Photo-thermal Dual Curing of Polysilane/diarylfluorene Blends -Fabrication of Films with High and Tunable Refractive Indices-

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We have developed the crosslinked films of diphenyl- or dinaphthylfluorene having acryl units with polymethylphenylsilane in the presence of a photoradical initiator upon irradiation at 405 nm with thermal treatments at around 100 °C. The photopolymerization of the acrylates effectively enhanced by the photo-thermal dual curing technique. Polysilane moieties were incorporated into the film by the termination reaction between the acrylate radicals and Si radicals generated by the slight photo-decomposition of the Si-Si bonds. We have successfully fabricated the films with high refractive indices (n_D : 1.62) and the refractive index values were tunable by irradiation at 254 nm by the effective decomposition of the Si-Si bonds of the polysilanes. The reaction mechanism is discussed based on real-time FT-IR measurements. The prepared films have a high thermal stability (temperature for 5% weight loss, T_{d5} : 300 °C).

Keywords: Photo-thermal dual curing, Fluorene, Acryl, Polysilane, High refractive index, High thermal stability

1. Introduction

The photo-thermal dual curing technique has attracted much attention due to the enhanced photoreactivity to fabricate specially-controlled and temporally-controlled functional materials [1-6]. Thus, significant efforts have focused on designing a photo-thermal dual curing system having excellent chemical and physical properties [1-6].

Based on this point of view, we have developed a photo-thermal dual curing technique to fabricate functional materials [5,6]. We reported the application to screen printing technology using the photo-thermal dual curing system [6]. The new formulation of acrylic anchor resins contains a base polymer, which consists of hydrophilic units and solvent-absorbing units. As crosslinkers, multifunctional acrylates were employed. The acrylic anchor resins coated on poly(ethylene

terephthalate) films were effectively cured by simultaneous photo-irradiation and baking below 80 °C. Using the photo-thermal dual cured anchor layer, an 8- μ m sized silver circuit was successfully printed without defects on a poly(ethylene terephthalate) film [6].

In this study, the photo-thermal dual curing technique was applied to the photocrosslinking of diphenylfluorene and polysilane blends [7-12] as potential functional coatings with a high thermal stability, high transparency, and high refractive indices. We have developed the photo-induced acid-catalyzed crosslinking system of diepoxyfluorene/polysilane blends in the presence of PAGs upon irradiation [7-10]. In the system, the photo-induced acid catalyzed the crosslinking of epoxides and the terminal groups of the polysilanes. In this study, we applied the radically-induced

photo-thermal dual curing technique instead of the previously reported photo-induced acid-catalyzed crosslinking system [7-10]. A wide variety of photoinitiation systems by radical species can be applied compared to the cationic photocrosslinking system. We have developed the crosslinked films of diphenyl- or dinaphthylfluorene having acryl units with polymethylphenylsilane in the presence of a photoradical initiator upon irradiation at 405 nm with thermal treatments. The refractive indices were controlled by irradiation at 254 nm based on the degradation properties of the polysilanes [13-18]. The photocrosslinking and photodegradation properties were discussed in terms of the structures of the chemicals and irradiation conditions. The reaction mechanism is also discussed based on real-time FT-IR measurements.

2. Experimental

The structures of chemicals used are shown in Fig. 1. The photoradical initiators, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), were used as received. 7-(1,1-Dimethylethyl)-1,3-dihydro-1,3-dioxo-2H[1,4] benz-odithiino[2,3-f]isoindol-2-yl trifluoromethanesulfonate (PAG) [19] was kindly donated by Sanbo Chemical Ind., Ltd. A hexafunctional acrylate dipentaerythritol hexaacrylate (DPHA) was kindly donated by Shin-Nakamura Chemical Co., Ltd., and used without further purification. A tetrafunctional thiol pentaerythritol tetrakis(3-mercaptopbutylate) (PEMB) was obtained from Showa Denko K.K. and used as received. Polymethylphenylsilane (PMPS) ($M_n = 11000$), 9,9-bis[(3-acryloyloxy-2-hydroxypropoxy)phenyl]fluorene (BPFGA), 9,9-bis[6-(2-acryloyloxyethoxy)-2-naphthyl]fluorene (BNEFA), 9H-fluoren-9-ylidenebis(4,1-phenyleneoxy-2,1-ethanediyl) 3-mercaptopropionate (BPEFMP), 9H-fluoren-9-ylidenebis(4,1-phenyleneoxy-2,1-ethanediyl) 3-mercaptopbutyrate (BPEFMB), 9H-fluoren-9-ylidenebis(6,2-naphthyleneoxy-2,1-ethanediyl) 3-mercaptopbutyrate (BNEFMB), 9,9-bis[(3,4-diglycidyoxy)phenyl]fluorene (BCAFG), 9,9-bis[(6-glycidyoxy)-2-naphthyl]fluorene (BNFG), and 3,3'-[(1-fluorenylmethylene) bis(6,2-naphthylideneoxymethylene)] bis[3-methyl-oxetane] (BNFO) were obtained from Osaka Gas Chemicals Co., Ltd.

Sample films (ca. 1 μm) were prepared by spin-casting from polymer solutions containing fluorene derivatives, polymethylphenylsilane, and a

photoradical initiator onto a CaF_2 plate or silicon wafer. Cyclohexanone and diglyme were used as the solvents.

Photo-thermal dual curing was performed by irradiation at 405 nm using an LED laser (Ball Semiconductor, BP300, 300 mW, 48 mW/cm^2) along with baking using a conventional hot plate. Photodegradation was carried out at 254 nm using a low pressure mercury lamp (Sen SUV40UL-32, 40 W, 2 mW/cm^2) without a filter. The intensity of the light was measured by an Orc Light Measure UV-M02 and Ushio USR-45VA.

The irradiated films were soaked in tetrahydrofuran and the insoluble fraction was determined by comparing the film thickness before and after soaking in tetrahydrofuran for 10 min. The thickness of films was measured by interferometry (Nanometrics Nanospec M3000).

Fig. 1. Structures of chemicals used.

The UV-vis spectra were taken by a Shimadzu UV-2450. The real-time FT-IR measurements were carried out using a JASCO FT/IR-4200 equipped with a JASCO RS-200 thermal stage and a xenon lamp (Asahi Spectra, MAX-301, 300 W) through band-path filters at 405 nm or with a mirror which passes the light below 410 nm.

Conversion of the acryl and thiol units in the film was determined by the real-time FT-IR measurements using the peak at 1635 cm^{-1} ascribed to the acryl unit and at 2570 cm^{-1} ascribed to the thiol unit, respectively.

The refractive indices of the films were obtained

using an Abbe refractometer (ATAGO DR-04).

3. Results and discussion

3.1. Photo-thermal dual curing

UV curing is generally achieved by photopolymerization which is obtained by the utilization of photoinitiators and photocrosslinking agents. Photoinitiators are the key materials for the UV-curing processes. The first stage in the UV curing system is the absorption of a photon from the incident radiation by the photoinitiators. Light absorption by the photoinitiators requires that the emission line from the light source overlaps with an absorption band of the photoinitiators. Thus, the absorption spectrum of the photoinitiator must be carefully selected.

In a previous study [7], we successfully fabricated the blended films of PMPS and dinaphthylfluorene having epoxy and oxetane units with PAG [19] by irradiation at 405 nm and baking at 150 °C. The obtained films showed high refractive indices (n_D : 1.70) due to the high content of the naphthyl moieties. In this study, the typical acylphosphine-oxide-type, Norrish type I photoinitiators, TPO and BAPO, were used as photoradical initiators which are sensitive to 405-nm light. Figure 2 shows the UV-vis spectra of TPO and BAPO in acetonitrile. The molar absorption coefficient value of BAPO at 405 nm (ϵ_{405} : 520) is about 2.5 times higher than that of TPO (ϵ_{405} : 220).

Fig. 2. UV spectra of TPO (solid line) and BAPO (broken line) in acetonitrile (1.00×10^{-4} M).

In this study, photocrosslinking was carried out by irradiation at 405 nm using an LED laser which emits 405-nm light as shown in Fig. 3. Photodegradation was performed using a low pressure mercury lamp and a xenon lamp (Fig. 3).

In general, the photopolymerization of acrylates is strongly inhibited in the presence of oxygen.

The oxygen inhibition is known to be effectively suppressed by the use of the thiol-ene photocuring system due to regeneration of the thiyl radical in the presence of oxygen [20-23] (Scheme 1). Thus, application of the thiol-ene system may afford a high sensitivity.

Fig. 3. Power spectra of LED laser which emits 405-nm light (dotted line), low pressure mercury lamp (solid line), and xenon lamp (broken line).

Scheme 1. Reaction mechanism of thiol-ene system.

When the BPFGA/BPEFMP (132/68, wt/wt) blended film containing 0.5 wt% TPO was irradiated at 405 nm with a dose of 3000 mJ/cm² without heating, insolubilization was not observed. Thus, the photo-thermal dual curing technique was applied in this study. When the irradiation was performed with heating at 120 °C, insolubilization was observed (Table 1, column 1). When the irradiation wavelength was changed to 365-nm light, a low irradiation dose was required to produce about a 70% insoluble fraction (Table 1, column 2). The high sensitivity using 365-nm light is reasonable because of the light absorption of TPO as shown in Fig. 1. BPEFMB, a secondary thiol compound showed less reactivity than BPEFMP, a primary

Table 1. Photocrosslinking of polysilane/diarylf luorene blended films and their refractive indices.

Formulation (weight ratio)										Irradiation dose (mJ/cm ²)	Heating temp. (°C)	Heating time (sec)	Insoluble fraction (%)	n_F^a	n_E^b	n_D^c	n_C^d
PMPS	DPHA	BPFGA	BNEFA	BPEFMP	BPEFMB	BNEFMB	PEMB	TPO	BAPO								
		132		68				1		3000 ^f	120	1107	61	1.6205	1.6103	1.6050	1.5988
		132		68				1		1000 ^g	120	763	68	— ^h	— ^h	— ^h	— ^h
		134			66			1		3000 ^f	120	1107	6	1.6075	1.6023	1.5953	1.5907
		134			66			1		2000 ^g	120	1527	15	— ^h	— ^h	— ^h	— ^h
		163					37		1	6000 ^f	110	126	84	1.6007	1.5888	1.5818	1.5793
	77				123				1	6000 ^f	110	126	86	1.5839	1.5746	1.5690	1.5648
67	78						55		1	6000 ^f	120	126	77	1.5690	1.5570	1.5501	1.5427
67		109					25		1	6000 ^f	110	126	74	1.6325	1.6220	1.6128	1.6064
100		82					19		1	18000 ^f	120	378	28	1.6642	1.6516	1.6503	1.6244
67	23		78				33		1	18000 ^f	110	378	44	1.6352	1.6231	1.6147	1.6089
67		88			49				1	12000 ^f	120	252	24	1.6335	1.6233	1.6141	1.6110
67		84				49			1	12000 ^f	100	252	6	1.6444	1.6306	1.6222	1.6166

^aMeasured at 486 nm. ^bMeasured at 546 nm. ^cMeasured at 589 nm. ^dMeasured at 656 nm. ^eAbbe number: $(n_D - 1)/(n_F - n_C)$. ^fIrradiated at 405 nm. ^gIrradiated at 365 nm. ^hNot measured.

thiol compound (Table 1, columns 3 and 4). When PEMB, an aliphatic tetrafunctional thiol compound, was used and BAPO was used as a photoinitiator, the insoluble fraction increased up to 84% (Table 1, column 5) due to the high flexibility of PEMB and high sensitivity of BAPO. The incorporation of aromatic groups into the films is effective to increase their refractive indices. However, due to the low reactivity of BPEFMP and BPEFMB, we used PEMB as the thiol compound. The sensitivity of a DPHA/BPEFMB blend, in which DPHA is a hexafunctional acrylate aromatic thiol compound, was nearly equal to that of a BPFGA/PEMB blend (Table 1, columns 5 and 6). Due to the low refractive index of the DPHA/BPEFMB blend, the BPFGA/PEMB blend is best in terms of the sensitivity and the refractive index value.

The incorporation of PMPS into the blended films is effectively increased the value of the refractive indices (Table 1, columns 7-12). In terms of the sensitivity and the refractive index value, we concluded that the PMPS/BPFGA/PEMB (67/109/25, wt/wt/wt) blended film was the best among our tested films. The cured film has a high refractive index (n_D : 1.62).

3.2. Photodegradation

In a previous study [7], we reported that the photodecomposition of the Si-Si bonds of polysilanes effectively occurred upon irradiation at 254 nm, and a decrease of about a 0.04 refractive index was observed after the photodecomposition at 254 nm with a dose of 16000 mJ/cm².

Figure 4 shows the effect of the irradiation dose

on the UV spectral changes of the PMPS/BPFGA/PEMB blended films. The shoulder at around 330 nm ascribed to the Si-Si bonds decreased with the irradiation dose.

Fig. 4. UV spectral changes of PMPS/BPFGA/PEMB (67/109/25, wt/wt/wt) blended films containing 0.5 wt% BAPO. Bold line: no irradiation. Solid line: irradiated at 405 nm with a dose of 6000 mJ/cm² upon heating at 110 °C for 126 sec. Subsequent irradiations at 254 nm were carried out with a dose of 500 (broken line), 2000 (dot-dash line), and 8000 mJ/cm² (dotted line). Film thickness: 2 μ m.

About an 85% decrease was observed upon irradiation at 405 nm with a dose of 6000 mJ/cm² by heating at 110 °C for 126 sec. The slight decomposition of the Si-Si bonds during the crosslinking condition enhanced the insoluble fraction of the film as discussed in the reaction mechanism section (section 3.4). More than 90% of the shoulder disappeared after irradiation at 254

nm with a dose of 8000 mJ/cm². FT-IR measurements also revealed the decomposition of the Si-Si bonds in the blends as also discussed in section 3.4.

Table 2 shows the effect of the irradiation dose on the refractive index changes in the crosslinked PMPS/BPFGA/PEMB blended films irradiated at 254 nm. The crosslinked PMPS/BCAFG blended film showed a high refractive index ($n_D = 1.62$). The value of the refractive index decreased to 1.59 after irradiation at 254 nm with a dose of 18000 mJ/cm².

Table 2. Optical properties of photocrosslinked PMPS/BPFGA/PEMB (67/109/25, wt/wt/wt) blended films by irradiation at 254 nm.

Irradiation dose at 254 nm (mJ/cm ²)	n_F^a	n_E^b	n_D^c	n_C^d	v_d^e
0	1.6325	1.6220	1.6128	1.6064	23
1000	1.6288	1.6106	1.6094	1.5999	21
6000	1.6278	1.6106	1.6039	1.5981	20
12000	1.6214	1.6048	1.5978	1.5921	20
18000	1.6190	1.5888	1.5941	1.5876	19

^aMeasured at 486 nm. ^bMeasured at 486 nm. ^cMeasured at 589 nm. ^dMeasured at 656 nm. ^eAbbe number: $(n_D - 1)/(n_F - n_C)$.

3.3. Thermal stability

When using the dual curing system, the thermal stability of the crosslinked films was drastically enhanced compared to the previously reported cationic photocrosslinking system [7]. Figure 5 shows the TGA curves of photocrosslinked PMPS/BPFGA/PEMB blended film together with the previously reported photocrosslinked PMPS/BCAFG and PMPS/BNFG/BNFO films. The decrease that started at around 130 °C was observed for the photocrosslinked PMPS/BCAFG and PMPS/BNFG/BNFO films due to the decomposition of the PAG contained in the films.

The values of the 5% weight loss, T_{d5S} , were 301, 172, and 182 °C for the PMPS/BPFGA/PEMB blended film, the PMPS/BCAFG film and the PMPS/BNFG/BNFO film, respectively. The thermal stability of the BAPO as a photoinitiator enhanced the thermal stability of the blended film.

3.4. Reaction mechanism

As already mentioned, the UV-vis spectral changes in the PMPS/BPFGA/PEMB blended film revealed that less than 10% of the intensities of the shoulders at around 330 nm ascribed to the Si-Si

Fig. 5. TGA curves of photocrosslinked PMPS/BPFGA/PEMB (67/109/25, wt/wt/wt) blended film by irradiation at 405 nm with a dose of 6000 mJ/cm² upon heating at 110 °C for 126 sec (solid line), photocrosslinked PMPS/BCAFG (33/67, wt/wt) blended film [7] by irradiation at 405 nm with a dose of 1600 mJ/cm² and PEB at 110 °C for 6 min (broken line), and photocrosslinked PMPS/BNFG/BNFO (33/6.7/60, wt/wt/wt) blended film [7] by irradiation at 405 nm with a dose of 1600 mJ/cm² and PEB at 150 °C for 5 min (dotted line) in N₂. Heating rate: 10 °C/min.

bonds of PMPS were decreased when irradiated at 405 nm with a dose of 6000 mJ/cm² upon heating at 110 °C for 126 sec (Fig. 4).

The decomposition is very important in order to enhance the insoluble fraction as discussed below.

The FT-IR spectral changes revealed the reaction mechanism of the blended films. Figure 6 shows the FT-IR spectral changes of the PMPS/BPFGA/PEMB blended films. Upon irradiation at 405 nm, the peak at 1635 cm⁻¹ ascribed to the acryl units and at 2570 cm⁻¹ ascribed to the thiol units decreased with the irradiation dose. We can follow the conversions of the acryl units and the thiol units by in situ FT-IR spectroscopy (Fig. 7). The conversions of the thiol and acryl groups increased with the irradiation dose.

In this system, the acryl content was adjusted to two times higher than that of the thiol groups. During the initial stage, the thiol-ene reaction and homopolymerization of the acryl unit simultaneously proceeded. After irradiation at about 150 sec, homopolymerization of the acryl was suppressed and only the thiol-ene reaction

Fig. 6. FT-IR spectra of PMPS/BPFGA/PEMB (67/109/25, wt/wt/wt) blended film containing 0.5 wt% BAPO. Solid line: no irradiation. Broken line: irradiated at 405 nm for 600 sec with heating at 110 °C. Irradiation intensity: 1.41 mW/cm². Dotted line: irradiated at 250-400 nm using xenon lamp (see Fig. 1) for 600 sec after irradiation at 405 nm. Irradiation intensity: 4.9 mW/cm² for 365 nm. Film thickness: 1.1 μ m.

proceeded due to increased mobility of the films. The acceleration of the reaction of the thiol groups after irradiation at 400 sec may be due to the coupling reaction of the thiyl radicals to form S-S bonds.

Upon irradiation at 254 nm, the Si-Si bonds in PMPS easily photolyzed and the Si-O-Si bonds assignable at 1150 cm⁻¹ clearly increased.

Scheme 2 shows a plausible reaction mechanism of the PMPS/BPFGA/PEMB blended system. On irradiation at 405 nm, the photoinitiator photolyzed to produce radicals. The generated radicals subtract the hydrogen of the thiols to produce thiyl radicals as shown in Scheme 1. The thiyl radicals reacted with acryl groups to produce the thiol-ene reaction (Scheme 1) together with the homopolymerization of the acryl groups as observed in Fig. 7. The thiol-ene reaction and the homopolymerization produced networks containing

Fig. 7. Conversion of acryl (solid line) and thiol (dotted line) groups in PMPS/BPFGA/PEMB (67/109/25, wt/wt/wt) blended films containing 0.5 wt% BAPO measured by in-situ FT-IR spectroscopy. Irradiation intensity: 4.9 mW/cm² for 365 nm. Film thickness: 1.1 μ m.

Irradiation at 405 nm

major reaction

minor reaction

Irradiation at 254 nm

Scheme 2. Plausible reaction mechanism of PMPS/BPFGA/PEMB blended system.

BPFGA and PEMB moieties. As a minor reaction, the decomposition of the Si-Si bonds in PMPS generates Si radicals by the slight absorption at 405-nm light. The Si radicals terminate the thiol-ene reaction and the homopolymerization to produce PMPS/BPFGA/PEMB networks in the BPFGA/PEMB networks.

Upon irradiation at 254 nm, the Si-Si bonds in PMPS easily photolyzed to generate Si radicals. After sequential reactions of the Si radicals with O₂ in the atmosphere, scission of the O-O bonds, hydrogen abstraction, and condensation of the generated Si-OH groups, the Si-O-Si bonds are introduced into the blended films, which reduced the refractive indices.

4. Conclusion

We succeeded in preparing photocrosslinked polysilanes/diarylfuorenes blended films and controlled their refractive indices upon irradiation at 254 nm. We have successfully fabricated the films with high refractive indices (n_D : 1.62). Photodecomposition of the Si-Si bonds of the polysilanes effectively occurred upon irradiation at 254 nm. The decrease of about a 0.03 refractive index was observed after the photodecomposition at 254 nm with a dose of 18000 mJ/cm². The prepared films have a high thermal stability (temperature for 5% weight loss, T_{d5} : 300 °C).

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