

Refractive Index Changes of Doped Polymer Films Induced by the Photoelimination of Meso-Ionic Heterocyclic Compounds with and without a Sulfur Atom

Seiichiro MURASE, Masaki BAN and Kazuyuki HORIE*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

(Received August 4, 1999; accepted for publication September 7, 1999)

We measured refractive index changes of doped polymer films induced by photoelimination of meso-ionic heterocyclic compounds. A poly(methyl methacrylate) (PMMA) film containing 30 wt% 3-phenyl-1,2,3,4-oxatriazole-5-thione (3POTT) showed a large refractive index change of -0.02 during photoirradiation, at a wavelength far from the resonant region. PMMA films containing meso-ionic compounds with a sulfur atom in the meso-ionic ring showed large refractive index changes during photoirradiation, while PMMA films containing 3-phenyl-1,2,3,4-oxatriazole-5-one, which possess no sulfur atoms in the meso-ionic ring, showed relatively small changes in refractive index. This difference may be due to the existence of a sulfur atom in the meso-ionic ring. We estimated the specific refractions of the eliminating groups, and we found that both the existence of a sulfur atom and the position of the sulfur atom in the meso-ionic group affect the specific refractions.

KEYWORDS: refractive index change, photoreaction, meso-ionic compounds, phenyl-oxatriazole-thione, dye-doped polymer film, photoeliminable group, microlens, waveguide lithography, holography

1. Introduction

Photochemical reaction is an important process in the fabrication of refractive index patterns in polymer films. Compared to other processes, such as those which involve photorefractive effects and nonlinear optical effects, where the refractive index modulation is very small and can be induced transiently, photochemical reaction induces larger refractive index modulation in a polymer film and the modulation remains after the photoreaction. Therefore, photochemically induced refractive index changes in polymer films have been given much attention for various applications, such as optical memories, switching devices, holography and waveguide lithography.

Photochemical reactions can be categorized into two types of reactions, reversible ones and irreversible ones. Photochromic compounds are well known to induce reversible photoisomerization and have been studied by many groups for application in write-read-erase (WRE) recording devices.¹⁻⁹⁾ On the other hand, photopolymerization, photolocking and other irreversible photochemical reactions are applicable to read-only optical memories, holography, microlenses, and waveguide lithography.¹⁰⁻¹³⁾ For these applications, large refractive index changes induced by photochemical reactions in polymer films should be achieved, and transparency in a wide visible region is also desired. With the properties of large refractive index change and transparency, the polymer system becomes more applicable to various optical devices.

The refractive index, n , of a compound can be related to the molar refraction, R , the molar mass, M , and the density, ρ , by the Lorentz-Lorenz equation, eq. (1) by¹⁴⁾

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} \quad (1)$$

We can introduce this equation into a polymer film using the mean molar refraction, \bar{R} , expressed as eq. (2), where x is the mole fraction of molecule A in the polymer film B given in base moles.

$$\bar{R} = xR_A + (1 - x)R_B \quad (2)$$

Generally, the molar refraction of a compound with no delocalized electrons is described only by the summation of atomic or atomic group refractions. However, the molar refraction of a compound with delocalized electrons, i.e., resonance structure, is described by the summation of atomic refractions and the contribution of resonance effects. Therefore, compounds with delocalized electrons have larger molar refractions and larger refractive indices. We can induce refractive index changes in a polymer film by introducing a compound that changes its molar refraction and/or molar mass and/or density during a photochemical reaction. Photochromic compounds have a large resonance structure and the resonance structure changes during the photochemical reaction, which leads to changes in molar refraction and therefore in the refractive index. Photo-cross-linking in a polymer film induces the density change of the polymer film, which leads to an increase in the refractive index. By using these processes effectively, large refractive index changes can be achieved.

Photoinduced refractive index changes of polymer films containing various photochromic compounds were reported by several authors,²⁻⁶⁾ and they obtained refractive index changes of 10^{-3} – 10^{-2} during photoreaction. However, photochromic dyes have absorption bands in the longer wavelength region.

We have already obtained the large refractive index changes of -0.01 and -0.037 at 633 nm by the photoisomerization of norbornadiene derivatives^{15,16)} and the photodimerization of poly(vinyl cinnamate) (PVCm) film,¹⁷⁾ respectively, maintaining transparency throughout the entire visible wavelength region. Here, it is considered that large refractive index changes were achieved because largely delocalized π -conjugations of photoreactive compounds are lost during the photoreactions. In other words, large decreases in the molar refraction induced by the photoreaction lead to large decreases in the refractive index. Using the same concept, Beeson *et al.*¹⁸⁾ obtained large changes in refractive index of -0.026 by photobleaching (4-*N,N*-dimethylaminophenyl)-*N*-phenyl nitron doped in poly(methyl methacrylate) (PMMA) film.

In our previous paper,¹⁹⁾ we introduced photoeliminable

*To whom all correspondence should be addressed.

groups, such as α -diazoketone derivatives and azido compounds, into polymer films. Since the photoeliminable groups release nitrogen molecules and are accompanied by the loss of resonance structure during photoreaction, decreases in both the molar refraction of the dopant and the density of the polymer film additively contribute to decreases in the refractive index, which lead to the large refractive index changes of polymer films containing various α -diazoketone derivatives. The refractive index change of the polymer film containing 20 wt% 2-diazo-1-indanone (2DI) was -0.015 during photoirradiation. In the course of the study, we found that the loss of nitrogen molecules from various dopants, especially dopants with meso-ionic $=N^+=N^-$ groups, contributes to large refractive index changes of doped polymer films during photoirradiation.

In the present study, we investigated new materials, *meso-ionic heterocyclic compounds*, for making large refractive index patterns in polymer films because of their interesting electronic structure. 3-Phenyl-oxatriazole-5-one (3POTO) is a meso-ionic heterocyclic compound and it is known that, during photoirradiation, 3POTO releases a carbon dioxide molecule to form mainly phenyl azide which is further photolyzed to produce nitrene, or 3POTO is transformed to phenyl isocyanate (Fig. 1).²⁰ In this course, the meso-ionic heterocyclic ring disappears and is accompanied by large changes in resonance structure and in molar mass. This suggests that both the molar refraction and the density of the polymer film containing meso-ionic compounds, such as 3POTO, decrease during photoirradiation; therefore, we can expect large changes in the refractive index of polymer film containing various meso-ionic compounds during photoirradiation.

2. Experimental

2.1 Materials

We used three meso-ionic compounds, 3-phenyl-oxatriazole-5-one (3POTO), 3-phenyl-oxatriazole-5-thione (3POTT) and 3-phenyl-thiatriazole-5-one (3PTTO), in which the heteroatoms in the meso-ionic heterocyclic ring are different. Conventionally, 3POTO is prepared by the nitrosation of phenylhydrazomethanedisulfonate salt or by the coupling of substituted nitromethane ions with phenyldiazonium ions or phenyl isocyanate. Here, we simply synthesized 3POTO from phenylthiosemicarbazide with nitrous acid by performing two steps, combining two reported procedures.^{21,22} 3POTT and 3PTTO were synthesized as described in the literature.²³ Their chemical structures are shown in Fig. 2. The photolysis of 3POTO has been reported, as shown in Fig. 1.²⁰ On the other hand, photoreactions of meso-ionic compounds containing a sulfur atom in the heterocyclic ring, such as 3POTT and 3PTTO, have not been reported. In many cases of photoreactions of heterocyclic ring compounds, the photoreaction

itself occurs irrespective of whether the atoms in the heterocyclic ring are oxygen or sulfur, but the process and/or products of the photoreaction may be different. Although we do not yet know the processes and products of the photoreaction of 3POTT and 3PTTO, it was confirmed from absorption spectra that both 3POTT and 3PTTO undergo some chain-scission reactions under photoirradiation. We used commercially available PMMA after reprecipitation as a polymer.

2.2 Absorption spectrum and refractive index measurements

The photoreaction was carried out 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 by an m-line method.²⁴ The probe beam used for refractive index measurements is a tunable He-Ne laser (LSTP-1010, Research Electro-Optics). Films for refractive index measurements with a thickness of approximately $3 \mu\text{m}$ were prepared by a barcoater method⁸) from approximately 10 wt% solutions of PMMA film 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.

In order to investigate the process of the photoreactions of 3POTT and 3PTTO compared to 3POTO, we measured the IR spectra of PMMA films containing 3POTT or 3PTTO during photoirradiation. Since the photoreaction of 3POTO proceeds through phenyl azide, a peak from azido groups in the phenyl azide at about 2100 cm^{-1} should appear in the IR spectra of the PMMA film containing 3POTO during photoirradiation. On the basis of this type of measurement, we can see whether or not the photoreactions of 3POTT and 3PTTO proceed through phenyl azide. The photoirradiation as carried out using a 450 W high-pressure mercury lamp with a UV29 filter in order to prevent the phenyl azide formed during photolysis of the meso-ionic compounds from contributing to another photolysis due to corresponding UV irradiation.

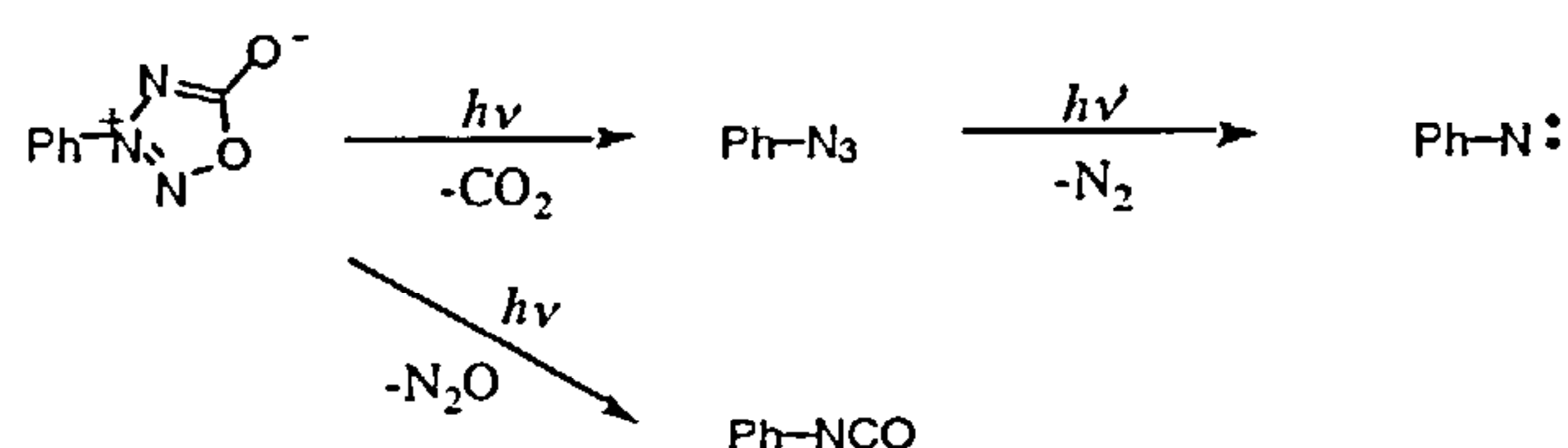


Fig. 1. Photochemical reaction scheme of 3POTO.

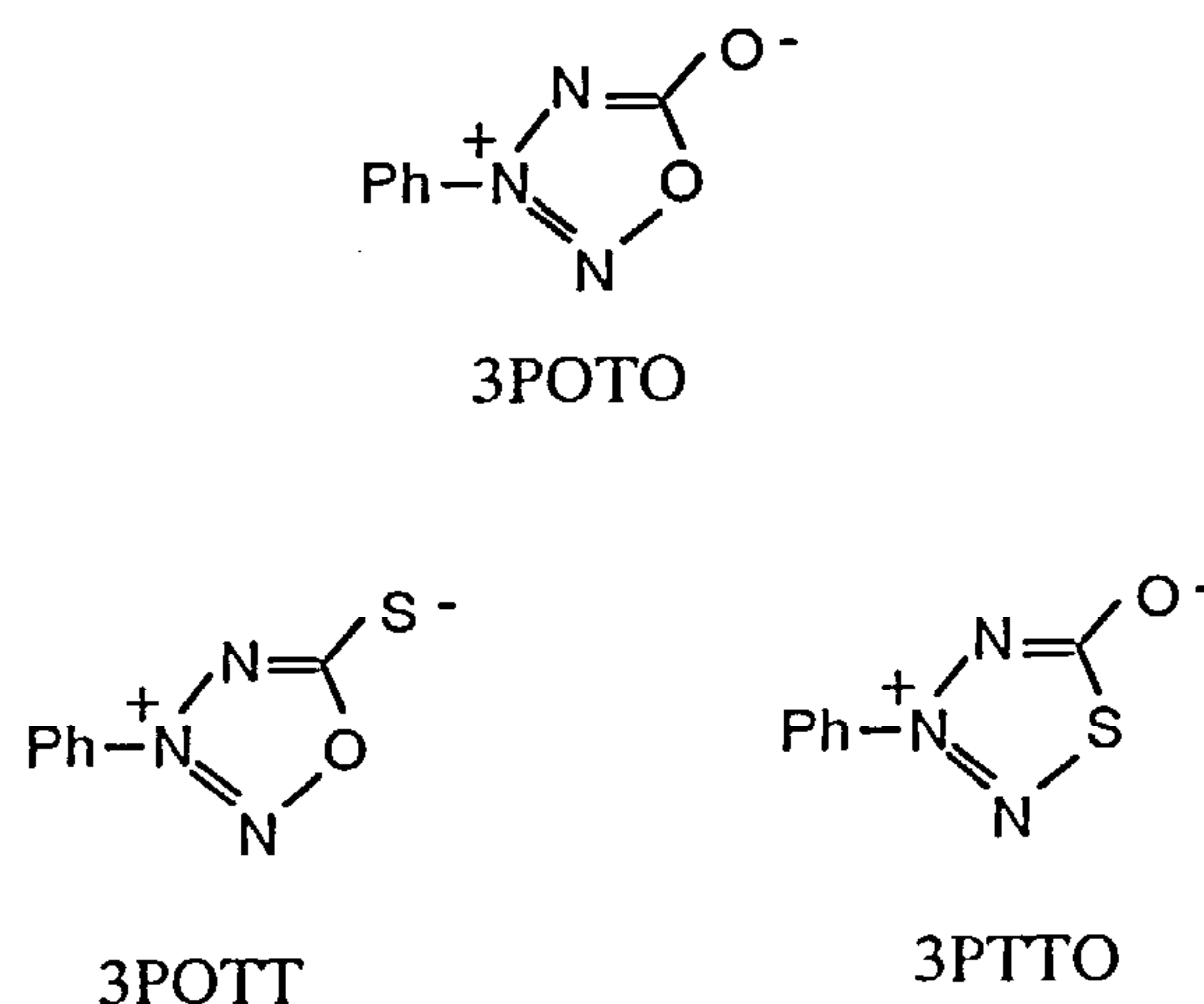


Fig. 2. Chemical structure of meso-ionic compounds.

3. Results and Discussion

3.1 Absorption spectra of meso-ionic compounds before and after photoirradiation

The changes in absorption spectra of 3POTO, 3POTT and 3PTTO are shown in Fig. 3. 3POTO has an intense peak at 265 nm ($\epsilon = 1.1 \times 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$), and after UV irradiation the absorption peak greatly decreased with an increase in absorption around 350 nm [Fig. 3(a)]. Isosbestic points were observed at 240 and 300 nm. 3POTT, which possesses a sulfur atom in the meso-ionic ketone site, has an intense absorption peak at 257 nm ($\epsilon = 2.1 \times 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$) and a broad peak around 390 nm [Fig. 3(b)]. After photoirradiation, the absorption greatly decreased, which suggests that 3POTT undergoes a photochemical reaction. 3PTTO, with a sulfur atom in the meso-ionic ring, showed similar behavior in absorption spectra before ($\epsilon = 1.0 \times 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$ at 271 nm) and after photoirradiation [Fig. 3(c)]. The absorption spectra of 3POTT and 3PTTO before irradiation are different from those of 3POTO in that 3POTT and 3PTTO have absorption bands in longer wavelength regions due to the sulfur atom in the meso-ionic moiety. 3POTT has an absorption band around 390 nm and 3PTTO has an absorption shoulder at 350 nm, which cannot be observed in the absorption spectrum of 3POTO. On the other hand, the absorption spectra of these three meso-ionic compounds after photoirradiation are not very different. This suggests that the photoproducts of these three meso-ionic compounds, 3POTO, 3POTT and 3PTTO, are similar.

3.2 Refractive index changes of PMMA film containing meso-ionic compounds during photoirradiation

The refractive indices of PMMA films containing various meso-ionic compounds decreased after photoirradiation

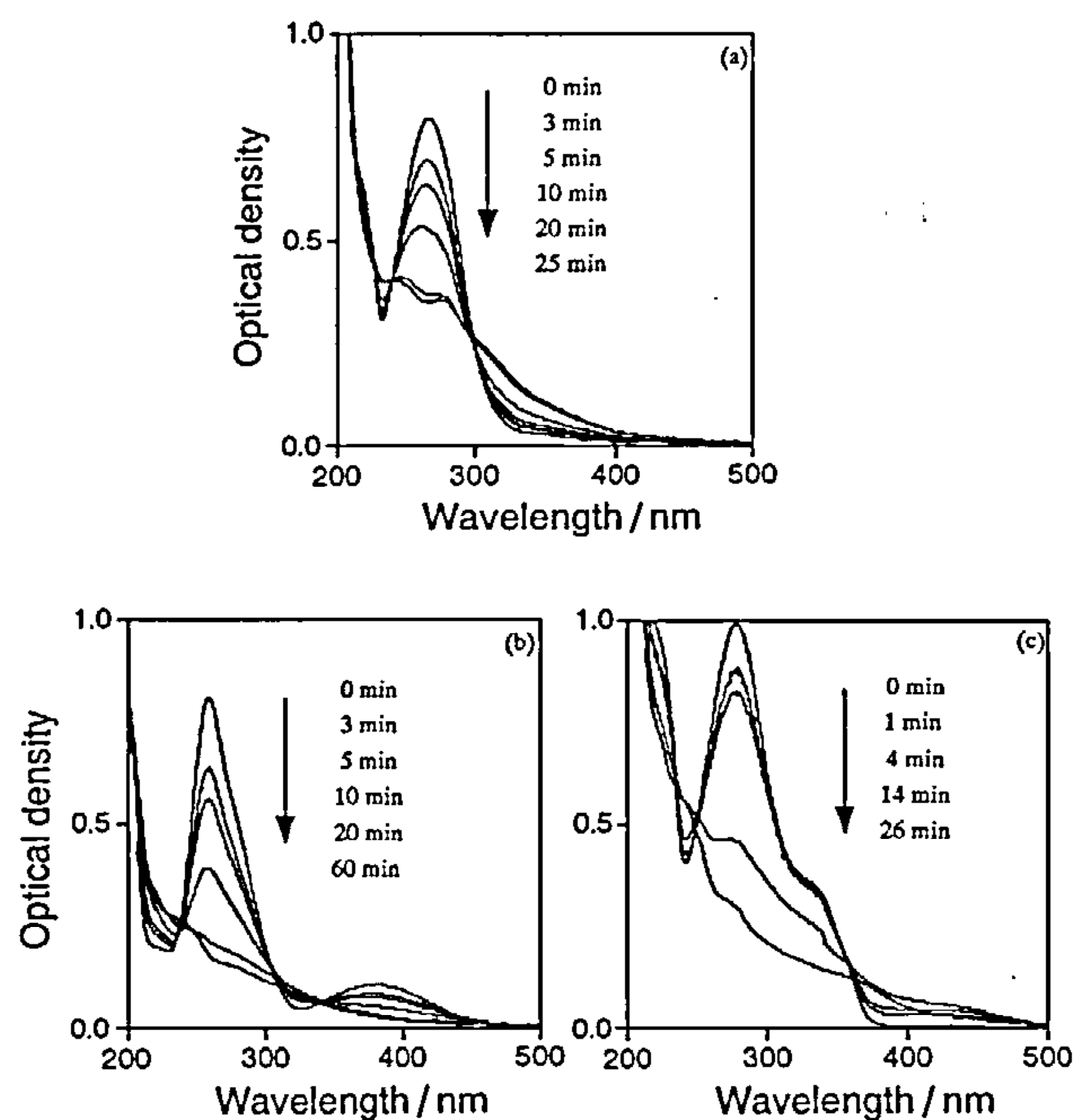
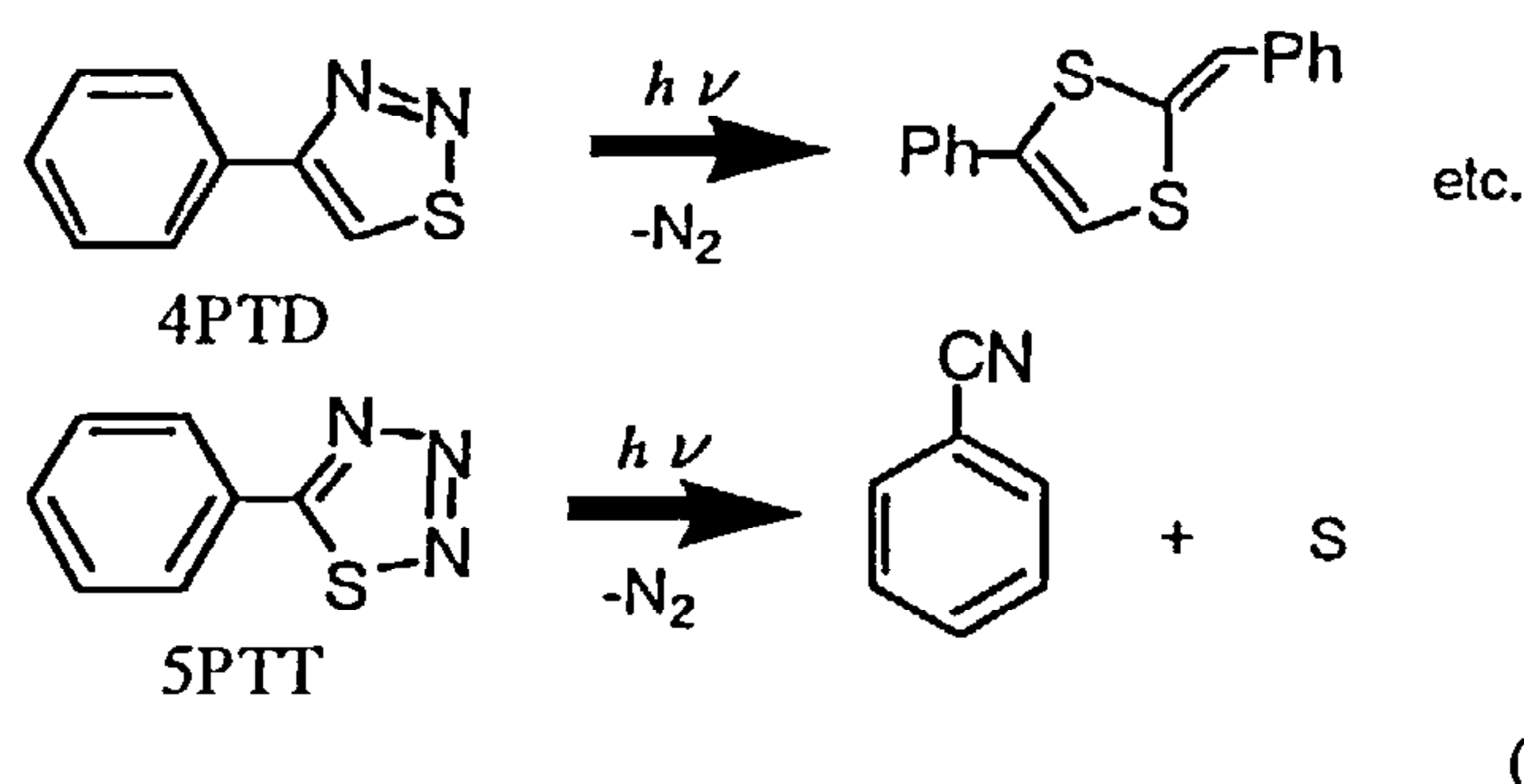


Fig. 3. Absorption spectra of meso-ionic compounds in acetonitrile before and after photoirradiation: (a) 3POTO in $8.0 \times 10^{-5} \text{ mol/L}$ solution: (b) 3POTT in $4.0 \times 10^{-5} \text{ mol/L}$ solution: (c) 3PTTO in $8.0 \times 10^{-5} \text{ mol/L}$ solution. Arrows show the direction of change during photoirradiation. photoirradiation times are shown beside the arrows.

due to the decreases in absorption. Refractive indices and refractive index changes of PMMA films containing 5 wt% meso-ionic compounds are shown in Table I. PMMA films containing 5 wt% meso-ionic compounds with a sulfur atom, 3POTT and 3PTTO, showed large refractive index changes of -0.0040 and -0.0032 during photoirradiation, respectively, while a PMMA film containing 5 wt% 3POTO, which possesses no sulfur atom, showed only a small change in refractive index of -0.0015 during photoirradiation. The difference in the refractive index changes is attributable to the difference in heteroatoms in the meso-ionic ring. Refractive indices of 3POTT and 3PTTO before irradiation are larger than that of 3POTO due to a sulfur atom, which has larger molar refraction, in the meso-ionic moiety and therefore, the refractive index changes of 3POTT and 3PTTO are larger than that of 3POTO during photoirradiation. In our previous paper,¹⁹⁾ we measured the refractive index changes during photoirradiation of PMMA films containing heterocyclic compounds with a sulfur atom in the heterocyclic ring, 4-phenyl-1,2,3-thiadiazole (4PTD) and 5-phenyl-1,2,3,4-thiatriazole (5PTT) [eq. (3)].



The refractive index changes of PMMA films containing 5 wt% 4PTD and 5PTT were -0.0014 and -0.0015 , respectively; these values were very small, as in the case of 3POTO. This suggests that it is not the existence of a sulfur atom but the existence of a sulfur atom in the *meso-ionic* heterocyclic moiety that is an important factor for large refractive index changes. In other words, large refractive index changes can be obtained by introducing compounds which possess a photoreactive meso-ionic group with a sulfur atom into polymer films.

Figure 4 shows the relationship between the weight fractions of 3POTT in PMMA films and the refractive indices or refractive index changes of PMMA films before and after photoirradiation. The samples with a larger wt% of 3POTT were irradiated for longer time periods to complete the refractive index change. Up to 30 wt% doping, the refractive indices and refractive index changes of PMMA films before and after photoirradiation are in proportion to the weight fractions of 3POTT in PMMA. This finding suggests that 3POTT exhibits quite high solubility to PMMA. Other photoreactive compounds, such as 2DI and β -azidostyrene (β -AS), exhibit

Table I. Refraction indices of PMMA films containing 5 wt% of meso-ionic compounds before and after photoirradiation (at 633 nm, in TE Mode).

	3POTO	3POTT	3PTTO
n before irradiation	1.4945	1.4985	1.4977
n after irradiation	1.4930	1.4945	1.4945
$-\Delta n$	0.0015	0.0040	0.0032

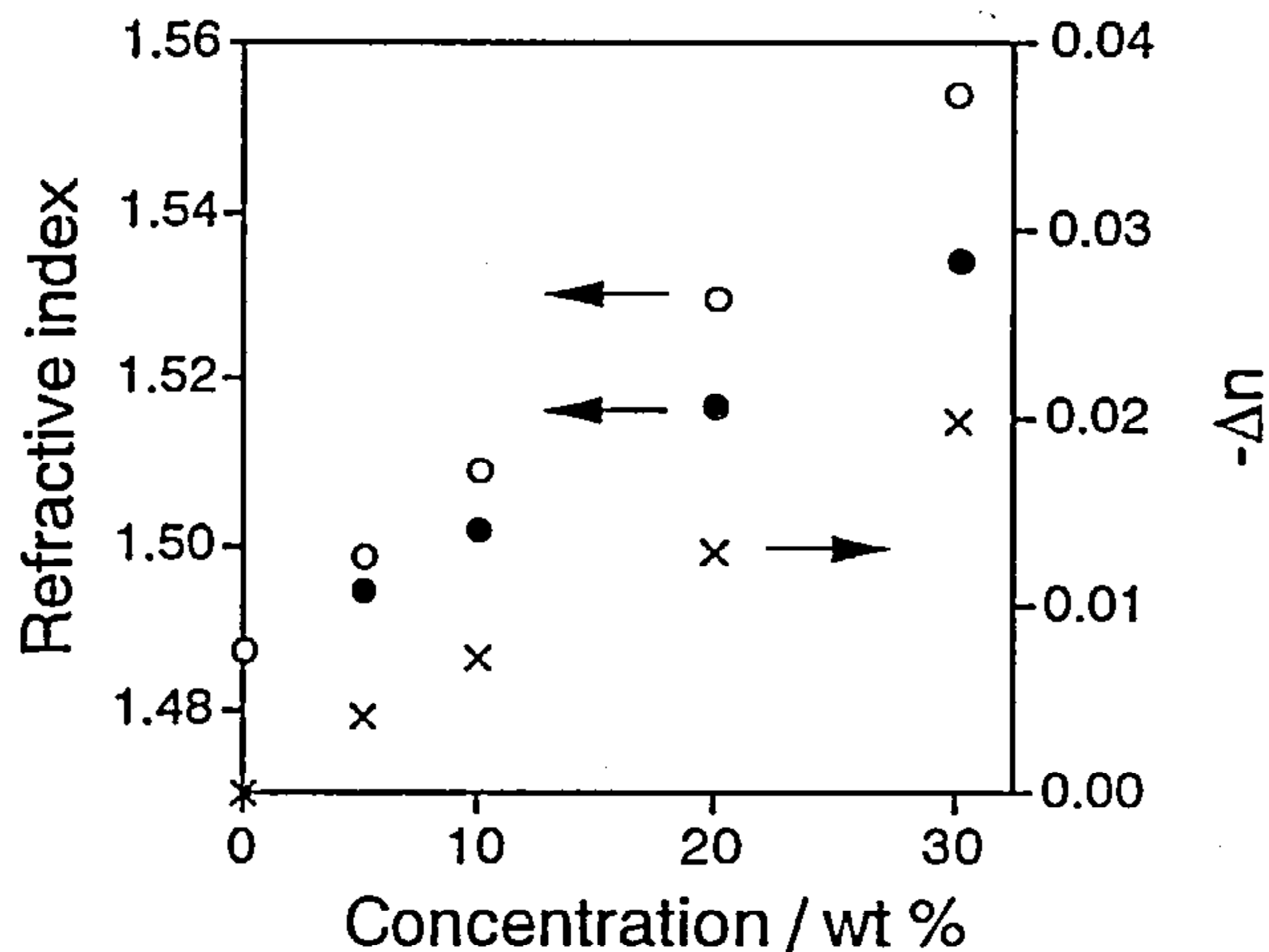


Fig. 4. Refractive indices (○, ●) and refractive index changes (×) of PMMA films containing various weight fractions of 3POTT before (○) and after (●) photoirradiation. Irradiation times are 1 h (5, 10 wt%), 2 h (20 wt%) and 3 h (30 wt%).

fairly good solubility to PMMA, but the refractive indices of PMMA films containing more than 20 wt% 2DI or β -AS no longer showed a linear relationship to the weight fractions, probably due to partial crystallization induced by the microscopic aggregation of dopants in the PMMA films.¹⁹⁾ Compared to these results, 3POTT shows remarkable solubility to PMMA and we can therefore obtain larger refractive index changes of PMMA films containing 3POTT during photoirradiation because we can introduce 3POTT with high weight fractions to PMMA films maintaining a reasonably high quality of PMMA films. Eventually, we could obtain a large refractive index change of -0.02 in the PMMA film containing 30 wt% 3POTT during photoirradiation.

The process of the photoreactions of 3POTT and 3PTTO were revealed by the measurement of IR spectra during photoirradiation to be not through phenyl azide. The PMMA film containing 3POTO showed a peak from an azide group at 2100 cm^{-1} during photoirradiation, while the PMMA films containing 3POTT or 3PTTO did not show any peaks around 2100 cm^{-1} . 3POTO releases carbon dioxide (CO_2) during photoirradiation and forms phenyl azide. If 3POTT or 3PTTO releases carbon oxide sulfide (COS) during photoirradiation, it is quite possible that phenyl azide is formed during photoirradiation and that azide peaks should appear in the IR spectra. These results suggest that the photoreactions of 3POTT and 3PTTO may proceed through a different process from 3POTO. This can influence the refractive index changes of the PMMA films.

3.3 Effects of eliminating molecules on refractive index changes

The molar refraction, which is related to the refractive index by the Lorentz-Lorenz equation, is an effective parameter for relating two properties, the refractive index and its chemical structure, as mentioned above. Molar refraction changes, which well describe the changes in electronic structure of photoreactive compounds, are reasonably well related to the changes in the refractive index during photoreactions. However, in the case of photoelimination where the molar mass of the photoreactive compound varies, the molar refraction changes cannot describe the refractive index changes of

Table II. Specific refraction of photoeliminable ester groups with and without a sulfur in the meso-ionic rings.

	-COO-	-CSO-	-COS-
Specific refraction (cm^3/g)	0.141	0.247	0.209

the polymer film containing photoreactive compounds accurately, because the molar refraction changes include the effect of mass changes. Therefore, we introduce the specific refraction, r , ($r = R/M$) instead of the molar refraction, R , as shown in eq. (4).¹⁹⁾

$$r \cdot \rho = \frac{n^2 - 1}{n^2 + 2} \quad (4)$$

Since the specific refraction eliminates the contribution of the change in molar mass to the change in molar refraction, the change in specific refraction, Δr , can accurately describe the changes in electronic structure of the photoreactive compound. By using the parameter r , we discuss the effect of the eliminating molecule on the refractive index changes. Three photoreactive compounds, 3POTO, 3POTT and 3PTTO, are meso-ionic heterocyclic compounds with the substitution by a phenyl group at 3-position and the only differences are the heteroatoms in the ester-like structure, $-\text{CO}^--\text{O}-$, $-\text{CS}^--\text{O}-$ and $-\text{CO}^--\text{S}-$, respectively. Considering these ionized ester groups as three ester groups, $-\text{COO}-$ and $-\text{CSO}-$ and $-\text{COS}-$, we can calculate the contribution of the loss of these ester groups from the meso-ionic rings to the specific refractions by using the summation of atomic refractions. The specific refractions of these ester groups are shown in Table II. The specific refractions of the ester groups containing a sulfur atom are larger than that of $-\text{COO}-$, which suggests that a sulfur atom contributes more to the specific refraction than an oxygen atom. This result is in good agreement with the refractive index changes of the PMMA films containing meso-ionic compounds. The specific refraction of $-\text{CSO}-$ is larger than that of $-\text{COS}-$, which leads to a larger refractive index before irradiation and larger refractive index changes of the PMMA film containing 3POTT than 3PTTO. This suggests that the position of a sulfur atom in the meso-ionic ring is also an important factor for the refractive index change. Thus, the differences in specific refractions of ester groups effectively contribute to the refractive index changes of the PMMA films containing meso-ionic compounds. The total changes in refractive index during photoreaction are achieved by the summation of various effects, such as the loss of eliminating molecules with high specific refractions, the loss of resonance structure, and the decreases in density of PMMA films.

4. Conclusions

We measured the refractive index changes of PMMA films containing photoeliminable groups with meso-ionic heterocyclic rings during photoirradiation. Polymer films containing 3POTT or 3PTTO, which possess a sulfur atom in the meso-ionic ring, showed large decreases in refractive index during photoirradiation, while a polymer film containing 3POTO, which possesses no sulfur atom in the meso-ionic ring, showed only a small change in refractive index. This may be explained by the existence of a sulfur atom in the meso-ionic ring. We can obtain a large refractive index

change of -0.02 by UV photoirradiation to the PMMA film containing 30 wt% 3POTT.

The specific refractions of the eliminating molecules were estimated using the summation of atomic refractions. The specific refractions of ester groups with a sulfur atom turned out to have large specific refractions compared to those with no sulfur atom, which leads to the differences in refractive index changes. We found that the position of the sulfur atom in the meso-ionic compound also relates to the specific refractions and the refractive index changes.

Acknowledgments

We greatly appreciate the assistance of Drs. S. Machida and H. Shirota during this study.

- 1) T. Kardinahl and H. Franke: *Appl. Phys. Lett.* **67** (1995) 795.
- 2) P. Rochon, T. Gosselin, A. Natansohn and S. Xie: *Macromolecules* **60** (1992) 4.
- 3) A. Natansohn, P. Rochon, T. Gosselin and S. Xie: *Macromolecules* **25** (1992) 2268.
- 4) A. Natansohn, S. Xie and P. Rochon: *Macromolecules* **25** (1992) 5531.
- 5) N. Tanio and M. Irie: *Jpn. J. Appl. Phys.* **33** (1994) 1550.
- 6) N. Tanio and M. Irie: *Jpn. J. Appl. Phys.* **33** (1994) 3942.
- 7) W. J. Tomlinson, E. A. Chandross, R. L. Fork, C. A. Pryde and A. A. Lamola: *Appl. Opt.* **11** (1972) 533.
- 8) S. Morino, S. Machida, T. Yamashita and K. Horie: *J. Phys. Chem.* **99** (1995) 10280.
- 9) S. Morino and K. Horie: *ACS Symp. Ser.* **672** (1997) 260.
- 10) H. Franke: *Appl. Opt.* **23** (1984) 2729.
- 11) C. Xu, K. M. Stengel, L. W. Shacklette and J. T. Yardley: *J. Lightwave Technol.* **14** (1996) 1704.
- 12) E. A. Chandross, C. A. Pryde, W. J. Tomlinson and H. P. Wever: *Appl. Phys. Lett.* **24** (1974) 72.
- 13) V. P. Pham, T. Galstyan, A. Granger and R. A. Lessard: *Jpn. J. Appl. Phys.* **36** (1997) 429.
- 14) *Optical Properties of Polymers*, ed. G. H. Mecten (Elsevier Applied Science, London and New York, 1989).
- 15) S. Morino, T. Watanabe, Y. Magaya, T. Yamashita, K. Horie and T. Nishikubo: *J. Photopolym. Sci. Technol.* **7** (1994) 121.
- 16) K. Kinoshita, K. Horie, S. Morino and T. Nishikubo: *Appl. Phys. Lett.* **70** (1997) 2940.
- 17) S. Murase, K. Kinoshita, K. Horie and S. Morino: *Macromolecules* **30** (1997) 8088.
- 18) K. W. Beeson, K. A. Horn, M. McFarland and J. T. Yardley: *Appl. Phys. Lett.* **58** (1991) 1955.
- 19) S. Murase and K. Horie: *Macromolecules* **32** (1999) 1103.
- 20) C. Bjerre, C. Christophersen, B. Hansen, N. Harrit, F. M. Nicolaisen and A. Holm: *Tetrahedron* **35** (1979) 409.
- 21) R. N. Hanley, O. W. David and C. A. Ramsden: *J. Chem. Soc. Perkin 1* (1979) 736.
- 22) K. Masuda, T. Kamiya and K. Kashima: *Chem. Pharm. Bull.* **19** (1979) 559.
- 23) R. N. Hanley, O. W. David and C. A. Ramsden: *J. Chem. Soc. Perkin 1* (1979) 732.
- 24) P. K. Tien: *Appl. Opt.* **10** (1971) 2395.