HMDN with MMA under the same conditions ([2,2′-azobis(isobutyronitrile) (AIBN)] = 5 mmol/L; 60 °C, 6 h) gave a copolymer in 3.3% yield ($M_n = 7.7 \times 10^4$, $M_w/M_n = 4.8$; see Table 1). Prolonged polymerization drastically increased not only the polymer yield but also the M_n. The ^{1}H NMR spectrum of the copolymer obtained is depicted in Figure 1. There are signals attributable to the protons of the diarylnitrone pendant [δ (ppm) = 13.0 (OH), 7.6 (CH=N), 7.2 (overlap with the solvent signals, Ph−H), 7.1 (Ph−H), 6.6−6.9 (Ph−H)], and no other signals are observed in the lower magnetic field region than 4.0 ppm. This finding demonstrates that steric hindrance of the two methyl groups almost completely suppressed the 1,3-dipolar cycloaddition of MMA to the nitrone moiety, and even the addition of propagating radical to this moiety was effectively inhibited by the steric bulkiness.

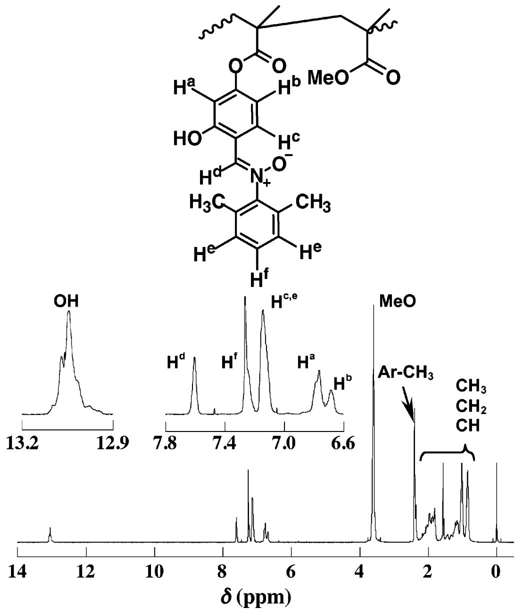

Figure 1. ^{1}H NMR spectrum of polymer obtained by copolymerization ([α-(2-hydroxy-4-methacryloyloxyphenyl)-*N*-(2,6-dimethylphenyl)nitrone]/[methyl methacrylate] = 13.1/86.9) in $CDCl_3$ containing tetramethylsilane.

In this polymerization the induction period seems to be long. Although the reason for this long induction period may be found in the radical capture by the $-CH{=}N^+(-O^-)-$ moiety or the inhibition by the phenolic hydroxy group of HMDN, we propose another reason. In our system the polymerization proceeds in a reaction tube which was placed in an oil bath (60 °C). The insufficient stirring is very likely to cause heterogeneity in the polymerization mixture. In fact, the results in Table 1 were obtained when the depth of the polymerization mixture in the tube was longer than 3 cm, whereas the shorter depth of this mixture (<1 cm) gave no polymer. The possibilities of reaction heat accumulation and gel effects will be discussed in the near future.

The HMDN−MMA copolymer exhibits a UV absorption spectrum with maxima at 344 and 294 nm (Figure 2). This spectrum is very similar to that of the model nitrone HDN having absorption maxima at 346 and 291 nm. The absorbance ratio at their absorption maximum wavelengths allowed us to estimate the concentration

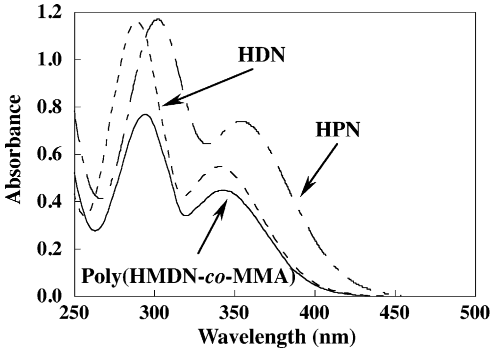

Figure 2. UV absorption spectra of copolymer of α-(2-hydroxy-4-methacryloyloxyphenyl)-*N*-(2,6-dimethylphenyl)nitrone (HMDN) and methyl methacrylate (MMA) ([HMDN]/[MMA] = 17.3/82.7, 5.96×10^{-2} g/L), α-(2-hydroxyphenyl)-*N*-(2,6-dimethylphenyl)nitrone (HDN, 1.0×10^{-4} mol/L), and α-(2-hydroxyphenyl)-*N*-phenylnitrone (HPN, 1.0×10^{-4} mol/L)[8] in $CHCl_3$.

of the diarylnitrone pendant in the copolymer as 1.4×10^{-3} mol/g. This value agrees well with that evaluated from the area ratio of given ^{1}H NMR signals (1.2×10^{-3} mol/g), allowing that negligible decomposition of the diarylnitrone pendant occurs during the copolymerization.

In conclusion, we succeeded in obtaining a copolymer with sufficient amounts of the hydroxy-substituted diarylnitrone pendants in good yield without undergoing the 1,3-dipolar cycloaddition and radical addition to the nitrone moiety by introducing steric bulkiness using the two methyl groups on the *N*-phenyl side. Additionally, the refractive index of the copolymer obtained in this study may be controlled by irradiation because the polymer has the photoreactive nitrone moiety. One of the problems is whether before photoisomerization steric hindrance of the two ortho methyl groups renders the perpendicular orientation of the *N*-phenyl and C=N−O planes possible to greatly weaken the π-conjugation. The finding that the UV absorption maxima of the HMDN−MMA copolymer and HDN are shifted to shorter wavelengths compared with that of α-(2-hydroxyphenyl)-*N*-phenylnitrone (HPN),[8] as shown in Figure 2, substantiates the weakened π-conjugation and, hence, allows us to predict that the photoreactivity as well as the extent to which refractive index is changed is influenced by this drop in π-conjugation.

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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) Lekishvili, N. G.; Nadareishvili, L. I.; Zaikov, G. E.; Khananashvili, L. M. *Polymers and Polymeric Materials for Fiber and Gradient Optics*; VSP: Utrecht, 2002.
(3) Kada, T.; Obara, A.; Watanabe, T.; Miyata, S.; Liang, C. X.; Machida, H.; Kiso, K. *J. Appl. Phys.* **2000**, *87*, 638−642.
(4) Kinoshita, K.; Horie, K.; Morino, S.; Nishikubo, T. *Appl. Phys. Lett.* **1997**, *70*, 2940−2942.
(5) Kato, Y.; Muta, H.; Takahashi, S.; Horie, K.; Nagai, T. *Polym. J.* **2001**, *33*, 868−873.
(6) Kato, Y.; Horie, K. *Macromol. Chem. Phys.* **2002**, *203*, 2290−2295.
(7) Kondo, H.; Tanaka, K.; Kubo, K.; Igarashi, T.; Sakurai, T. *Heterocycles* **2004**, *63*, 241−247.
(8) Tanaka, K.; Shima, K.; Kondoh, H.; Igarashi, T.; Sakurai, T. *J. Appl. Polym. Sci.*, in press.
(9) Heinenberg, M.; Ritter, H. *Macromol. Chem. Phys.* **1999**, *200*, 1792−1805.
(10) Heinenberg, M.; Menges, B.; Mittler, S.; Ritter, H. *Macromolecules* **2002**, *35*, 3448−3455.
(11) Iwamura, M.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 856−860.
(12) Iwamura, M.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 860−863.
(13) Al-Jaroudi, S. S.; Perzanowski, H. P.; Wazeer, M. I. M.; Ali, S. A. *Tetrahedron* **1997**, *53*, 5581−5592.

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