Large Photoinduced Refractive Index Increase in Polymer Films Containing Phenylazide Maintaining Their Transparency and Thermal Stability

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ABSTRACT: We realized large photoinduced refractive index increases of poly(methyl methacrylate) (PMMA) films containing phenylazide (PAZ) through photochemical and thermal processes. The refractive index increase of the PMMA film containing 30 wt% PAZ through the processes is as much as 0.0161 with transparency in a wide visible region both before and after photoirradiation and with moderate thermal stability. These excellent performances suggest the applicability of PAZ doped PMMA films for optical devices.

KEY WORDS   Refractive Index Increase / Photocleavage / Phenylazide / M-line Method / Polymer Film / Poly(methyl methacrylate) (PMMA) / Nitrene / Optical Device /

Organic polymers have received considerable attention as materials for opto-electronics applications because of their processability and reasonable cost performances. Some organic polymers have already been applied to optical devices, such as optical fibers, microlenses, liquid crystal display components and polymer light emitting diodes.[1,2] The possibility of organic polymers for opto-electronics applications is not limited, and developments of organic polymers have been more and more promoted.

A photochemical reaction is an important process in the fabrication of refractive index patterns in polymer films. The photochemical reaction can induce larger refractive index modulation in polymer films and the modulation remains after the photoreaction, leading to the permanent change in refractive index. Therefore, photochemically induced refractive index changes in polymer films have been attracting much attention for various applications, such as optical memories, switching devices and optical waveguides.

We can use various kinds of photoreactions, such as photoisomerization, photodimerization, photoelimination, and photopolymerization. These reactions bring about the changes in electronic structure of photoreactive compounds, which result in the refractive index changes of polymer films. Photoisomerization of photochromic compounds is one of the attractive candidates for making refractive index patterns in polymer films reversibly.[3–9] However many photochromic compounds become colored after photoisomerization with absorption bands in the visible region, which may disturb the transmittance of probing light in optical devices. On the other hands, by using irreversible photochemical reactions such as photoelimination and photopolymerization, large refractive index changes of polymer films have been realized with transparency both before and after photoirradiation in a wide visible region.[10–19] Among them, Photoelimination brings about the changes not only in electronic structure of photoreactive compounds and also in the density of the polymer films, which leads to larger refractive index changes.[16,17] The refractive indices of the photoirradiated area decreased in many cases, however, the increases in refractive index of the photoirradiated area are necessary for some applications. In some cases, the presence of remaining doped reactants, which have not reacted in the films, may cause thermal or chemical instability in optical devices.

Phenylazide (PAZ) is a photoeliminable compound and releases a nitrogen molecule during photoreaction to form a nitrene that induces various reactions, mainly insertion to a C–H bond. PAZ is thermally stable below its boiling temperature. In general, polymer films containing a photoeliminable compound exhibit decreases in refractive index during the photoreaction as mentioned above, however the polymer films containing some azido derivatives did not decrease but increased their refractive indices by photoirradiation.[16,20] Moreover, since PAZ is volatile, we can remove unreacting PAZ from the non-irradiated area of the polymer films at a moderate condition, which gives not only large refractive index increase but also thermal stability on patterned polymer films.

In the present study, we exhibited large refractive index increases in polymer films containing various concentrations of PAZ by photoirradiation and a postbake

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process at a moderate condition, keeping transparency in a wide visible region and thermal stability. The refractive indices of polymer films after various processes were measured and the relationship between the refractive index changes and the processes is discussed.

EXPERIMENTAL

Materials

Materials for the experiments are commercially available or synthesized according to reported procedures. Phenylazide (PAZ) was synthesized from phenylhydrazine with sodium nitrite and HCl and purified through silica column chromatography.[21] Commercially available poly(methyl methacrylate) (PMMA) was used as a polymer matrix after reprecipitation. The photoreaction of PAZ is shown in Figure 1. During photoirradiation, PAZ releases a nitrogen molecule to form a nitrene that induces various chemical reactions in the PMMA film, where the main reaction may be the insertion to a C–H bond of the PMMA chains. *N*-Ethylaniline (NEA) as a model compound of the reaction product was supplied by Wako Pure Chem. Ind. and used without further purification.

Film Preparations

Films for refractive index measurements with a thickness of approximately 3 μm were prepared with a barcoater method onto fused silica substrates from about 10 wt% chloroform solutions of PMMA containing various concentrations of PAZ or NEA. The films containing PAZ can be categorized into four types according to the following photochemical and/or thermal processes applied to the films.

Film (a) is a film which was prepared with the above barcoater method and dried under atmospheric pressure at room temperature for 14 h. Film (a) contains various wt% of PAZ. Film (b) is a film prepared by the photoirradiation on Film (a) with a 450 W high-pressure mercury lamp with a UV25 filter for 3 h. Film (c) was

prepared from Film (b) by thermal drying under a reduced pressure at 105 °C for 3 h. Film (d) is a reference film which was prepared by thermal drying of Film (a) under a reduced pressure at 105 °C for 3 h. It should be noted that during the processes preparing Film (c) and Film (d), the unreacting dopant, PAZ, can be removed from PMMA films completely. The photoreaction of PAZ can be followed through IR spectra and we made sure the complete decomposition of PAZ in the Film (b) by the disappearance of a peak at 2130 cm^{-1}, which is identical to azido groups in the IR spectra.

Absorption Spectrum and Refractive Index Measurements

The absorption spectra of the PMMA films containing PAZ during photoirradiation were measured with a Jasco V-570 UV/VIS/NIR spectrophotometer.

The refractive indices of the PMMA films containing PAZ or NEA were measured by using an m-line method.[8] The probe beam for the measurements is a tunable He-Ne laser (LSTP-1010, Research Electro Optics). We measured the refractive indices of the PMMA films in TE (in-plane) mode at 632.8 nm. We also measured the refractive indices on the TM (out-of-plane) polarization for respective samples, but only a very small anisotropy was observed as expected from intrinsically isotropic nature of amorphous PMMA.

RESULTS AND DISCUSSION

The change in absorption spectra of a PMMA film containing 10 wt% of PAZ during photoirradiation is shown in Figure 2. During photoirradiation, the ab-

Figure 1. The photoreaction scheme of PAZ in PMMA.
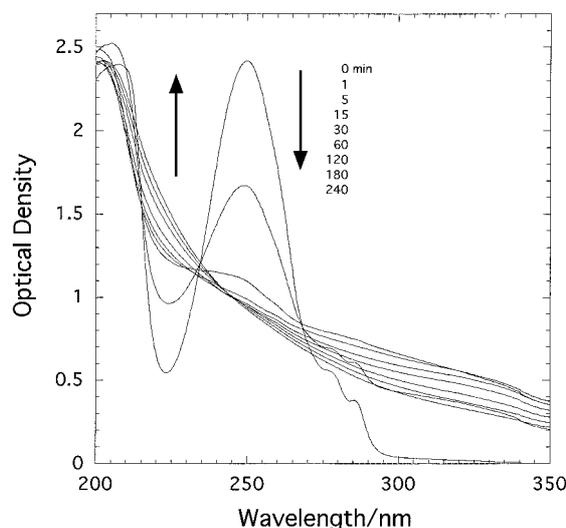
Figure 2. Absorption spectra of PMMA films containing 10 wt% of PAZ before and during photoirradiation. Arrows show the direction of change during photoirradiation. Photoirradiation times are shown beside the arrow.

Table I. Refractive indices of the PMMA films containing various initial concentrations of PAZ before and after photochemical and thermal processes

	Process[a]		n_{TE} for films with various wt% of PAZ		
	(1)	(2)	10 wt%	20 wt%	30 wt%
Film (a)	—	—	1.4961	1.5006	1.5041
Film (b)	○	—	1.4993	1.5046	1.5082
Film (c)	○	○	1.4956	1.5007	1.5040
Film (d)	—	○	1.4875	1.4878	1.4879
	Δn[b]		0.0081	0.0129	0.0161

[a](1): Photoirradiation by a 450 W high-pressure mercury lamp with a UV25 filter for 3 h. (2): Heating under a reduced pressure at 105 °C for 3 h. [b]$\Delta n = n_{TE}$[Film (c)]$-n_{TE}$ [Film (d)].
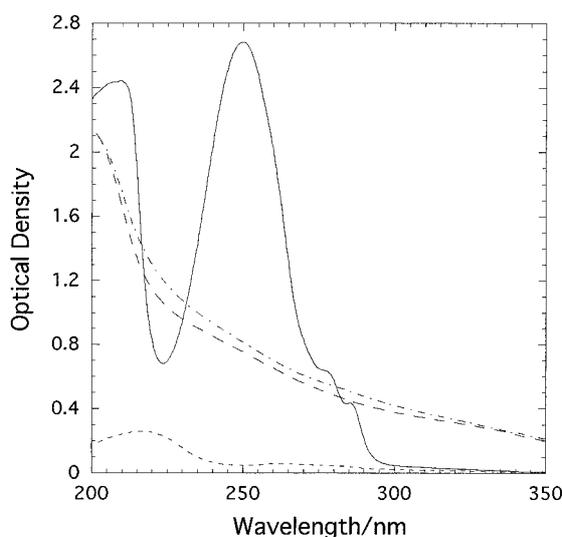
Figure 3. Absorption spectra of the PMMA films containing 10 wt% of PAZ before photochemical and thermal processes (Film (a): ——), after photoirradiation without further thermal process (Film (b): − − −), after photoirradiation and thermal drying process (Film(c): −·−·−·), and after thermal drying process without photoirradiation (Film (d): - - - -).

sorption peak of PAZ at 250 nm decreased in several minutes, while an absorption tail around 300–350 nm appeared. After 5 min photoirradiation, the absorption tail gradually decreased again and the decrease in the absorption tail saturated around 240 min photoirradiation. This change corresponds to the process from Film (a) to Film (b) described above.

Figure 3 shows the absorption spectra of the PMMA films containing 10 wt% of PAZ before and after photochemical and/or thermal processes. The absorption peak at 250 nm of the PMMA film containing 10 wt% of PAZ before photoirradiation completely disappeared after photoirradiation and an absorption tail around 300–350 nm appeared (Film (b)). An absorption spectrum of Film (d) with 3 h thermal drying on unirradiated Film (a) at 105 °C under a reduced pressure exhibits that PAZ can be removed completely with this process. The absorption spectrum of Film (c), being prepared through the heating process on photoirradi-

ated Film (b), seems to be almost the same as that of photoirradiated Film (b). So we expected the refractive indices of Film (b) and Film (c) would not be so different.

Refractive indices, n, of the PMMA films containing 10 wt% of PAZ before and after the various photochemical and/or thermal processes (Film (a) to Film (d)) are given in Table I. Before both photochemical and thermal process, Film (a) has a large refractive index at the TE mode, n_{TE} = 1.4961, compared to the value for non-doped PMMA film (n_{TE} = 1.4875). After 3 h photoirradiation to Film (a), the refractive index of Film (b) became to be 1.4993, with the increase by 0.0032 compared to that of Film (a). This increase in refractive index was somewhat surprising for us, because we expected that the molar refractions of PAZ and aniline derivatives, possible photoproducts of PAZ, may not be so different from each other and moreover the density of the film after photoirradiation may decrease due to the loss of nitrogen molecules during the photoreaction. Film (c) shows smaller refractive index, n_{TE} = 1.4956, than Film (b) by 0.0037. This means that low-molecular-weight compounds, which were produced by photoirradiation and was not inserted to the C–H bonds of the PMMA chains, were removed by the heating process. The thickness of the films for refractive index measurements decreased by several percents during the heating process from Film (b) to Film (c). Film (d) shows the same refractive index as the undoped PMMA film, n_{TE} = 1.4875, which exhibits complete removal of PAZ from the PMMA film through the thermal process on Film (a). As a result, we could obtain the refractive index modulation of 0.0081 between Film (c) and Film (d).

Table I also shows the refractive indices of PMMA films containing 20 and 30 wt% of PAZ before and after the photochemical and/or thermal processes. As is shown in Figure 4, the refractive indices of the PMMA films for the same stage of processes increase as the concentration of PAZ increases, on the other hands, the refractive index history among four types of films,
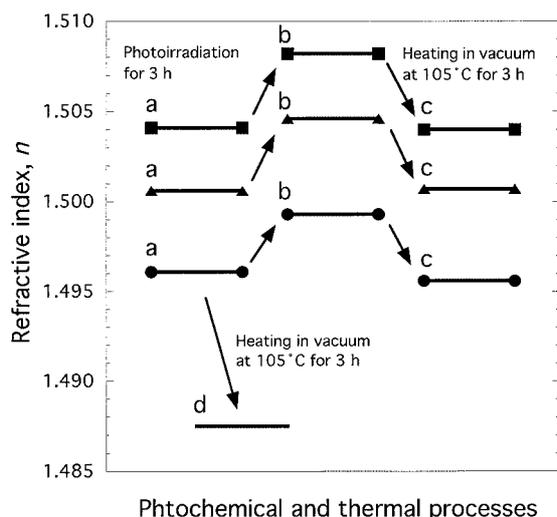
Figure 4. The change in refractive indices of the PMMA films containing 10 wt% (●), 20wt% (▲), and 30 wt% (■) of PAZ during photochemical and thermal processes.

Table II. Refractive indices of the PMMA films containing various initial concentrations of *N*-ethylaniline (NEA) compared to those of Film (b)

Dopant	n_{TE}		
	10 wt%	20 wt%	30 wt%
NEA	1.4998	1.5050	1.5053
Film (b) with PAZ	1.4993	1.5046	1.5082

Film (a)–(d), is similar in every initial concentration of PAZ. For example, the refractive indices of Film (a) and Film (c) are almost the same in every concentration and those of Film (d) with three different PAZ concentrations possess the same value around 1.4875 as for the undoped PMMA film. Considering a practical use of these processes in the refractive index patterning of PMMA films, the thermal process must be carried out on the whole film area. Therefore the refractive index modulation between Film (c) and Film (d) in the experiments should be important. Thus we could obtain a large refractive index change of 0.0161 during photochemical and thermal processes on the PMMA film containing 30 wt% PAZ with further thermal stability and transparency in a wide visible region.

The refractive indices of the PMMA films containing various concentrations of *N*-ethylaniline (NEA) are summarized in Table II. The refractive indices of the PMMA films containing NEA are quite similar to those of Film (b), which supports the expectation that PAZ in Film (a) reacted through the photochemical process to become mainly aniline derivatives in Film (b). From the result of 25–30% decreases in the refractive index difference from the pure PMMA film for Film (c) compared to Film (b), we also see that about 25–30% of photoproducts in Film (b) could not be inserted to the
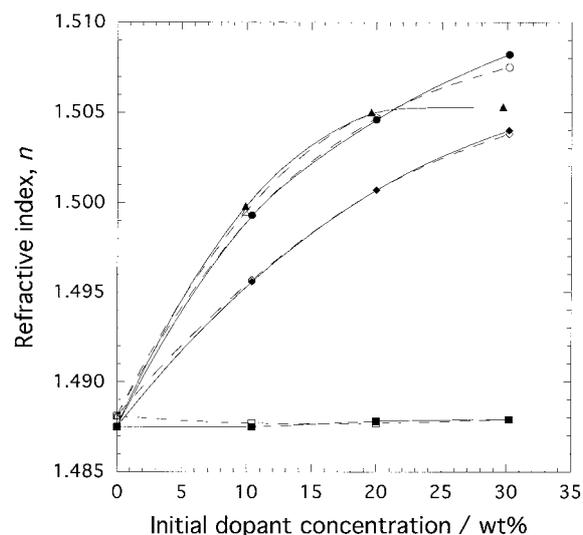
Figure 5. Refractive indices of PMMA films containing various initial concentrations of PAZ after photochemical and/or thermal processes, Film (b) (○, ●), Film (c) (◇, ◆), Film (d) (□, ■), and those containing *N*-ethylaniline (NEA) (△, ▲). Closed and open symbols correspond to refractive indices in TE and TM modes, respectively.

C–H bonds of the PMMA chains and became to be low-molecular-weight compounds, which could be easily removed by evaporation through the heating process. Figure 5 shows the relationship between the initial concentrations of PAZ or NEA in the PMMA films and the refractive indices of the PMMA films after various processes. The refractive indices of the PMMA films increase as the weight fraction of the dopants increases and this increase in refractive indices is not linear. However the difference in the refractive indices between Film (c) and Film (d) continues to increase over 20 wt% and thus we realized a large refractive index change of 0.0161.

CONCLUSION

We realized a large refractive index increase as much as 0.0161 of the PMMA film containing 30 wt% PAZ through successive photochemical and thermal drying processes. The large refractive index change of the PMMA films is accompanied with moderate thermal stability and transparency in a wide visible wavelength region. Thus we can exhibit an effective method of fabricating large refractive index patterns with thermal stability and transparency on polymer films through simple photochemical and thermal processes.

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