

Fabrication of Photocrosslinkable Polysilane/diarylfluorene Blended Films with Tunable Refractive Indices

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Abstract

We have devised the photocrosslinked films of diphenyl- or dinaphthylfluorene having epoxy or oxetane moieties and polysilanes blends in the presence of a photoacid generator on irradiation at 405 nm. Photo-decomposition of Si-Si bonds of polysilanes was successfully suppressed during irradiation of the visible light. The cationic photocrosslinking properties of the blends were strongly affected by PEB conditions and irradiation dose. Polysilane moieties were incorporated with the film by the termination reaction of the polymerization with the terminal OH groups. We have successfully fabricated the films with high refractive indices (n_d : 1.70) and the refractive index values were tunable by irradiation at 254 nm by the decomposition of Si-Si bonds of polysilane.

Introduction

Photo-induced control of the network structures of polymers has attracted much attention due to its versatility of special and temporal control in order to fabricate functional materials^{1,2}. Based on this point of view, recent research regarding the design of polymer networks by dual irradiations has been reviewed². Especially, a photo-degradable system after photopolymerization, photopolymerizable system after photolysis, and photo-cross-linkable system after photopolymerization were introduced. In terms of the photo-degradable system after photopolymerization, a chain length analysis of the networks can be applied in addition to the fabrication of the replicated resin molds³. In terms of photo-cross-linkable system after photopolymerization, a novel methacrylate containing a chalcone unit was synthesized and the photopolymerization was controlled by the choice of the photoinitiators and irradiation wavelength⁴. In terms of photopolymerizable system after photolysis, a photocrosslinkable system sensitive to 405-nm light was successfully devised using a novel photoacid generator^{5,6}. This system is applicable to novel photosensitive materials.

We have become interested in the photocrosslinking of diphenylfluorene and polysilane blends⁷⁻¹¹ as potential functional coatings with a high thermal stability, high transparency, and high refractive indices. Thus, we have developed the photo-induced acid-catalyzed cross-linking system of diepoxyfluorene/polysilane blends in the presence of PAGs by irradiation⁷⁻⁹. In the system, the photo-induced acid catalyzed the crosslinking of the epoxides and the terminal groups of the polysilanes. In

this study, we extended the previous studies⁷⁻⁹ to fabricate films with high and tunable refractive indices. We have formed photocrosslinked films of diphenyl- or dinaphthylfluorene having epoxy or oxetane moieties and polysilanes blends in the presence of a photoacid generator by irradiation at 405 nm. The refractive indices were controlled by irradiation at 254 nm using the degradation properties of the polysilanes¹²⁻¹⁷. The photocrosslinking and photodegradation properties were discussed in terms of the structures of the chemicals and irradiation conditions.

Experimental

Materials

N-Trifluoromethanesulfonyloxy-7-*tert*-butyl-thianthrene-2,3-dicarboxylic imide (PAG)⁵ was kindly donated by Sanbo Chemical Ind., Ltd. Polymethylphenylsilane (PMPS) ($M_n = 11000$), hyperbranched polyphenylsilylene [(PSy1, $M_n = 1100$) and (PSy2, $M_n = 1300$)], 9,9-bis[(3,4-diglycidyloxy)phenyl]fluorene (BCAFG), 9,9-bis[(6-glycidyloxy)-2-naphthyl]fluorene (BNFG), and 3,3'-[(1-fluorenylmethylene)bis(6,2-naphthylideneoxymethylene)]bis[3-methyloxetane] (BNFO) were obtained from Osaka Gas Chemicals Co., Ltd. The structures of these chemicals used are shown in Fig. 1.

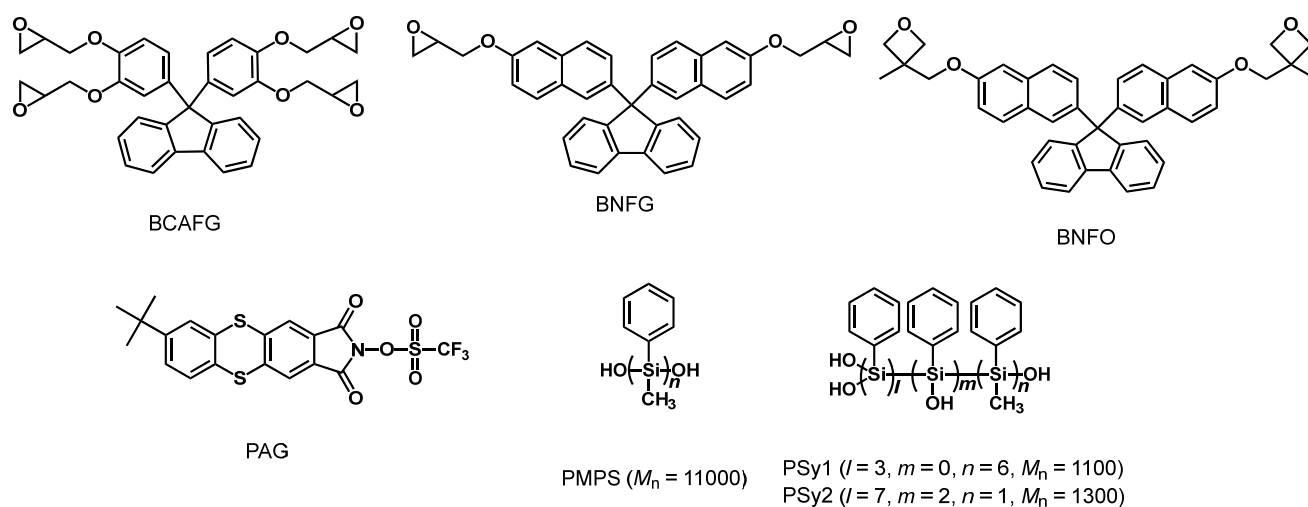


Fig. 1. Structures of chemicals used in this study.

Sample films (ca. 1 μm) were prepared by spin-casting from polymer solutions containing fluorene derivatives, polysilanes, and PAG onto a CaF₂ plate or silicon wafer. Cyclohexanone and diglyme were used as the solvents.

Irradiation was performed at 405 nm using an LED laser (Ball Semiconductor, BP300, 300 mW, 48 mW/cm²) and at 254 nm using a low pressure mercury lamp (Sen SUV40UL-32, 40 W, 2 mW/cm²)

without a filter. 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 and the insoluble fraction was determined by comparing the film thickness before and after soaking in tetrahydrofuran for 10 min. The thickness of the films was measured by interferometry (Nanometrics Nanospec M3000).

The UV-vis spectra were taken 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 using an Abbe refractometer (ATAGO DR-04).

Results and discussion

Photocrosslinking

In a previous study⁷, we successfully fabricated the photocrosslinked PMPS/BCAFG (13/87, wt/wt) blended film without damaging the Si-Si bonds of PMPS in the film. The PMPS content strongly affects the refractive indices of the films, but also the photocrosslinking reactions. Clear films were obtained with up to a 50 wt% PMPS content. When the PMPS/BCAFG (33/67, wt/wt) blended film containing 5 wt% PAG was irradiated at 405 nm with a dose of 1600 mJ/cm² and baked at 110 °C for 6 min, insolubilization was observed. The effect of the post-exposure-bake (PEB) temperature on the insoluble fractions of the polysilanes/BCAFG blended films irradiated with a dose of 1600 mJ/cm² was observed. The insoluble fractions increased with the PEB temperature. Insolubilization was not observed for unirradiated samples after heating below 110 °C. When the polysilanes/BCAFG samples were baked above 120 °C without irradiation, insolubilizations were observed. The generation of the acid by the decomposition of PAG promotes the crosslinking reactions of BCAF. Table 1 summarizes the optimum conditions for the preparation of the photocrosslinked polysilanes/diarylfuorene blended films together with their refractive indices. Incorporation of naphthyl units into the blended films can effectively increase the refractive indices. However, the reactivity of BNFG, a difunctional epoxide, and BNFO, a difunctional oxetane derivative, were lower than that of BCAF, a tetrafunctional epoxide, due to the low functionality of BNFG and BNFO (Table 1, columns 4 and 5). When the PMPS/BNFG (33/67, wt/wt) and the PMPS/BNFO (33/67, wt/wt) blended film containing 5 wt% of PAG were baked at 150 °C, insolubilization was observed for both films. We consider that we overcome the low photo-contrast by mixing epoxy to oxetane moiety. The addition of oxetane to the epoxide is known to increase the reactivity of cationic photopolymerizations¹⁸⁻²⁰. When the PMPS/BNFG/BNFO (33/6.7/60, wt/wt/wt) blended film containing 5 wt% of PAG was irradiated at 405 nm with a dose of 1600 mJ/cm² and baked at 150 °C for 5 min, insolubilization was observed. No insolubilization was observed without irradiation. The photocrosslinked film showed a high refractive index (n_d : 1.70).

Photodegradation

Figure 2 shows the effect of the irradiation dose on the UV spectral changes of the PMPS/BCAFG blended films irradiated at 254 nm. The shoulder at around 330 nm ascribed to the Si-Si bonds decreased with the irradiation dose. More than 70% of the shoulder disappeared after irradiation with a dose of 16000 mJ/cm². When using PSy1 and PSy2 instead of PMPS, a decrease in the shoulder during irradiation was also observed. FT-IR measurements also revealed the decomposition of the Si-Si bonds in the blends as discussed below.

Table 1. Optimum photocrosslinking conditions of polysilane/diarylfuorene blended films and their refractive indices.

PMPS	PSy1	PSy2	BCAFG	BNFG	BNFO	PAG	Irradiation dose at 405 nm (mJ/cm ²)	Heating temp. (°C)	Heating time (min)	Insoluble fraction (%)	n_F^a	n_D^b	n_C^c	v_d^d
33			67			5	1600	110	6	92	1.645	1.619	1.617	22
	33		67			5	1600	110	6	78	1.641	1.622	1.618	27
		33	67			5	1600	110	6	76	1.640	1.621	1.616	26
33				67		5	1600	110	6	0	- ^e	- ^e	- ^e	- ^e
33					67	5	1600	110	6	0	- ^e	- ^e	- ^e	- ^e
33				6.7	60	5	1600	150	5	78	1.723	1.688	1.689	17

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

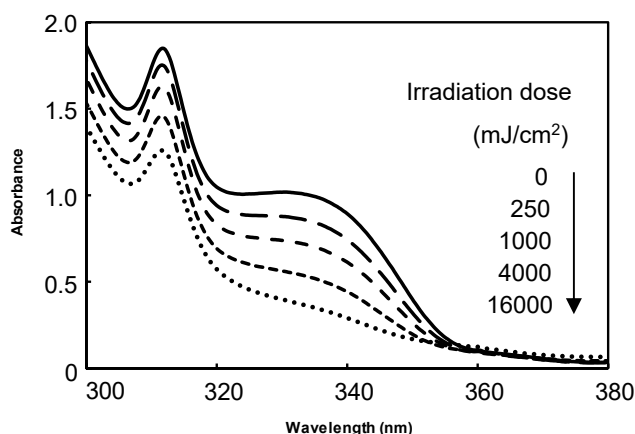


Fig. 2. Effect of irradiation at 254 nm on UV spectral changes of PMPS/BCAFG (33/67, wt/wt) blended films containing 5 wt% PAG. 405-nm irradiation dose: 1600 mJ/cm². PEB condition: 110 °C for 6 min. Film thickness: 1.1-1.3 μm.

Figure 3 shows the effect of the irradiation dose on the refractive index changes of the PMPS/BCAFG blended films irradiated at 254 nm. The crosslinked PMPS/BCAFG blended film showed a high refractive index ($n_a = 1.62$). The refractive index value decreased to 1.58 after irradiation at 254 nm with a dose of 16000 mJ/cm². Using PSy1 and PSy2 instead of PMPS, a decrease in the refractive indices during irradiation was also observed. The structures of the polysilanes did not strongly affect the decreased values.

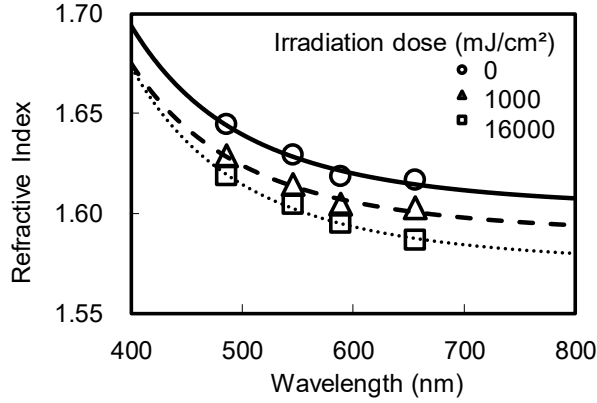


Fig. 3. Effect of irradiation dose at 254 nm on refractive index changes of PMPS/BCAFG (33/67, wt/wt) blended films containing 5 wt% PAG.

Tables 2 and 3 summarize the effect of the irradiation dose on the refractive index changes of the PMPS/diaryluorene blended films irradiated at 254 nm. The crosslinked PMPS/BNFG/BNFO (33/6.7/60, wt/wt/wt) blended films (Table 3) showed a high refractive index ($n_d = 1.70$). The refractive index value decreased to 1.66 after irradiation at 254 nm with a dose of 64000 mJ/cm².

Table 2. Optical properties of photocrosslinked PMPS/BCAFG (33/67, wt/wt) blended films upon irradiation at 254 nm.

Irradiation dose at 254 nm (mJ/cm ²)	n_F^a	n_D^b	n_C^c	ν_d^d
0	1.645	1.629	1.619	22
1000	1.629	1.614	1.605	23
16000	1.610	1.595	1.584	19

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

Table 3. Optical properties of photocrosslinked PMPS/BNFG/BNFO (33/6.7/60, wt/wt/wt) blended films upon irradiation at 254 nm.

Irradiation dose at 254 nm (mJ/cm ²)	n_F^a	n_D^b	n_C^c	ν_d^d
0	1.723	1.698	1.689	17
1000	1.718	1.691	1.682	19
4000	1.707	1.685	1.676	21
16000	1.695	1.672	1.662	20
64000	1.683	1.657	1.651	21

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

Reaction mechanism

The UV-vis spectral changes of the PMPS/BCAFG blended films revealed that less than 10% of the intensities of the shoulders at around 330 nm ascribed to the Si-Si bonds of PMPS decreased upon irradiation and baking at 110 °C for 6 min. The UV-vis spectral changes of the PSy1/BCAFG and PS2/BCAFG blended films were slightly observed like the PMPS/BCAFG ones.

As already mentioned, effective scissions of the Si-Si bonds in the blended films were clearly observed upon irradiation at 254 nm as shown in Fig. 2.

The FT-IR spectral changes revealed the reaction mechanism of the blended films. Figure 4 shows the FT-IR spectral changes of the photocrosslinked PMPS/BCAFG blended films upon irradiation at 254 nm. The broad peak at around 3400 cm^{-1} ascribed to the Si-O-H stretching and at 1100 cm^{-1} ascribed to the Si-O-Si stretching increased with the irradiation dose. On the other hand, the peak at around 1500 cm^{-1} ascribed to the phenyl ring slightly decreased.

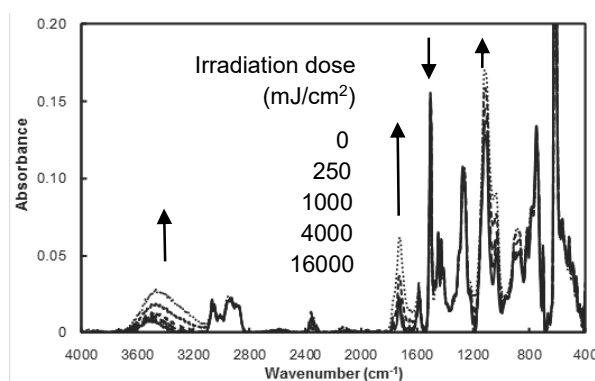
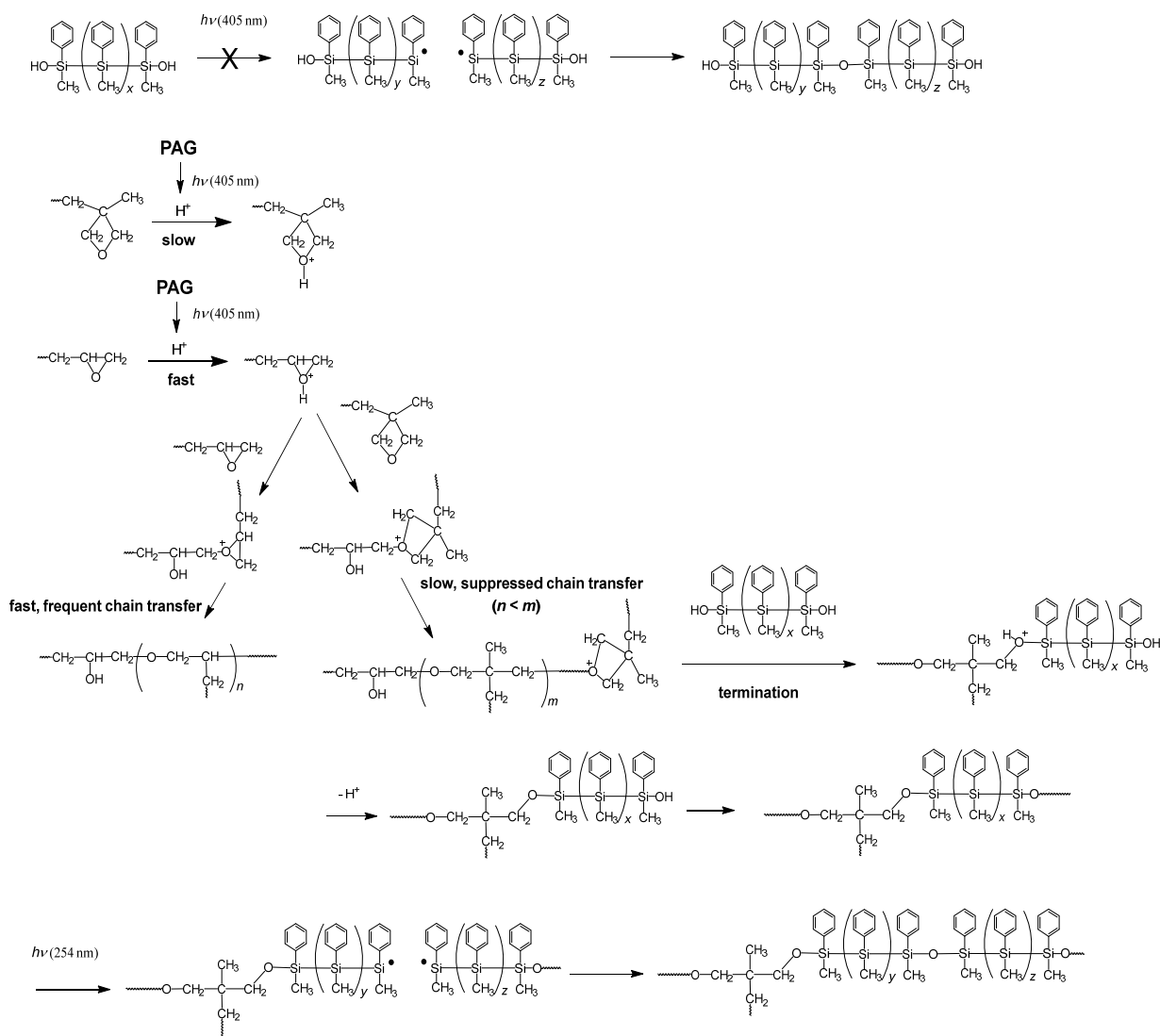


Fig. 4. Effect of irradiation at 254 nm on FT-IR spectral changes of PMPS/BCAFG (33/67, wt/wt) blended films containing 5 wt% PAG. 405-nm irradiation dose: 1600 mJ/cm^2 . PEB condition: 110 °C for 6 min. Film thickness: 1.1-1.3 μm .

Scheme 1 shows a plausible reaction mechanism of the PMPS/BNFG/BNFO blended system. Upon irradiation at 405 nm, PAG photolyzed to produce an acid. The generated acid promotes the crosslinking reactions which were mainly due to the acid-catalyzed polymerization of the epoxy and oxetane moieties. It is known that initiation of the epoxy is faster than that of oxetane in the cationic polymerization¹⁸⁻²⁰. The polymerization induced the insolubilization of the films due to the nature of the difunctional compounds of BNFG and BNFO. The chain length of the oxetane polymer is higher than that of epoxy polymer, i.e., $m > n$ in Scheme 1¹⁸⁻²⁰. Mixing BNFG and BNFO in the blended films effectively enhanced the photocrosslinking reactions. The termination of the polymerization by the terminal OH groups of the polysilanes also occurred as a minor reaction. We consider that the Si-Si bonds in the polysilanes were not photolyzed by the visible light.

Upon irradiation at 254 nm, the Si-Si bonds in PMPS easily photolyzed to generate Si radicals¹²⁻¹⁴. After sequential reactions of the Si radicals with O_2 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 in the blended films which reduced the refractive indices (see Fig. 3, Tables 2 and 3).



Scheme 1. Plausible reaction mechanism of PMPS/BNFG/BNFO blended system.

Conclusions

We succeeded in the preparation of photocrosslinked polysilanes/diarylfuorenes blended films and controlled their refractive indices upon irradiation at 254 nm. We have successfully fabricated films with high refractive indices (n_d : 1.70). Photodecomposition of the Si-Si bonds of polysilanes effectively occurred on irradiation at 254 nm. A decrease of about 0.04 of refractive indices was observed after the photodecomposition at 254 nm. The changes in the refractive indices were not strongly affected by the structures of the polysilanes.

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