Highly Sensitive Photocrosslinking System Using Fluorene Derivatives Having Vinyl Ether or Epoxy Moiety

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Photocrosslinking properties of fluorene-9,9'-bis(4-ethoxyphenyl vinyl ether) (FBPEVE)/fluorene-9,9'-bis(4-phenoxyethyl glycidyl ether) (FBPEG) blend and FBPEVE/poly (glycidyl methacrylate) (PGMA) blend were investigated. Photocrosslinking of FBPEVE/PGMA or FBPEVE/FBPEG blended films containing a photoacid generator (PAG) was observed at lower irradiation dose than that of PGMA, FBPEG, or FBPEVE. The high sensitivity of blended films is due to the enhancement of the conversion of both epoxy and vinyloxy moieties compared with the conversion of simple epoxy in FBPEG or vinyloxy moiety in FBPEVE. The photocrosslinked films showed good thermal stability.

Keywords: photocrosslinking, fluorene, vinyl ether, epoxide, photoacid generator, high sensitivity, reaction mechanism

1. Introduction

Fluorene derivatives have been attracted much attention due to their unique electronic and physical properties. The research topics have concerned with organic light emitting devices [1-4], non-linear optical properties [5], thermal stability [6-8], low birefringence [9], and gas permselectivity [10]. Therefore, thin films composed of fluorene derivatives are applicable to functional materials such as electronic devices, surface protective coatings, gas separation membrane, and so on. Photocrosslinking of fluorene derivatives is one of the most promising methods to prepare chemically and/or thermally stable films. In this respect, photocrosslinking system using fluorene-9,9'-bis(4-phenoxyethyl glycidyl ether) (FBPEG) and poly(vinyl phenol) [11, 12] or poly(methyl phenyl silane) [13, 14] has been studied. The blended films showed high thermal stability. However, more research to improve the sensitivity of the blended films is necessary for the practical use.

Vinyl ether derivatives are among the most

reactive monomers for cationic polymerization. Thus, photo-induced acid-catalyzed crosslinking of vinyl ether groups was employed for the preparation of the blended films. Photocrosslinking of fluorene derivatives having vinyl ether moiety, fluorene-9,9'-bis(4-phenoxyethyl vinyl ether) (FBPEVE), was carried out using *N*-trifluoromethanesulfonyloxy-1,8-naphthalene imide (NITf) as a photoacid generator (PAG). Regrettably, the insolubilization of FBPEVE/NITf blended films was not observed due to low acidity of triflic acid generated from NITf. Using I-line sensitive PAGs generating stronger acid than triflic acid is one of the promising methods to circumvent this problem. However, development of the PAGs was very difficult.

Vinyl ether/epoxy blends were also studied in terms of the combination of the high reactivity of vinyl ethers with the good physical properties of epoxides [15-19]. Recently, Kim et al. reported that a blended system of diepoxide and vinyl ether showed high photoreactivity. They mentioned

that the cross-propagation of epoxide and vinyl ether was the main factor for the high reactivity of the blends [19].

In this paper, photocrosslinking properties, reaction mechanism, and thermal properties of two vinyl ether/epoxy blended systems, FBPEVE/poly(glycidyl methacrylate) (PGMA) and FBPEVE/fluorene-9,9'-bis(4-phenoxyethyl glycidyl ether) (FBPEG), were investigated.

2. Experimental

2.1. Materials

Fluorene derivatives, FBPEVE (mp. 79 °C) and FBPEG (softening temperature: ca. 50 °C), were supplied from Osaka Gas Co., Ltd. NITf ($\epsilon = 380$ (L/mol · cm) at 365 nm in acetonitrile) was purchased from Midori Kagaku. Poly(glycidyl methacrylate) (PGMA) ($M_n = 21000$, $M_w/M_n = 2.0$) was prepared by the conventional radical polymerization using azobis(isobutyronitrile) as an initiator.

2.2. Photocrosslinking

All sample films were prepared on silicon wafer by spin-casting from solutions of cyclohexanone containing PGMA or FBPEG, FBPEVE, and NITf. The sample films were dried on a hot plate at 90 °C for 1 min. The thickness of films was about 0.5 μm except for the sample films for FT-IR measurements (1.0 μm). Irradiation was performed at 365 nm in air using a medium-pressure mercury lamp (Ushio UM-102, 100 W) with a TOSHIBA UV-D36B filter. The intensity of the light was measured with an Orc Light Measure UV-M02. Insoluble fraction was determined by comparing the film thickness before and after developments in THF. Thickness of films was measured by interferometry (Nanometrics Nanospec M3000).

2.3. Measurements

^1H NMR spectra were observed at 270 MHz using a JEOL GX-270 spectrometer. FT-IR measurements were carried out using a JASCO IR-410. In-situ FT-IR measurements were carried out by using Litho Tech Japan PAGA-100. Size exclusion chromatography (SEC) was carried out in THF on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex GMN_{HR}-H + GMN_{HR}-N; 8.0 mm i.d. x 30 cm each) and a differential refractometer JASCO RI1530. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated based on a polystyrene calibration.

3. Results and Discussion

3.1. Photocrosslinking of FBPEG/FBPEVE blends

Insolubilization was reported for FBPEG film containing 2 wt% of triphenylsulfonium triflate when irradiated at 254 nm with a dose of 36 mJ/cm² and followed by a PEB treatment at 140 °C for 2 min [11]. However, thickness of the crosslinked films was limited less than 0.2 μm for 254 nm light exposure. The strong absorption ascribed to phenyl rings of a fluorene moiety diminishes the transmittance of the film. Figure 1 shows the UV-vis spectrum of FBPEG/FBPEVE (3:1,w/w) blended film containing 3 wt% of NITf with 0.5 μm thick. Absorbance of the film at 365 nm was 0.096. A micron-order thick film as coating layers is possible by using 365 nm light exposure.

Fig. 1. UV-vis spectrum of FBPEG/FBPEVE (3:1,w/w) blended film containing 3 wt% of NITf. Film thickness: 0.5 μm .

When sample films were irradiated at 365 nm, NITf decomposed to generate triflic acid. Protonation of epoxy and vinyl ether units occurred and subsequent acid-catalyzed polymerization of epoxy and vinyl ether units proceeded. A precise reaction mechanism for the photocrosslinking of

the system is discussed below.

Figure 2 shows the relationship between insoluble fraction and PEB temperature for FBPEG/FBPEVE blended films with various weight fraction. Insolubilization was observed for FBPEG film and FBPEG/FBPEVE (X:1, w/w, X= 2, 3, 5 and 10) blended films when the films were irradiated and baked at 100 ~ 160 °C for 10 min. The insoluble fraction decreased with the increase of the weight fraction of FBPEVE in the blended films. Insolubilization of FBPEVE and FBPEG/FBPEVE (1:1 w/w) films were not observed when irradiated and baked at 60 ~ 160 °C for 10 min.

Fig. 2. Effect of PEB temperature on insolubilization of FBPEG/FBPEVE blended films containing 3 wt% NITf. FBPEG (●). FBPEG/FBPEVE (X:1, w/w) : X=10 (△), 5 (◇), 3 (□), 2 (×), 1 (▽), 0 (○). Irradiation dose: 200 mJ/cm². PEB time: 10 min.

To investigate the low reactivity of FEPEVE, SEC measurement was carried out. FEPEVE film containing 3 wt% NITf was irradiated at 200 mJ/cm² and baked at 100 °C for 10 min before the measurement. The conversion of vinyl group of the sample was estimated to be ca. 40% using FT-IR spectroscopy. A large peak (MW ~ 600) and a small peak (MW ~ 1000) were observed as shown in Fig. 3. The large peak (MW ~ 600) is ascribed to an unreacted FBPEVE and other species, for example, an adduct of water and FBPEVE. FBPEVE showed a peak at 600 in SEC measurement. The small peak (MW ~ 1000) in Fig. 3 indicates the formation of oligomers of FBPEVE. The low fraction of the oligomer in the system may be due to the low acidity of the initiating species generated from NITf compared to that generated from triphenylsulfonium

hexafluoroantimonate used for the photopolymerization of vinyl ethers.

Fig. 3. SEC curve of irradiated and baked FBPEVE containing 3 wt% NITf. Irradiation dose: 200 mJ/cm². PEB: 100 °C for 10 min.

Fig. 4. Effect of irradiation dose on insolubilization of FBPEG/FBPEVE blended films containing 3 wt% NITf. FBPEG (●). FBPEG/FBPEVE (X:1, w/w) : X=10 (△), 5 (◇), 3 (□), 2 (×), 0 (○). PEB: 100 °C for 10 min.

However, insolubilization was observed for FBPEG/FBPEVE (X:1, w/w, X= 2, 3, 5 and 10) blended films irradiated and baked at 80 °C for 10 min. Insolubilization of FBPEG was not observed at the same baking condition. The insoluble fraction increased with the weight fraction of FBPEG in the blended films. The result clearly indicates that FBPEG/FBPEVE blended system is more effective for photocrosslinking than FBPEG. Figure 4 shows

the relationship between insoluble fraction and irradiation dose for FBPEG/FBPEVE blended films with PEB treatment at 100 °C for 10 min. Sensitivity of FBPEG/FBPEVE (X:1, w/w, X= 2, 3, 5, and 10) blended films (ca. 10 mJ/cm²) was higher than that of PBPEG film (ca. 20 mJ/cm²). Insoluble fraction of the FBPEG/FBPEVE (2:1, w/w) blended films showed the highest value when irradiated at 10 mJ/cm². Optimum blend ratio was 2/1 by weight for FBPEG/FBPEVE blended system.

3.2. Photocrosslinking of PGMA/FBPEVE blends

PGMA/FBPEVE blended films were expected to show higher sensitivity than FBPEG/FBPEVE films due to multi-functionality of epoxy unit in PGMA/FBPEVE blended films. Moreover, PGMA/FBPEVE blends are useful for a representative system of FBPEG/FBPEVE blends.

Figure 5 shows the relationship between insoluble fraction and PEB temperature for PGMA/FBPEVE blended films irradiated at 200 mJ/cm² with various weight fractions. Insoluble fraction of the films increased with the weight fraction of PGMA in the blended film. THF-soluble fractions of irradiated and baked PGMA/FBPEVE blended films were investigated. The fractions contained mainly unreacted FBPEVE. PGMA was not detected in the fractions by FT-IR and SEC analysis.

Fig. 5. Effect of PEB temperature on insolubilization of PGMA/FBPEVE blended films containing 3 wt% NITf. PGMA (●). PGMA/FBPEVE (X:1, w/w) : X = 2 (○), 1 (△), 0.5 (◇), 0.33 (□). Irradiation dose: 200 mJ/cm². PEB time: 10 min.

Figure 6 shows the relationship between insoluble fraction and irradiation dose for PGMA/FBPEVE blended films with PEB

treatment at 100 °C for 10 min. Improvement of the sensitivity of PGMA/FBPEVE blended films was clearly observed compared with the non-blended films. Insolubilization of PGMA film was observed when irradiated at 5 mJ/cm², whereas PGMA/FBPEVE (X:1, w/w, X= 2, 1, 0.5, and 0.33) blended films became insoluble when irradiated at 1 mJ/cm². Insoluble fractions of the films irradiated at < 1 mJ/cm² were not measured due to experimental limitation. PGMA/FBPEVE (1:1, w/w) blended film showed the highest sensitivity. Sensitivity enhancement by addition of FBPEVE in blended films was more clearly observed for PGMA/FBPEVE blended system than FBPEG/FBPEVE one.

Fig. 6. Effect of irradiation dose on insolubilization of PGMA/FBPEVE blended films containing 3 wt% NITf. PGMA (●). PGMA/FBPEVE (X:1, w/w) : X = 2 (○), 1 (△), 0.5 (◇), 0.33 (□). PEB: 100 °C for 10 min.

3.3. Reaction mechanism studied by in-situ FT-IR measurement

In-situ FT-IR spectroscopy is a useful technique to analyze the reaction mechanism.

Figure 7 shows the in-situ FT-IR spectral changes of irradiated PGMA/FBPEVE (1:1, w/w) blended film containing 3 wt% NITf on baking at 120 °C. The peak at 918 cm⁻¹ ascribed to epoxy of PGMA and the peak at 1610 cm⁻¹ ascribed to C=C stretching of vinyl ether moieties in FBPEVE decreased with PEB treatments. Figure 8 shows the conversion of epoxy in the PGMA/FBPEVE (1:1, w/w), vinyl ether in the PGMA/FBPEVE (1:1, w/w) blended film, epoxy in a PGMA film, and vinyl ether in a FBPEVE film. The conversion of both epoxy and vinyl ether in the blended films showed higher value than those in the non-blended

films. The crosslinking mechanism of the blended system shown in Scheme 1 was discussed based on the result of in-situ FT-IR analyses.

Fig. 7. In-situ FT-IR spectral changes of a PGMA/FBPEVE (1:1, w/w) blended film containing 3 wt% NITf on baking. Film thickness: 1.0 μm . Irradiation dose: 200 mJ/cm^2 . PEB temperature: 120 $^{\circ}\text{C}$.

Fig. 8. Conversion of epoxy in PGMA film (bold line), epoxy in PGMA/FBPEVE (1:1, w/w) blended film (solid line), vinyl ether in FBPEVE film (bold-dotted line), and vinyl ether in PGMA/FBPEVE (1:1, w/w) blended film (dotted line) containing 3 wt% of NITf measured by in-situ FT-IR spectroscopy. Irradiation dose: 200 mJ/cm^2 . PEB temperature: 120 $^{\circ}\text{C}$.

When the films were irradiated, NITf in the film decomposed to produce triflic acid (eq 1). The protonation of vinyl ether (eq 2) or epoxide (eq 3)

Scheme 1.

occurred. The rate of equation 2 is much faster than that of equation 3 due to high reactivity of vinyl ethers compared with epoxy units. From the results shown in Fig. 8, the rate of epoxy-vinyl ether cross-propagation, i.e. the reaction of epoxy and alkoxy-carbenium ion (eq 5) and the reaction of vinyl ether and oxonium ion (eq 6), is larger than the rate of epoxy-epoxy homopropagation, i.e., the reaction of epoxy and oxonium ion (eq 7). Moreover, the reactions concerning vinyl ether, shown in eqs 2, 4, and 6, occur only the initial stage. To assume that the conversion of vinyl ether in the blended film is similar with that in the FBPEVE film, about 40% of the vinyl ether in the blended film was consumed by the reaction of vinyl ether-vinyl ether homopropagation (eq 4). The conversion of vinyl ether in PGMA/FBPEVE blended film reached to be ca. 60%. Thus, ca. 20% of vinyl ether was consumed by reactions shown in eqs 5 and 6 in the initial stage. The mole ratio of epoxy/vinyl ether in the blended film is ca. 2/1. About 10% of epoxy in the blended film can be consumed by epoxy-vinyl ether cross-propagation as shown in eqs 5 and 6. After the reactions concerning vinyl ether (eqs 4, 5, and 6) ceased, epoxy-epoxy homopropagation, (eq 7) proceeded. The rate of epoxy-epoxy homopropagation in the blended film was much

larger than that in the PGMA film. The acceleration of epoxy-epoxy homopropagation rate is considered to be a main factor of the high sensitivity of the blended films.

Table 1. Conversion of epoxy and vinyl ether units in PGMA film, FBPEVE film, and PGMA/ FBPEVE blended film^{a)}.

composition of film (w/w)		conversion(%)			
		PEB ^{b)} at 80 °C		PEB ^{b)} at 120 °C	
PGMA	FBPEVE	epoxy	vinyl ether	epoxy	vinyl ether
0	1	-	31	-	43
1	1	37	44	75	62
3	1	37	51	75	53
10	1	36	- ^{c)}	70	- ^{c)}
20	1	38	- ^{c)}	69	- ^{c)}
1	0	14	-	31	-

^{a)} Irradiation dose: 200 mJ/cm². ^{b)} PEB time: 10 min.

^{c)} Not determined due to low peak intensity.

It is interesting to evaluate the composition dependence of FEPEVE in the blended films on sensitivity enhancement. Table 1 summarizes the conversion of epoxy and vinyl ether in the blended films having different composition. When the weight ratios of PGMA/FBPEVE in the blended films were in the range of 1/1 to 20/1, the conversion of epoxy in the blended film was higher than that in PGMA. When the films were baked at 80 °C, the conversion of epoxy in PGMA/FBPEVE blended films (36 ~ 38%) was 2 ~ 3 times higher than that in PGMA film (14%). When baked at 120 °C, the conversion of epoxy in PGMA/FBPEVE blended films (69 ~ 75%) was also 2 ~ 3 times higher than that in PGMA film (31%). In terms of the reaction mechanism, the conversion of epoxy in the blended films due to crossover reaction of epoxy and vinyl ether (eqs 5 and 6) is reduced with FBPEVE fraction in the blended films. Thus, there is no doubt that epoxy-epoxy homopropagation (eq 7) is accelerated by adding FBPEVE to PGMA.

Investigation of PEB temperature dependence of the reaction rate of epoxy in the blended films is one of the powerful techniques to clarify the reaction mechanism. Apparent activation energy (*E_a*) of conversion of epoxy in PGMA and PGMA/FBPEVE blended film was determined using Arrhenius plots between 1/*T* and ln *k* of conversion of epoxy in the films. The acceleration effect of the blended films can be seen for the

sample baked at 80 ~ 140 °C. Table 2 summarizes the reaction rate constant of epoxy (*k*) and *E_a* values for PGMA film and PGMA/FBPEVE blended films. The *E_a* value for PGMA (46 kJ/mol) is larger than those for PGMA/FBPEVE blended films (24 ~ 28 kJ/mol). Composition dependence of the PGMA/FBPEVE blended films on their *E_a* values was not clearly observed. The *E_a* values for PGMA/FBPEVE blended films correspond to the epoxy-vinyl ether cross-propagation step (eqs 5 and 6). The *E_a* value for PGMA film was due to epoxy-epoxy homopropagation (eq 7).

Table 2. Activation energy *E_a* and reaction rate constant *k* of epoxy in PGMA film and PGMA/FBPEVE blended film^{a)}.

composition of film (w/w)		k (mmol g ⁻¹ s ⁻¹)				Ea (kJ mol ⁻¹)
		PEB temperature (°C)				
PGMA	FBPEVE	80	100	120	140	
1	0	0.44	0.80	2.0	4.2	46
1	1	1.6	2.4	3.8	6.5	28
3	1	2.3	3.6	5.7	9.6	29
10	1	2.6	4.1	6.6	9.6	27
20	1	2.8	3.9	6.1	9.1	24

^{a)} Irradiation dose: 200 mJ/cm².

Conversion of epoxide in PGMA films and PGMA/FBPEVE (1:1, w/w) films with various irradiation dose and with various PEB conditions was examined. When PGMA films were irradiated at 20 mJ/cm² and baked at 80 °C, conversion of epoxy was 9%. On the other hand, 10% of conversion in the blended film was obtained when the film was irradiated at 1 mJ/cm² and baked at 80 °C. When PGMA film and PGMA/FBPEVE (1:1, w/w) films were baked at 100 °C, conversion of epoxy in PGMA film irradiated at 20 mJ/cm² (15%) gave a similar value of conversion of epoxy in PGMA/FBPEVE (1:1, w/w) films irradiated at irradiated at 1 mJ/cm² (16%). Moreover, conversion of epoxy in PGMA film irradiated at 200 mJ/cm² (20%) gave a similar conversion of epoxy in PGMA/FBPEVE (1:1, w/w) films irradiated at irradiated at 2 mJ/cm² (21%). When the films were baked at 120 °C, conversion of epoxy in PGMA film irradiated at 20 mJ/cm² (22%) gave a similar conversion of epoxy in PGMA/FBPEVE (1:1, w/w) films irradiated at irradiated at 1 mJ/cm² (23%). Thus, sensitivity of PGMA/FBPEVE (1:1, w/w) films is 20 ~ 100 times higher than that of PGMA film.

Table 3. Conversion of epoxy in PGMA film and PGMA/FBPEVE blended film.

composition of film (w/w)		PEB temperature ^{a)} (°C)	conversion(%)			
PGMA	FBPEVE		irradiation dose (mJ/cm ²)			
			1	2	20	200
1	0	80	_b)	_b)	9	14
1	1	80	10	13	26	37
1	0	100	_b)	_b)	15	20
1	1	100	16	21	41	54
1	0	120	_b)	_b)	22	31
1	1	120	23	36	56	75

^{a)} PEB time: 10 min. ^{b)} Not determined.

3.4. Thermal properties of photocrosslinked FBPEG/FBPEVE and PGMA/FBPEVE blended films

The thermal degradation of the crosslinked FBPEG/FBPEVE and PGMA/FBPEVE blended films was investigated by TGA measurements. The crosslinked FBPEG/FBPEVE blended films were prepared as follows: FBPEG/FBPEVE blended film with NITf was irradiated with 200 mJ/cm² and baked at 100 °C for 5 min. A similar procedure was employed for the sample preparation of PGMA/FBPEVE blended films except for the PEB treatment at 140 °C for 10 min. The temperatures for 5 wt% loss of the films are summarized in Table 4. Crosslinked FBPEG/FBPEVE and PGMA/FBPEVE blended films showed better thermal stability than corresponding non-blended films. FBPEG/FBPEVE (10:1, w/w) blended film showed the highest thermal stability. This was due to the high weight content of fluorene moieties in the film and relatively high crosslinking density as can be seen in Figs. 2 and 4. Crosslinked blended films showed good thermal stability irrespective of the different reactivity for crosslinking.

4. Conclusion

The photocrosslinking of fluorene derivatives having epoxy and vinyl ether moieties was investigated. The blended system showed high sensitivity compared with non-blended system. In-situ FT-IR study of PGMA/FBPEVE blends was carried out. The observation revealed that the high sensitivity is accomplished by two main factors; (1) the enhancement of conversion of epoxide and vinyl ether by the crossover reactions of epoxy and vinyl ether, and (2) acceleration of

Table 4. Temperature for 5 wt% loss (Td₅) of photocrosslinked FBPEG film, PGMA film, FBPEG/FBPEVE blended film, and PGMA/FBPEVE blended film.

composition of film (w/w)			Td ₅ (°C)
FBPEG	PGMA	FBPEVE	
1	0	0	249 ^{a)}
3	0	1	252 ^{a)}
10	0	1	329 ^{a)}
0	1	0	230 ^{b)}
0	1	1	238 ^{b)}
0	1	2	248 ^{b)}

^{a)} Crosslinking condition; Irradiation dose: 200 mJ/cm². PEB: 100 °C, 5 min. ^{b)} Crosslinking condition; Irradiation dose: 200 mJ/cm². PEB: 140 °C, 10 min.

epoxy-epoxy homopropagation by adding vinyl ether moieties. The sensitivity of PGMA/FBPEVE blended films was 20 to 100 times higher than that of PGMA film. Crosslinked FBPEG/FBPEVE blended films and PGMA/FBPEVE blended films showed better thermal stability than FBPEG film and PGMA film, respectively.

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