Large Photoinduced Refractive Index Changes of Transparent Polymer Films Containing Photoeliminable Diazo and Azido Groups

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ABSTRACT: We measured photoinduced refractive index changes of polymer films containing various compounds, such as α-diazoketone derivatives, azide derivatives, and others which induce the loss of nitrogen molecules during photoirradiation. PMMA films containing 20 wt % of 2-diazo-1-indanone (2DI) and *β*-azidostyrene (*β*-AS) showed large refractive index changes of 0.015 during photolysis, keeping transparency throughout the entire visible region. The fact that the chemical structure of the substituents at α-position of the diazo group and hence the resonance effect do not affect the photoinduced changes in refractive indices much indicates the major contribution of the elimination effect of nitrogen molecules to the refractive index changes. Azide derivatives except for *β*-AS showed small refractive index changes which may be related to the chemical structure of the photoproducts. Discussion is given on the estimation of the molar refraction and the contribution of the changes in electronic structure and in density to the refractive index of the systems.

Introduction

Recently, organic polymers have received considerable attention as substances for various optical components, such as holographic image recordings, optical memories, optical waveguides, and other optical elements because of their interesting advantages compared to inorganic substances in their processability and reasonable prices. To control optical properties of polymer films, we can use various methods. For example, electrooptical effects, photorefractive effects, and optical nonlinear effects induce transient modulation in optical properties of polymer films. On the other hand, a photochemical reaction in a polymer film changes various properties such as its solubility, absorption, and refractive index, and these modulations are not transient. The refractive index modulation induced by a photochemical reaction remains after irradiation. So photochemically induced refractive index changes can be used to make refractive index patterns in a polymer film.

We know two kinds of photochemical reactions, reversible ones and irreversible ones. Photoisomerization is a reversible one and is applicable to write−read−erase (WRE) recordings and switching devices.[1−7] Typical compounds used for photoisomerization are azobenzene, spirobenzopyran, and diarylethene derivatives. Photopolymerization, photolocking, and photoelimination are irreversible reactions, and can be used for read-only holographic memories, waveguide lithography, microlenses, and other optical elements.[8−12] For these applications, large photoinduced refractive index changes in polymer films are desired. Transparency in a wide visible region is also very important. Since the relationship between refractive index spectra and absorption spectra is described by the Kramers−Kronig transformation,[7] it is rather difficult to realize both large refractive index changes and transparency in a wide visible region at the same time. Thus we may have to balance these two factors.

Photoinduced refractive index changes of polymer films doped with various photochromic materials were reported previously by several authors. Tanio and Irie[3] obtained the refractive index change of 10^{-3} by isomerization of some diarylethenes. Natansohn et al.[2] realized large changes in refractive index of 10^{-2} by isomerization of electron donor−acceptor substituted azobenzene groups. However, a number of photochromic dyes have absorption bands in the visible wavelength region after photoirradiation.

We have obtained so far large refractive index changes of −0.01 and −0.037 at 633 nm by using photoisomerization of norbornadiene derivatives[13] and photodimerization of poly(vinyl cinnamate) (PVCm) film,[14] respectively, keeping transparency throughout the whole visible region. Beeson et al.[15] reported large refractive index changes of 0.026 by photobleaching of (4-*N*,*N*-dimethylaminophenyl)-*N*-phenyl nitrone doped in poly(methyl methacrylate) (PMMA) film. These large changes in refractive index are due to the loss of *π*-conjugation by photoreaction that leads to large changes in electronic delocalization. These are very large values for refractive index changes at wavelengths far from the resonant region. Thus large refractive index changes and transparency can be compatible to a certain degree.

For the simultaneous realization of large refractive index change and transparency, photoeliminations of molecules such as nitrogen or carbon dioxide are very interesting. It is well-known that α-diazoketone and azide derivatives have been studied and used as positive-tone and negative-tone photoresists, respectively, as the former photochemically transform to carboxylic acids and the latter generate nitrenes to cross-link the polymer chains.[16,17] Photoelimination may induce not only the loss of *π*-conjugation but also the loss of eliminating molecules. These losses lead to decreases in both the molar refraction and the density of the polymer film so the refractive indices of the polymer film are expected to decrease additively.

In the present study, we measured photoinduced refractive index changes in polymer films containing photoreactive compounds, such as α-diazoketone derivatives, azide derivatives, and other compounds which induce the loss of nitrogen molecules by photoirradia-

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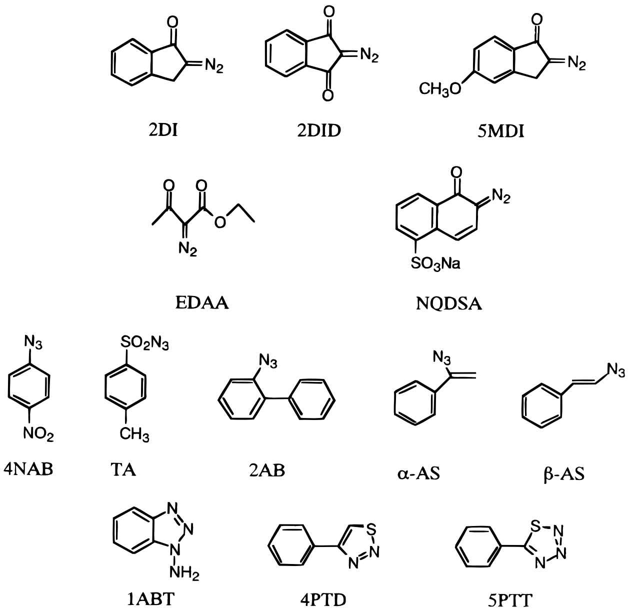


Figure 1. Chemical structure of photoeliminable groups, α-diazoketone derivatives, azide derivatives, and other compounds.

tion. We also investigated the relationship between the changes in refractive index and the molecular structure by using a molar refraction as a parameter connecting the refractive index and the molecular structure.

Experimental Section

Materials. We used α-diazoketones, azides and other compounds as photoreactive materials. 2-Diazo-1-indanone (2DI),[18] 2-diazo-1,3-indanedione (2DID),[19] 5-methoxy-1-indanone (5MDI),[20] ethyl diazoacetoacetate (EDAA), **1**, 2-naphthoquinone-2-diazide-5-sulfonic acid sodium salt (NQDSA) as α-diazoketone derivatives and 4-nitro-1-azidobenzene (4NAB),[21] tosyl azide (TA), 2-azidobiphenyl (2AB), α-azidostyrene (α-AS), and *β*-azidostyrene (*β*-AS) as azide derivatives, and 1-aminobenzotriazole (1ABT),[22] 4-phenyl-1,2,3-thiadiazole (4PTD),[23] and 5-phenyl-1,2,3,4-thiatriazole (5PTT)[24] were synthesized as described in the literature or general procedures except for EDAA and NQDSA. EDAA and NQDSA were commercially obtained. Chemical structures are shown in Figure 1. As a polymer, we used commercially available PMMA after reprecipitation. Diazo compounds are thermally unstable and many decompose at room temperature. However diazo compounds with carbonyl groups at the α-position of diazo groups are comparatively stable and do not decompose at room temperature. Azido compounds are also stable, especially for phenyl azides. Diazo compounds have quite high quantum yields (ϕ) on photolysis. We measured ϕ on photolysis of α-diazoketone derivatives in PMMA films and obtained high values of 0.61 (2DI), 0.96 (2DID), and 0.79 (EDAA) at room temparature.

Absorption Spectrum and Refractive Index Measurements. The photoreaction was carried out by using a 450 W high-pressure mercury lamp with an appropriate filter. The absorption spectra of the photoreactive compounds before and after photoirradiation were measured in acetonitrile solutions. The refractive indices of the polymer films were measured using an m-line method.[7,25] The probe beam for refractive index measurements is a tunable He−Ne laser (LSTP-1010, Reseach Electro Optics). Films for refractive index measurements with a thickness of about 3 μm were prepared by using a barcorter method[7] from about 10 wt % solutions of PMMA containing photoreactive compounds with various weight fractions for PMMA in methylene chloride on fused silica substrates. We measured the refractive indices of the polymer films containing photoreactive compounds before and after irradiation in TE modes at 632.8 nm. We also measured the refractive indices on the TM polarization for some samples, but there exists only a very small anisotropy (n_{TM} are larger than n_{TE} by about 0.0005) as is true in a PMMA film both before and after photoirradiation.

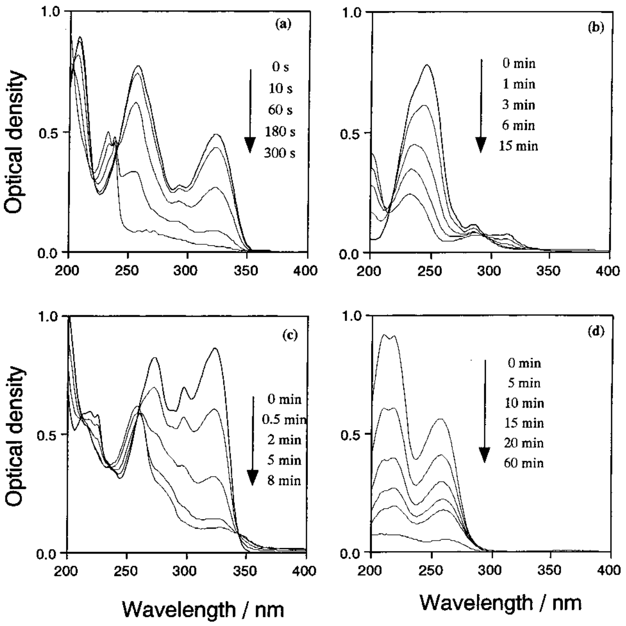


Figure 2. Absorption spectra of α-diazoketone derivatives in acetonitrile solutions before and after photoirradiation: (a) 2DI in 5.0 × 10^{-5} mol/L solution; (b) 2DID in 1.4 × 10^{-5} mol/L solution; (c) 5MDI in 5.0 × 10^{-5} mol/L solution; (d) EDAA in 5.0 × 10^{-5} mol/L solution. Arrows show the direction of change during photoirradiation. Photoirradiation times are shown beside the arrows.

NMR Measurements of Photoproducts. The products obtained by the photolysis of 2DI and 2DID were identified by NMR spectra. Photoreactions were carried out as solutions in methyl trimethyl acetate (MTA) because the chemical structure of MTA is quite similar to that of PMMA. After photoreaction, MTA solutions were evaporated, the residues were dried under reduced pressure, and their NMR spectra were measured.

Density Measurements of Films. The densities of PMMA films containing 2DI and 2DID before and after photoreaction were determined by using a float method. The density of a mixed solution of cyclohexane and carbon tetrachloride is described in eq 1,[26] where ρ^{25} is the density of the mixed

$$\rho^{25} = 0.32732 \times 10^{-8}C^4 - 0.24564 \times 10^{-6}C^3 + 3.5653 \times 10^{-5}C^2 + 0.37169 \times 10^{-2}C + 0.77387 \quad (1)$$

solution at 25 °C and C is the weight fraction of carbon tetrachloride in the mixed solution. PMMA is not soluble either in these two solvents or in the mixed solution. We could measure the density of polymer films by changing the mixing ratio of these two solutions.

Results and Discussion

Photoinduced Refractive Index Changes of PMMA Films with α-Diazoketone Derivatives. The changes in absorption spectra of 2DI, 2DID, 5MDI, and EDAA before and after irradiation are shown in Figure 2. 2DI has intense absorption peaks at 325 nm ($\epsilon = 1 \times 10^4$ L cm^{-1} mol^{-1}) and 255 nm ($\epsilon = 1.6 \times 10^4$ L cm^{-1} mol^{-1}), and after UV irradiation the absorption peaks decreased almost completely. An isosbectic point was observed at 240 nm. Accompanied by the decrease in absorption, the refractive indices of doped PMMA films decreased. Figure 3a shows the relationship between the weight fractions of 2DI in PMMA films and the refrac-

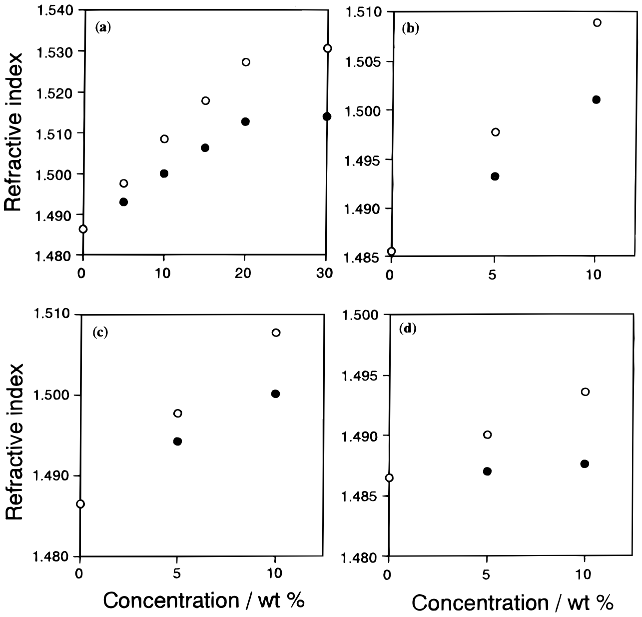


Figure 3. Refractive indices of PMMA films containing various weight fractions of α-diazoketone derivatives before (open circle) and after 30 min of photoirradiation (filled circle): (a) 2DI; (b) 2DID; (c) 5MDI; (d) EDAA.

tive indices before and after photoreaction. Up to 20 wt % doping, the refractive indices of PMMA films are in proportion to the weight fractions of 2DI in PMMA. However the refractive index of PMMA film doped with 30 wt % of 2DI no longer bears a linear relation to the weight fraction due to partial crystallization induced by microscopic aggregation of 2DI molecules in the PMMA film. Eventually we obtained large changes in refractive index of −0.015 by photoirradiation of the PMMA film doped with 20 wt % of 2DI. This is very large for refractive index changes induced by a photochemical reaction in a nonresonant wavelength region and is enough to make a channel waveguide. 2DID has an intense absorption peak at 245 nm ($\epsilon = 4.2 \times 10^4$ L cm^{-1} mol^{-1}), and after irradiation, a large decrease in the absorption peak was observed as in the case of 2DI. Although the peak wavelength is much shorter than that of 2DI, the peak intensity is much larger. The refractive indices of 2DID-doped PMMA films before and after irradiation (Figure 3b) are almost the same as those of 2DI. The changes in refractive index are of course equal to those of 2DI. 5MDI has a methoxy group at the para position to a carbonyl group on the benzene ring and has more intense absorption bands about 325 nm (Figure 2c) than 2DI. The refractive indices of doped PMMA films are also larger than those of 2DI. However, the refractive index changes (Figure 3c) are almost equal to or somewhat smaller than those of 2DI. EDAA has no aromatic ring and has absorption bands at a much shorter wavelength region (Figure 2d), but shows reasonably large refractive index changes in PMMA films (Figure 3d). These suggest that the substituents (the carbonyl groups at α-position etc.) do not affect the refractive indices and the refractive index changes as much. The comparison in refractive index changes of various α-diazoketone derivatives in PMMA is summarized in Table 1. We can see that the refractive index changes are not affected by their substituents very much. Though naphthoquinonediazide derivative (NQD-SA) has a long π-conjugation system and loses it during photoreaction, the refractive index change is not that much larger compared to those of other α-diazoketone derivatives. From these results, we suggest that the loss of the nitrogen molecules mainly contributes to the refractive index changes of α-diazoketone derivatives.

Table 1. Refractive Indices and Refractive Index Changes of PMMA Films Containing Various α-Diazoketone Derivatives before and after Photoirradiation (at 633 nm, in TE Mode)[a]

	5 wt %			10 wt %		
	n_b	n_a	$-\Delta n$	n_b	n_a	$-\Delta n$
PMMA	1.4865					
2DI/PMMA	1.4976	1.4932	0.0044	1.5088	1.4999	0.0089
2DID/PMMA	1.4978	1.4932	0.0046	1.5089	1.501	0.0078
5MDI/PMMA	1.4987	1.4949	0.0038	1.5078	1.5002	0.0076
EDAA/PMMA	1.4900	1.4870	0.0030	1.4935	1.4876	0.0059
NQDSA/PHEMA[b]	1.5164	1.5109	0.0055			

[a] n_b = refractive index before irradiation; n_a = refractive index after irradiation. [b] Poly(hydroxyethyl methacrylate).

Estimation of Molar Refractions of 2DI and 2DID. We introduce a molar refraction as a parameter to relate two properties, the refractive index of a molecule and its chemical structure. The molar refraction is described by the Lorentz−Lorenz equation, eq 2.[27] where R is the molar refraction, n is the refractive

$$R = \frac{n^2 - 1}{n^2 + 2} V, \quad V = \frac{M}{\rho} \tag{2}$$

index, V is the molar volume, M is the molar mass, and ρ is the density. To calculate the molar refractions of the doped polymer matrixes, we define the mean molar refraction $\bar{R}$ described in eq 3,[28] where $\bar{R}$ is the mean

$$\bar{R} = x\, R_A + (1 - x)\, R_B \tag{3}$$

molar refraction, x is the mole fraction of molecule A in the polymer film B given in moles of polymer base. $\bar{R}$ can also be described by using the Lorentz−Lorenz equation with the mean molar mass and the density of the polymer film.

As is in eq 2, the molar refraction of a compound is determined by the refractive index and the molar volume of the compound. Generally the molar refractions of the compounds that have no resonance structure in the molecule are described by the summation of atomic refractions. However the molar refractions of the compounds with resonance structure (e.g., π-conjugation) are described by the summation of atomic refractions and the contribution of resonance effects. In the case of the photoreactions, such as photoisomerization, where the molar mass and the density of the polymer film almost do not change at all after photoreaction, the refractive index changes are related only to the changes in molar refraction. In other cases of photodimerization and photoelimination, the refractive index changes are related not only to the changes in molar refraction but also to the changes in the density and/or molar mass.

We estimated the molar refractions of 2DI and 2DID. For this estimation, the products during the photolysis of 2DI and 2DID in PMMA films and the density of doped PMMA films were measured. Schemes showing photolysis and the products are depicted in Figure 4. As is well-known, an α-diazoketone derivative releases a nitrogen molecule and yields a carbene during photolysis and then forms a ketene by the Wolff rearrangement to yield a carboxylic acid by the addition of water.[16] After the photolysis in MTA, 2DI was found with NMR

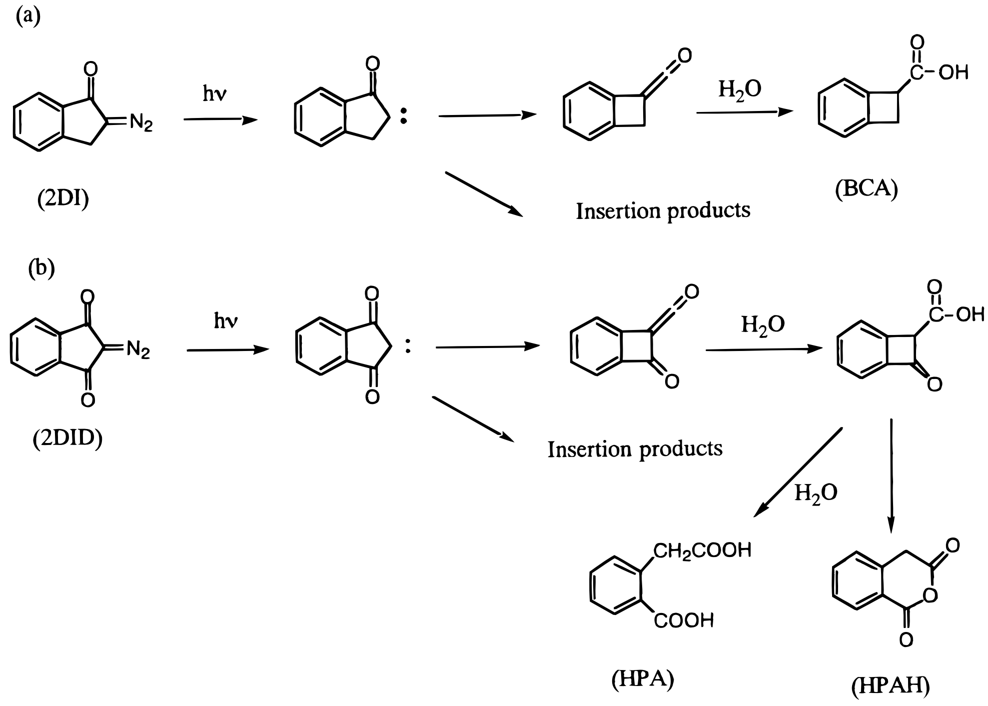


Figure 4. Photoreaction schemes and photoproducts of 2DI (a) and 2DID (b) in MTA solutions.

Table 2. Density of PMMA Film and PMMA Films Containing 5 wt % of 2DI or 2DID before and after Photoirradiation

	density (g/cm^3)	
	before irradiation	after irradiation
PMMA	1.189	
2DI/PMMA	1.204	1.201
2DID/PMMA	1.205	1.208

Table 3. Molar Refractions and Molar Refraction Changes of 2DI and 2DID before and after Photoreaction

	2DI	2DID
R before irradiation (cm^3/mol)	48.29	47.57
R after irradiation (cm^3/mol)	37.97	36.44
$-\Delta R$ (cm^3/mol)	10.31	11.14

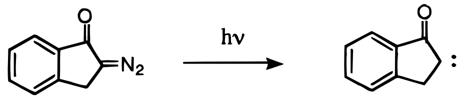
Table 4. Molar Refraction Changes and Specific Refraction Changes of α-Diazoketone Derivatives during Photoelimination of Nitrogen Molecules

	2DI	2DID	EDAA	EDA	PVCm
$-\Delta R$ (cm^3/mol)	10.31	11.34			5.19
$-\Delta R_e$ (cm^3/mol)	11.23	10.65	9.33	8.55	
$-\Delta r_e \times 10^2$(cm^3/g)	2.06	2.02	1.85	1.73	2.98[a]

[a] This value is Δr for PVCm during photodimerization.

to form benzocyclobutene-1-carboxylic acid (BCA) and other insertion products in a ratio of 25:75. This is in good agreement with the reported value.[29] 2DID formed in MTA homophthalic acid (HPA), homophthalic anhydride (HPAH), and other products including the insertion products in a ratio of 20:50:30. The photolysis of 2DID yielded more products with water addition than that of 2DI. This may more or less affect the changes in refractive index because of the difference in the amount of added water whose refractivity is very large. Table 2 shows the density of the PMMA films doped with 5 wt % of 2DI or 2DID before and after photoirradiation. The density of 2DI/PMMA decreases after photolysis due to the loss of nitrogen molecules. On the other hand, the density of 2DID/PMMA increases a little. This may be due to the amount of added water during the photolysis that increases the molar mass of 2DID and thus the density of the polymer film. These density changes may also affect the changes in refractive index of doped polymer films.

Using these results together with eqs 2 and 3, we calculated the molar refractions of 2DI and 2DID before and after photolysis. As is shown in Table 3, the molar refractions of 2DI and 2DID decreased markedly after photolysis. We obtained changes in molar refraction (ΔR) of -10.31 and -11.14 cm^3/mol for 2DI and 2DID, respectively. Recently we obtained large refractive index changes of -0.037 by photodimerization of poly(vinyl cinnamate) film where ΔR was -5.19 cm^3/mol.[14] Compared to this result, it is noteworthy that 2DI and 2DID induce very large changes in molar refraction during photolysis, which led to large changes in refractive indices. The molar refraction changes for only the elimination of nitorogen molecules (ΔR) of 2DI (eq 4)



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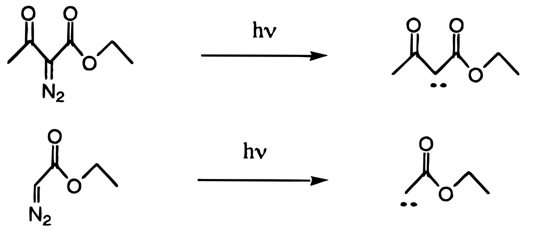
and 2DID were also estimated by assuming that the carbenes were the only photoproducts. The molar refractions of the corresponding carbenes were calculated by using the summation of atomic refractions. We obtained $\Delta R_e = -11.23$ and -10.65 cm^3/mol for 2DI and 2DID (Table 4). These are almost the same values as ΔR. We also calculated the molar refractions of α-diazoketone derivatives having no aromatic rings. EDAA and ethyl diazoacetate (EDA) showed large changes in molar refraction (ΔR_e) of -9.33 and -8.55 cm^3/mol, respectively, during the loss of nitrogen molecules (eq 5). This indicates that the loss of nitrogen molecules contributes strongly to the changes in molar refraction and the substituents have little effect on the values ΔR and ΔR_e. This is in good agreement with the fact that the refractive index changes were not affected by the substituents as mentioned before.



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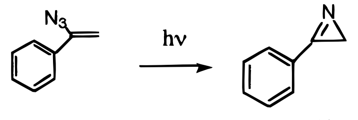
PMMA Films Containing Azide and Triazol Analogues. An azide derivative also releases a nitrogen molecule during photolysis, as does an α-diazoketone derivative, and then it forms a nitrene that induces various chemical reactions, mainly insertion to a C−H bond. Aromatic azides are stable and induce losses of both a nitrogen molecule and π-conjugation from an azido group to a benzene ring. This suggested that we should expect large changes in refractive index resulting from the photolysis of azide compounds. However, the PMMA film containing 5 wt % of 4NAB showed a very small change in refractive index of less than 10^{-3} by photoirradiation. In case of other azides, TA and 2AB, we also obtained only small changes in refractive index as well (−0.0007 and +0.0008 for 5 wt % of TA and 2AB in PMMA films, respectively). This can be explained as follows. During photolysis, azide derivatives in PMMA film release nitrogen molecules, and π-conjugation from an azido group to a benzene ring disappears. Hitherto, the process is similar to the case of α-diazoketone derivatives, so the refractive indices of the polymer films should decrease markedly. However, the products during the photolysis of azides are not the same as those of the α-diazoketone derivatives. An amine has formed by the insertion of a nitrene to a C−H bond. The amine may increase the refractive index of the polymer film after photoirradiation. Eventually, these effects on the changes in refractive index cancel each other and lead to almost no changes in refractive index of the polymer film. All the tendencies for these azides have been ascertained by the behavior of their absorption spectra. For example, 4NAB shows an intense absorption peak at 310 nm which decreases during photoirradiation as shown in Figure 5. However, unlike those for α-diazoketone derivatives, the peaks of 4NAB do not completely disappear and moreover new absorptions that may belong to the photoproducts arise. To sum up, the absorption of azides does not change enough to affect the change in refractive index at 633 nm, far from the absorption peak. This can be explained by the Kramers−Kronig transformation.[7]

α-Azidostyrene (α-AS) and β-azidostyrene (β-AS) are vinyl azides and are known not to produce an amine during photolysis as shown in eqs 6 and 7.[30,31]



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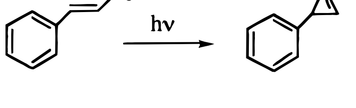

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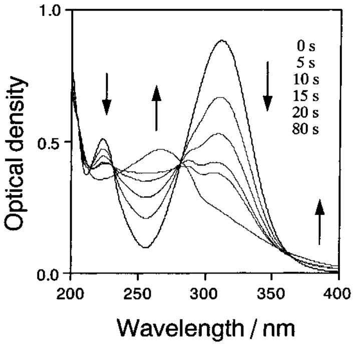


Figure 5. Absorption spectra of 4NAB in 5.0 × 10^{-5} mol/L acetonitrile solution before and after photoirradiation. Arrows show the direction of change during photoirradiation. Photoirradiation times are shown beside the arrow.

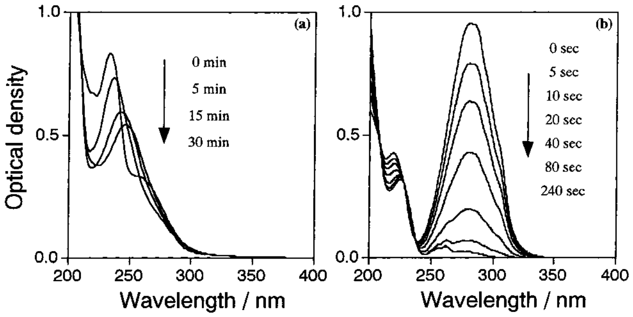


Figure 6. Absorption spectra of α-AS and β-AS in acetonitrile solutions before and after photoirradiation. (a) α-AS in 5.9 × 10^{-5} mol/L solution, (b) β-AS in 3.5 × 10^{-5} mol/L solution. Arrows show the direction of change during photoirradiation. Photoirradiation times are shown beside the arrows.

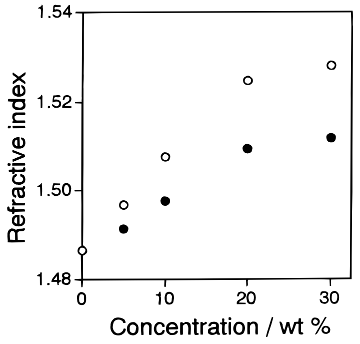


Figure 7. Refractive indices of PMMA films containing various weight fractions of β-AS before (open circle) and after 30 min of photoirradiation (filled circle).

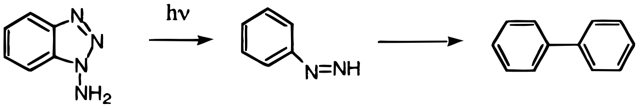
The changes in absorption spectra of α-AS and β-AS before and after photoirradiation are shown in Figure 6. We can see large differences in these two spectra. β-AS has an intense absorption peak at 280 nm ($\epsilon = 2.7 \times 10^4$ L cm^{-1} mol^{-1}) and the absorption decreased completely after irradiation. On the other hand, α-AS has an intense peak at 233 nm ($\epsilon = 1.5 \times 10^4$ L cm^{-1} mol^{-1}), and after irradiation the absorption peak did not decrease largely but shifted to a larger wavelength. The behavior in absorption spectra of α-AS and β-AS is similar to that of other azido and diazo compounds, respectively. The refractive indices of the PMMA film doped with various weight fractions of β-AS before and after photoirradiation are shown in Figure 7. As the weight fraction of β-AS becomes higher, the relationship between the refractive indices and the weight fractions of β-AS becomes nonlinear as in the case of 2DI. The refractive index changes of the PMMA film doped with 5 and 20 wt % of β-AS are −0.0054 and −0.015, respectively, which are almost the same as or somewhat larger than those of 2DI. On the other hand, the PMMA film doped with 10 wt % of α-AS showed small changes in refractive index of −0.0015, which can be expected

Table 5. Refractive Indices and Refractive Index Changes of PMMA Films Containing 10 wt % of Vinyl Azides before and after Photoirradiation (at 633 nm, in TE Mode)

	α-azidostyrene/PMMA	β-azidostyrene/PMMA
n before irradiation	1.5057	1.5076
n after irradiation	1.5042	1.4978
$-\Delta n$	0.0015	0.0098

from its absorption spectra (Table 5). These differences in refractive index between α-AS and β-AS are due to the differences in electronic structure both before and after irradiation, i.e., the electronic structure before irradiation of β-AS shows larger conjugation than that of α-AS and the electronic structure after irradiation of β-AS provides smaller conjugation than that of α-AS.

Two nitrogen molecules are lost during the photolysis of 1ABT, as shown in eq 8. One nitrogen molecule is lost on photolysis and then another nitrogen molecule is lost thermally.[32] In the process, the degree of delocalization of π-electrons changes accompanied by the loss of two nitrogen molecules. So we expected that the refractive indices of the polymer film containing 1ABT changes to some extent. In fact, PMMA films doped with 5 wt % of 1ABT showed large changes in the refractive index of −0.0045 during photolysis. This value is the same as that of 2DI and it is very large for a photoinduced refractive index change in a nonresonant region.



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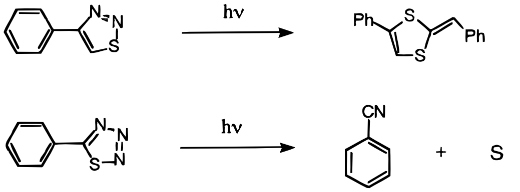
4PTD and 5PTT possess three and four contiguous heteroatoms in a five-membered aromatic ring, respectively. They release nitrogen molecules, and the aromatic rings disappear during photolysis as shown in eq 9.[33,34] Therefore, we introduced these compounds to the polymer films, expecting a large refractive index change during photolysis. However, PMMA films containing 5 wt % of 4PTD and 5PTT showed small changes in refractive index of −0.0014 and −0.0015 during photolysis, respectively. These results might be explained by the tendency that the compounds produced during the photolysis have large molar refractions compared to the case of α-diazoketone derivatives which suppresses the decrease in refractive indices of PMMA films after photoirradiation, and hence the changes in refractive index become relatively small. These results suggest that materials which give rise to the products of large molar refractions after photolysis are not suitable for making large refractive index patterns.



(9)

Factors Affecting the Photoinduced Refractive Index Changes. The refractive index changes in doped polymer films induced by photoelimination of a part of dopants, such as α-diazoketone derivatives, are not much influenced by the substituents of the dopants which change the resonant structure of the dopants but are strongly influenced by the loss of nitrogen molecules from the films. The loss of nitrogen molecules decreases the molar refractions of photoreactive compounds and the density of the polymer film, resulting in large decreases in the refractive index of the polymer film. These decreases in both the molar refractions of the dopants and the density of the polymer film contribute to the refractive index decreases in the polymer film. In the case of a photoreaction such as photoisomerization, where the thickness of the polymer film before and after photoirradiation does not change, the molar volume of the polymer film does not change, so the refractive index changes correspond directly to the molar refraction changes as is shown in eq 2. Since the molar refraction is described as the summation of atomic and/or atomic group refractions, the refractive index changes are related to the changes in electronic structure of the photoreactive compounds. In other words, the refractive index changes of the polymer film are described only by the changes in electronic structure, especially for electronic delocalization, of photoreactive compounds. In contrast to the case of photoisomerization, photoelimination gives rise to thickness changes of the polymer film. Upon photolysis, nitrogen molecules are liberated in the polymer film and some nitrogen molecules may go out of the polymer film, making holes in the polymer film. These holes should not remain as they are, but they should be filled up to a certain degree by the polymer chains followed by a decrease in the thickness of the polymer film. The density of the polymer film does not decrease in proportion to the change in the mean molar mass of the polymer film, so the molar volume decreases. Thus the loss of nitrogen molecules during photolysis induces several effects on the decrease of the refractive index of the polymer film.

For simplicity, we define the specific refraction, *r*, as given by eq 10. By using *r*, we can describe the

$$r = \frac{R}{M} \quad r{\cdot}\rho = \frac{n^2 - 1}{n^2 + 2} \tag{10}$$

refractive index changes just by the changes in *r* and the density ρ. The *r* value is related to the electronic structure of the compounds, so we can divide the contribution for the changes in refractive index into two independent parameters, Δr and $\Delta\rho$ that show the changes in electronic structure and in the density of the polymer film, respectively. Here we caluculated the specific refractions of α-diazoketone derivatives during photoelimination of nitrogen molecules ($\Delta r_e = (R/M)_{\text{after}} - (R/M)_{\text{before}}$). As is shown in Table 4, all α-diazoketone derivatives have almost the same values of Δr as in the case of ΔR and ΔR_e, and have slightly smaller values of Δr_e than PVCm. This is different from the case of ΔR and ΔR_e where α-diazoketone derivatives have much larger values of ΔR than PVCm. Since ΔR and ΔR_e include the contribution of the changes in molar mass, ΔR and ΔR_e cannot represent the changes in electronic structure during photolysis exactly. Δr_e is a value where the effect of the molar mass changes has been reduced, so it represents the changes in electronic structure during the loss of nitrogen molecules more exactly. Consequently, the changes in the electronic structure of α-diazoketone derivatives during photoelimination of nitrogen molecules are comparable to or somewhat smaller than those of PVCm during photodimerization.

A PMMA film containing 2DI shows the density changes during photoirradiation, which, together with the changes in electronic structure, contribute to the large refractive index changes. At this point, 2DI is quite different from the case of PVCm where Δr and $\Delta\rho$ show effects in opposite directions, canceling the refractive index changes.

The contribution of Δr and $\Delta\rho$ to refractive index changes can be described separately as eq 11. We

$$\Delta\left(\frac{n^2-1}{n^2+2}\right) = \Delta(r\cdot\rho) \cong \rho(\Delta r) + r(\Delta\rho) \qquad (11)$$

introduced this equation to the PMMA film containing 2DI by using the mean specific refraction, $\bar{r}$, of the film and its change, $\Delta\bar{r}$, during photolysis in place of r and Δr, respectively, based on eq 3 together with the density, ρ, of the film. The contribution of the changes in electronic structure and density to the changes in refractve index was estimated for the photolysis of 5 wt % 2DI in PMMA film by using the values $\Delta\bar{r} = -2.86 \times 10^{-3}$ cm^3/g and $\bar{r} = -0.249$ cm^3/g. The results are $\rho(\Delta\bar{r}) = -3.44 \times 10^{-3}$ and $\bar{r}(\Delta\rho) = -7.46 \times 10^{-4}$, which suggest the major contribution of $\Delta\bar{r}$, in other words, the changes in electronic structure for the refractive index changes of the PMMA film containing 5 wt % of 2DI.

PMMA films containing 5 wt % of 1ABT showed a series of refractive index changes as follows.

$$n_{\mathrm{b}}\ (1.4957) \xrightarrow{h\nu} n_{\mathrm{a}}\ (1.4912) \xrightarrow{T_{\mathrm{g}}} n_{\mathrm{a}}$$

after annealing (1.4919)

After photolysis, a PMMA film containing 5 wt % 1ABT was annealed just above the glass transition temperature (T_g) resulting in a little increase in the refractive index. This indicates that the density of PMMA film containing 1ABT after photoirradiation is a little smaller than that before photoirradiation. Upon heating above T_g, micro-Brownian motion of the polymer chains is liberated with the increase of density of the polymer film to the value before photoirradiation, and hence the refractive index of the polymer film increases. However this increase ($\Delta n = 0.0007$) is small compared to the changes in refractive index during photolysis ($\Delta n = -0.0045$). This is in good agreement with the case of 2DI. Consequently, the contribution of Δr, which is mainly related to the changes in electronic structure, to the changes in total refractive index (80% and 85% in this case of 2DI and 1ABT in PMMA film, respectively) turned out to be much larger than that of $\Delta\rho$.

Conclusion

We measured the refractive indices before and after photoirradiation of PMMA films containing various compounds which release nitrogen molecules during photolysis. We obtained the refractive index changes of 0.015 by photolysis of a PMMA film containing 20 wt % of 2DI. This is a very large change of the refractive index induced by a photochemical reaction, and this polymer is transparent over the entire visible region. 2DI shows a high quantum yield of photoreaction ($\phi = 0.61$) in PMMA film and stability at room temperature. These results suggest the applicability of photoelimination in 2DI and other α-diazoketone derivatives to make various refractive index patterns.

Refractive index changes of α-diazoketone derivatives are of the same order of magnitudes regardless of the types of substituents even in the case of highly electronically delocalized NQDSA. This suggests that the release of nitrogen molecules mainly contributes to the refractive index changes of PMMA films containing α-diazoketone derivatives. On the other hand, azides and other compounds except for β-AS and 1ABT show only small changes in refractive index in PMMA films during photolysis. This is attributed to the nature of products during photolysis which have large molar refractions and induce the increase in the refractive index of the polymer film after photoirradiation.

The changes in molar refractions of 2DI and 2DID during photolysis are very large and would be the reason of large changes in refractive index of PMMA films. By calculating the specific refractions of various α-diazoketone derivatives, we could see the real and major effect of changes in electronic structure on the refractive index changes separated from that of density changes. The present results suggest that we can obtain large refractive index changes of a polymer film by photoelimination of the dopants which induce large changes in electronic structure by the release of eliminating molecules.

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