Fabrication of Photocrosslinked Diarylfluorene Films with Episulfide Groups using Photobase Generators

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We have developed photocrosslinked films containing a blend of dinaphthylfluorene having episulfide moieties and photobase generators by UV irradiation. The photogenerated amine from the photobase generators catalyzed the crosslinking reaction of the episulfide moieties. The photocrosslinking properties of the blends were significantly affected by the irradiation and baking conditions. We have successfully fabricated films with high refractive indices (1.714 at 589 nm) and a high thermal stability (5% weight loss temperature: 304 °C).

Keywords: Photocrosslinking, Fluorene, Episulfide, Photobase generator, High refractive index

1. Introduction

High refractive index materials are extensively studied for use as optical materials such as light emitting diodes or the lens for imaging sensors. Particularly, the high refractive index materials consisting of organic materials have attracted much attention due to their high processability [1-12]. Especially, diarylfluorene derivatives have been employed as both high refractive index materials and low birefringence materials due to their cardo structures, that is, each aromatic ring is perpendicularly located [1-12].

The introduction to the sulfur atom having a high molecular refractive index by the polymerization of episulfide moieties is known to effectively produce high refractive index materials [1,6,12-14]. Recently, Nie et al. reported that a novel high-refractive index episulfide-thiol polymer for nanoimprinting optical elements was successfully synthesized [1]. The refractive index of the polymer is 1.707 at 590 nm. The episulfide-thiol optical polymer should be a potential candidate for applications in optical and optoelectronic devices. Thus, we focused on the photocrosslinking of diarylfluorene having episulfided moieties, which allows the photopatterning of high refractive index materials. We previously reported the fabrication of photocrosslinked films of diphenyl-or dinaphthylfluorene having epoxy or oxetane moieties and polysilanes blends in the presence of a photoacid generator [15] by irradiation at 405 nm [10]. The refractive indices were controlled in the range from 1.657 to 1.698 at 589 nm by irradiation at 254 nm using the degradation properties of the polysilanes [10].

In this study, we employed photobase generators (PBGs) which produce amines by irradiation [16-20]. The photocrosslinked films containing dinaphthylfluorene derivatives having episulfide moieties were successfully fabricated. The optical and thermal properties of the photocrosslinked films were investigated. The photocrosslinking mechanism was also discussed in terms of the structures of the PBGs and irradiation conditions.

2. Experimental

N-Trifluoromethanesulfonyloxy-7-tert-butylthianthrene-2,3-dicarboxylic imide (Photoacid
generator, PAG) [15] was kindly donated by Sanbo Chemical Ind., Ltd. Polymethylphenylsilane (PMPS) (Mn = 11000), 9,9-bis[(6-glycidyloxy)-2-naphthyl]fluorene (BNFG), 3,3’-[1-fluorenymethylene bis(6,2-naphthylideneoxy)methylene] bis[3-methyloxetane] (BNFO), and 2,2’-[9H-fluoren-9-ylidenebis(4,1-phenyleneoxy)methylene]bis-thiolane (BNFS) were obtained from Osaka Gas Chemicals Co., Ltd. The PBGs, O-(2-phenylacetyl) 2-acetonaphthone oxime (PaAnO) [17] and 1,1’,1”-(O,O’,O”-\{1,3,5-benzenetriyltris[methyleneoxy-4,1-phenylene(1-oxo-2,1-ethanediyl)]\}) 2-acetonaphthone trioxime (AnO3) [19] were synthesized as reported. The structures of these chemicals are shown in Fig. 1.

Sample films (ca. 0.4 μm) were prepared by spin-casting from solutions containing fluorene derivatives, polysilanes, PAG and PBGs onto a CaF2 plate or silicon wafer. Cyclohexanone was used as the solvent.

Irradiation was performed using a medium pressure mercury lamp (Hamamatsu Photonics Photocure 200 (200 W) without a filter, at 405 nm using an LED laser (Ball Semiconductor, BP300, 300 mW, 48 mW/cm²) and at 365 nm using an LED lamp (CCS HLDL-50UV365-FN, 23 W, 2 mW/cm²). The intensity of the light was measured by an Orc Light Measure UV-M02 and Ushio USR-45VA.

Baking of the films was carried out using a conventional hot plate. The irradiated films were soaked in tetrahydrofuran for 2 min and the insoluble fraction was determined by comparing the film thickness before and after soaking. The thickness of the films was measured by interferometry (Nanometrics Nanospec M3000).

The UV-vis spectra were obtained by a Shimadzu UV-2450. The FT-IR measurements were carried out using a JASCO FT/IR-4600. The refractive indices of the films were measured by an Abbe refractometer (ATAGO DR-04) and a spectroscopic ellipsometer (J. A. Woollam Japan M-2000UI). Thermal decomposition behavior was investigated with a Shimadzu DTG 60 simultaneous thermogravimetry and differential thermal analyzer (TG-DTA) under nitrogen flow. Heating rate was 10 °C/min.

3. Results and discussion

3.1. Photocrosslinking

In a previous study [10], we successfully fabricated the photocrosslinked PMPS/BNFG/BNFO (33/6.7/60, wt/wt) blended films which showed a high refractive index (n_d = 1.70) using a photoacid generator. On the other hand, for the episulfide/amine thermal crosslinking system, Ochi et al. reported that the diphenylfluorene having episulfide moieties was cured with 1,3-bis(aminomethyl)cyclohexane by heating at 120 °C. The transparent cured episulfide resins, which have a high refractive index (n_d > 1.61) and relatively low birefringence, were obtained [6]. We expected that photosensitive episulfide/amine crosslinking films can be obtained using PBGs instead of amines.

We chose PaAnO, which generates benzylamine, and AnO3, which generates trifunctional primary amines after irradiation, as the PBGs. Scheme 1 shows the reaction mechanism for the generation of benzyl amine from PaAnO [16].
The insolubilization of BNFS was observed by irradiation using a medium pressure mercury lamp without a filter for 2 min with 12 mW/cm² at 365 nm followed by baking at 180 °C for 5 min. The insolubilization was enhanced by the addition of PaAnO and AnO₃ as the PBGs. To determine the optimum reaction conditions, the effect of the heating temperature, heating time, irradiation time, and functionality of the PBGs on the insoluble fraction was investigated. Figure 2 shows the effect of the heating temperature and heating time on the insolubilization of the BNFS films, BNFS/PaAnO (100/6, wt/wt) blended films, and BNFS/AnO₃ (100/7.5, wt/wt) blended films with or without irradiation.

![Fig. 2. Effect of (a) heating temperature and (b) heating time on insolubilization of BNFS films (○, ●), BNFS/PaAnO (100/6, wt/wt) blended films (□, ■), and BNFS/AnO₃ (100/7.5, wt/wt) blended films (△, ▲). Open symbol: irradiated by medium pressure mercury lamp without filter for 2 min. Irradiation intensity: 12 mW/cm² at 365 nm. Solid symbol: no irradiation. (a) Heating time: 5 min. (b) Heating temperature: 200 °C. Dissolution: THF for 2 min.](image)

The insoluble fractions of all the samples increased with the heating temperature and time after irradiation. Insolubilization was not observed for the nonirradiated samples after heating at 200 °C for 5 min. When the samples were heated above 220 °C without irradiation, insolubilizations were observed. Thus, we determined that the optimum heating condition was 200 °C for 5 min.

The insoluble fraction amounts of the samples were in the order, BNFS/PaAnO ≈ BNFS/AnO₃ > BNFS. The increased insoluble fractions were due to the crosslinking reaction of the episulfide and amine generated from the PBGs upon irradiation [6]. The reaction mechanism is discussed below.

Figure 3 shows the effect of the irradiation time on the insolubilization of the BNFS films, BNFS/PaAnO (100/6, wt/wt) blended films, and BNFS/AnO₃ (100/7.5, wt/wt) blended films. The insoluble fractions of the samples increased with the irradiation time, and were in the order, BNFS/PaAnO ≈ BNFS/AnO₃ > BNFS.

The effect of the PBG content on the insolubilization of the BNFS/PBG was investigated (Fig. 4). The insoluble fractions increased, reached the maximum values, then decreased with the PBG content regardless of the PBGs used. We consider that the peak below 10% may be due to the predominant polymerization of the episulfide. On the other hand, the increase above 30% may be due to the effect of the crosslinking reaction of the episulfide and amine. About 100% insolubilization using less than 10 wt% PaAnO may be due to the vaporization of unreacted or uncrosslinked PaAnO.
The effect of content of PBGs on insolubilization of BNFS/PaAnO blended films (□), and BNFS/AnO3 blended films (△). Irradiation was performed by medium pressure mercury lamp for 2 min without filter. Irradiation intensity: 12 mW/cm² at 365 nm. Heating conditions: 200 °C for 5 min. Dissolution: THF for 2 min.

Table 1 summarizes the optimum conditions for the preparation of the photocrosslinked BNFS/PBG blended films together with their refractive indices and thermal properties. Using BNFG, a previously reported epoxy compound, insolubilization was not observed with the addition of PaAnO (Table 1, column 1). When irradiation was performed at 365 nm, insolubilization of BNFS was not observed. This result strongly suggests that the insolubilization of BNFS requires the irradiation of light below 365 nm. Using 365 nm light, insoluble fraction of BNFS/AnO3 is greater than that of BNFS/PaAnO (Table 1, columns 8 and 11). The result suggests that effective crosslinking reactions occurred by the generation of a trifunctional amine by the photolysis of AnO3.

As previously reported [10], when the PMPS/BNFG/BNFO (33/6.7/60, wt/wt) blended film containing 5 wt% of PAG was irradiated at 405 nm with a dose of 1600 mJ/cm² and heated at 150 °C for 5 min, insolubilization was observed. The photocrosslinked film showed a high refractive index (nD: 1.698). The photocrosslinked BNFS/AnO3 film showed the highest refractive index (nD: 1.714) compared to the PMPS/BNFG/BNFO blended film and BNFG/BNFO blended film (nD: 1.668) (Table 1, columns 11-13). The photocrosslinked BNFS/AnO3 film showed a high thermal stability (Td5: 304 °C) as described in the next section.

3.2. Optical and thermal properties

Figure 5 shows the spectral refractive indices of the photocrosslinked BNFS/AnO3 (100/7.5, wt/wt) blended film. The nF, nD, and nC values were 1.742, 1.714, and 1.703, respectively. The abbe number νd of the film was 18.
3.3. Reaction mechanism

The FT-IR spectral changes revealed the reaction mechanism of the blended films. Figure 7 shows the FT-IR spectral changes of the BNFS/AnO3 blended films. After irradiation, the peak at around 1750 cm\(^{-1}\) ascribed to the C=O stretching of oximes disappeared and the peak around 1630 cm\(^{-1}\) ascribed to a ketone compound appeared. After heating, the peak at 1085 cm\(^{-1}\) ascribed to an episulfide unit [6,21] disappeared. The UV-vis spectral changes of the BNFS/AnO3 blended films suggested the formation of 2-acetonaphthone oxime by the increase in the absorption below 400 nm (Fig. 8).

Scheme 2 shows a plausible reaction mechanism of the BNFS/PBG blended system. Upon irradiation, PBG photolyzed to produce amines. The generated amines promote the crosslinking reactions which were mainly due to the amine-catalyzed polymerization of the
episulfide moieties. The polymerization induced the insolubilization of the films due to the nature of the difunctional compounds of BNFS. On the other hand, the photocrosslinking of BNFS occurred by irradiation below 365 nm. This reaction may be due to a cationic mechanism by the sulfide oxidation. This produced sulfonate may initiate cationic polymerization of episulfide via sulfonium cations [13].

Scheme 2. Plausible reaction mechanism of BNFS with PBG.

4. Conclusion

We succeeded in the preparation of photocrosslinked BNFS/PBG blended films by irradiation. We have successfully fabricated films with high refractive indices (nD: 1.70) and high thermal stabilities (Tg: 304 °C). Effect of AnO3 was similar with PaAnO upon irradiation using medium pressure mercury lamp, and more effective than PaAnO upon irradiation at 365 nm. The photocrosslinking of BNFS may proceed by cationic and anionic mechanisms upon irradiation below 365 nm.

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