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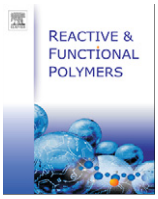

Photo-crosslinking of polymeric photobase generator bearing *O*-acyloxime moieties with low eliminating by-products and high sensitivity

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ABSTRACT

O-Acyloximes are a class of photobase generators (PBGs) that release a primary amine upon irradiation. The generated amine can be used as a crosslinker for polymers bearing epoxy groups, providing a novel photo-induced crosslinking system. However, *O*-acyloximes also release a ketone by-product that migrates and exudes from the crosslinked polymer. To reduce the migration and elimination of the ketone, 4-vinylacetophenone *O*-phenylacetyloxime (PaVO) was proposed as a monomeric PBG, and its copolymer with glycidyl methacrylate (PaVO-co-GMA) was compared to poly(glycidyl methacrylate) (PGMA) containing acetophenone *O*-phenylacetyloxime (PaApO) as a molecular PBG (PaApO/PGMA). Film thickness, infrared (IR), and ultraviolet (UV) spectral changes upon irradiation clarified the vaporization of photoproducts from the PaApO/PGMA films, while such behavior was not observed for the PaVO-co-GMA films. Furthermore, when PaVO-co-GMA was blended with PGMA, less irradiation energy was required for its crosslinking when compared to that of PaApO/PGMA, which contained the same molar ratio of the *O*-acyloxime unit.

1. Introduction

Photo-induced crosslinking is widely used to enhance the mechanical, thermal, and chemical-resistance properties of polymers via the formation of network structure. By applying light, spatial and dimensional control can be easily attained, often without heating. The excellent process ability of photo-induced crosslinking is advantageous in many fields, including imaging and surface modification. Recently, further attempts to post-crosslink engineering plastics [1,2], design degradable crosslinkers [3,4], and use for biomaterials [5] have been reported.

Photo-induced crosslinking often utilizes active species such as free radicals and acids that contribute to the bond formation in radical and cationic mechanisms. However, the radical mechanisms suffer from oxygen inhibition, and the residual acids often induce problems, such as metal corrosion in the cationic mechanism.

A photobase generator (PBG) is another photolabile active species that releases active bases upon irradiation. Generated bases can be used as catalysts for many reactions, such as polymerization, crosslinking, and depolymerization [6–8]. The PBG units that are introduced into polymer side-chains also induce crosslinking and polarity alterations that lead to a drastic solubility change of the polymers.

O-Acyloximes are known to release a primary amine upon irradiation, followed by hydrolysis [9–12]. As shown in Scheme 1, a ketone by-product is also produced in addition to the amine. In the use of negative-type photoresists and coatings, by-products often migrate in the macromolecular network and induce the reduction of film thickness after irradiation. During UV curing, by-products exude from the cured materials, which is a problem, especially in packaging and food applications [7,13].

In this paper, we demonstrate the effect of ketone by-product covalent bonding on the film reduction and photocrosslinking behavior of polymers bearing *O*-acyloxime moieties. We propose a novel *O*-acyloxime, 4-vinylacetophenone *O*-phenylacetyloxime (PaVO), which is anticipated to generate an amine without releasing a ketone after polymerization. Herein, PaVO was copolymerized with glycidyl methacrylate (GMA), and its behavior was compared to that of poly(glycidyl methacrylate) (PGMA), which contains corresponding low molecular weight PBG, acetophenone *O*-phenylacetyloxime (PaApO), in terms of spectral, film thickness, and solubility changes.

2. Experimental

2.1. Instruments

NMR, IR, and UV spectra were recorded using Jeol JNM-LA300, Jasco FT-IR4200, and Shimadzu UV2400 spectrometers, respectively. Thermal decomposition temperatures (T_d) and glass transition temperatures (T_g) were obtained using Shimadzu TGA-50 and

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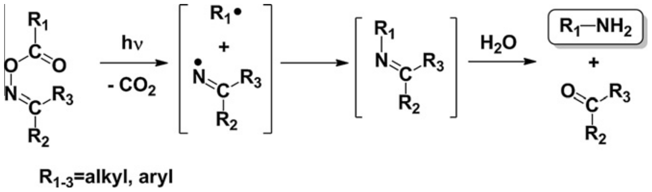


Scheme 1. The photoreaction of *O*-acyloximes.

DSC-60, respectively, with a heating rate at 10 K/min under N_2. Elemental analysis was performed using a Yanako MT-3 CHN recorder.

The molecular weights of the polymers were obtained after size exclusion chromatography (SEC) using Tosoh TSKgel GMH_{HR}-N and GMH_{HR}-H columns, a Jasco PU2080plus pump, a Jasco RI-2031plus detector, and a Jasco DG2080-53 degasser at 40 °C with tetrahydrofuran (THF) as the eluent and polystyrene standards.

An Ushio ULO-6DQ low pressure mercury lump was used as a 254 nm light source. The films were coated with a Mikasa 1H-D7 spincoater and baked on a Koike Seimitsu Kikai HM-15G hot plate. The thicknesses of the films on silicon plates were measured using a Nanometrics Nanospec/AFT M3000 interferometer.

2.2. Materials

Phenylacetyl chloride (Tokyo Chemical Industry), propylene glycol monomethyl ether acetate (PGMEA, Nacalai Tesque), chloroform (Wako Pure Chemicals, containing 150 ppm of amylene) and 2,2′-azobisisobutylonitrile (AIBN, Nacalai Tesque) were used as received. Triethylamine, THF, and GMA were distilled before use. 4-Vinylacetophenone was prepared from 4-bromoacetophenone and acetic anhydride as described in literature [14]: bp: 62–64 °C/1 mmHg (lit [14]: 63–64 °C/1 mmHg), IR (neat): 1680 cm^{-1} (C=O). PaApO was prepared from phenylacetyl chloride and acetophenone oxime as described in the literature [9]: mp: 44.5–45 °C (lit [9]: 42–43.5 °C).

2.3. 4-Vinylacetophenone oxime

In a flask, 6.87 g (47.0 mol) of 4-vinylacetophenone in 50 mL of ethanol and 4.90 g (70.5 mmol) of hydroxyammonium chloride in 40 mL of methanol were mixed. The mixture was cooled in an ice bath, and 24.3 g of sodium hydroxide was dissolved in 20 mL of water and added. After stirring at room temperature for 75 min and at 45 °C for 5 min, 1.2 N HCl was added until the pH became 4. The resulting solid was filtered, dried, and recrystallized from a toluene/hexane = 9/1 (vol/vol) mixture to afford 4.16 g of a colorless solid: yield 54.9%, mp: 119.5–120 °C, IR (KBr): 3325 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): 2.30 (3H, s, CH_3), 5.30 (1H, d, cis CH), 5.79 (1H, d, trans CH), 6.74 (1H, dd, *J* = 17.6 and 10.8 Hz, gemCH), 7.42 (2H, d, *J* = 8.4 Hz, meta), 7.60 (2H, d, *J* = 8.4 Hz, ortho), 9.46 (1H, broad s, OH). ^{13}C NMR ($CDCl_3$): 12.17, 114.72, 126.17, 126.31, 135.71, 136.16, 138.43, 155.67. The ^{1}H NMR peaks were assigned based on the literature [15].

2.4. 4-Vinylacetophenone O-phenylacetyloxime (PaVO)

In a 500 mL four-necked flask equipped with a drop funnel, 4.20 g (26.1 mmol) of 4-vinylacetophenone oxime and 3.63 mL (26.1 mmol) of triethylamine were dissolved in 120 mL of chloroform. Then, 3.45 mL (26.1 mmol) of phenylacetyl chloride and 15 mL of chloroform were added dropwise. Maintaining the solution <−5 °C with an ice bath, a phenylacetyl chloride solution was added dropwise over a period of 45 min. The flask was then stirred at room temperature for 1 h 45 min and heated at 50 °C for 10 min. The solution was subsequently washed with 1.2 N HCl, sat. $NaHCO_3$, and sat. NaCl aqueous solutions and dried over sodium sulfate. After being concentrated, the resulting tar was chromatographed using silica gel and chloroform to afford 6.42 g of a colorless solid, which was further purified via recrystallization twice from toluene/hexane = 9/1 (vol/vol). Finally, 3.50 g (12.5 mmol) of a colorless solid was obtained: Yield: 47.8%, mp: 63.5–64 °C. T_d (TGA onset): 224 °C. UV (CH_3CN): λ_{max} 276 nm (ε 2.45×10^4 L mol^{-1} cm^{-1}). ^{1}H NMR($CDCl_3$): δ (ppm) = 2.29 (3H, s, CH_3), 3.85 (2H, s, CH_2), 5.32 (2H, d, =CH), 5.82 (1H, d, =CH), 6.72 (1H, dd, *J* = 17.6 and 10.9 Hz, gemCH), 7.25–7.36 (5H, m, phenyl), 7.42 (2H, d, *J* = 8.3 Hz, meta), 7.70 (2H, d, *J* = 8.4 Hz, ortho). IR (KBr):1755 cm^{-1} (C=O). ^{13}C NMR($CDCl_3$): δ (ppm) = 14.16, 40.34, 115.43, 126.27, 127.19, 128.61, 129.29, 133.43, 133.84, 135.98, 139.75, 162.57, 168.86. Elemental analysis:Calcd. for $C_{18}H_{17}NO_2$; C: 77.40, H: 6.13, N:5.01. Found C: 77.46, H: 5.56, N: 5.07.

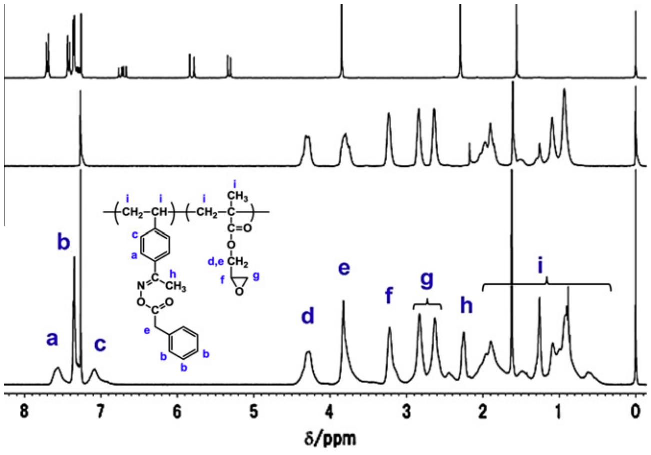


Fig. 1. The ^{1}H NMR ($CDCl_3$) spectra of PaVO (top), PGMA (middle), and PaVO-co-GMA (bottom).

Table 1
Polymerization conditions and characteristics of polymers.[a]

Polymer	PaVO (mol%)		Yield[c] (%)	M_n[d]	M_w/M_n[d]	T_g (°C)	T_d (°C)
	In feed	In polymer[b]					
PaVO-co-GMA	10	21	22	5000	1.54	55	234
PGMA	0	0	60	5400	1.64	50	337

[a] Polymerization at 60 °C for 4 h.
[b] From ^{1}H NMR spectrum.
[c] After reprecipitation.
[d] From SEC.

2.5. Polymerization

In a tube, total 35 mmol monomers, 51 mg (0.31 mmol) of AIBN, and 0.3 mL (1.3 mmol) of 1-dodecanethiol were dissolved in 5.9 mL of toluene. After degassing with freeze-pump-thaw cycles under N_2, the solution was heated at 60 °C for 4 h. The mixture was then cooled and poured into hexane. The obtained solid was reprecipitated three times from methanol and twice from hexane after being dissolved in THF. The polymerization conditions and characteristics of the purified polymers are summarized in Table 1.

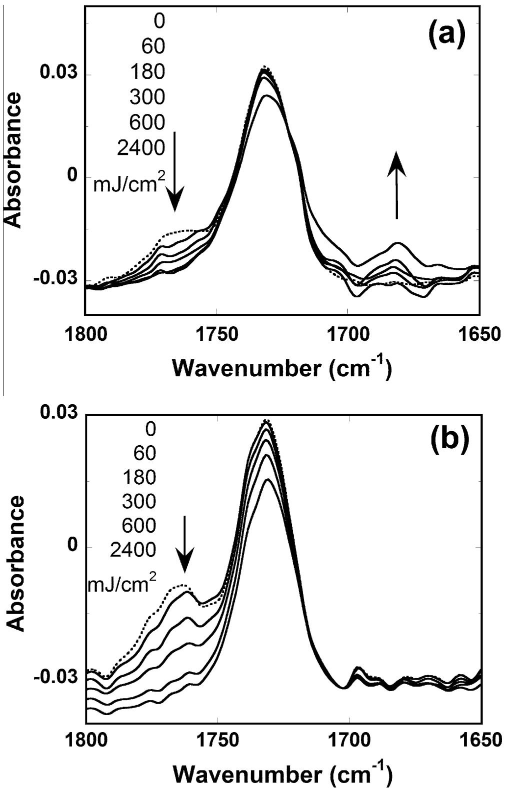


Fig. 2. The IR spectral changes of (a) PaVO-co-GMA and (b) PaApO/PGMA films upon irradiation at 254 nm. The numbers indicate irradiation energy. *O*-Acyloxime unit/epoxy unit = 21/79 (mol/mol). Film thickness before irradiation: 0.3–0.4 μm. The dotted lines demonstrate the spectra before irradiation.

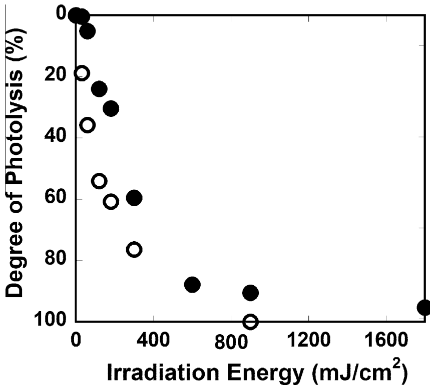


Fig. 3. The photolysis rates of the *O*-acyloxime units in the (○) PaVO-co-GMA and (●) PaApO/PGMA films based on an IR peak intensity at approximately 1765 cm^{-1}.

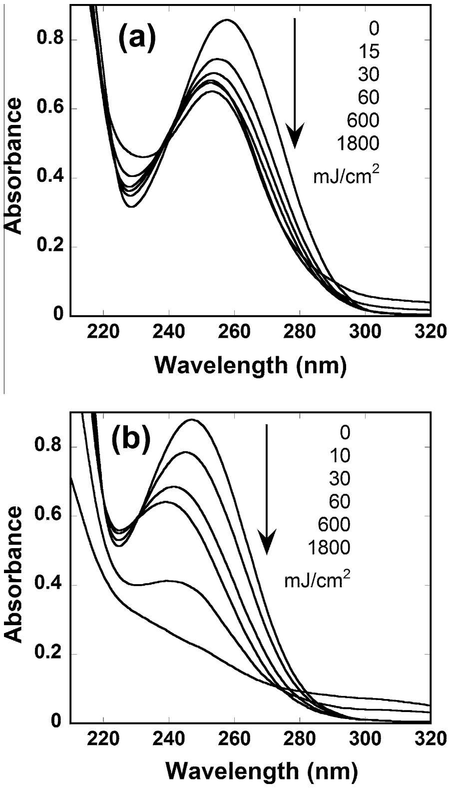


Fig. 4. The UV spectral changes of (a) PaVO-co-GMA and (b) PaApO/PGMA films upon irradiation at 254 nm. The numbers indicate irradiation energy. *O*-Acyloxime unit/epoxy unit = 21/79 (mol/mol). Film thickness before irradiation: 0.3–0.4 μm.

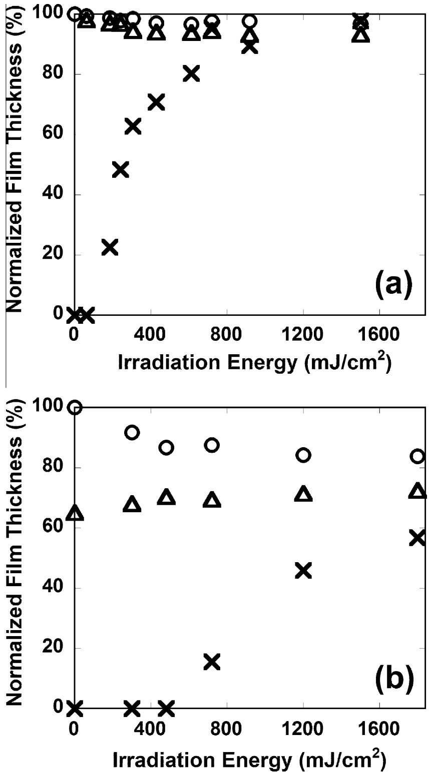


Fig. 5. The changes in film thickness for (a) PaVO-co-GMA and (b) PaApO/PGMA films upon irradiation, followed by heating at 140 °C for 10 min and soaking in THF for 10 min. (○) After irradiation, (△) after heating, and (×) after soaking in THF respectively, based on thickness after prebake. *O*-Acyloxime unit/epoxy unit = 21/79 (mol/mol).

2.6. Film state evaluation

The polymers and additives were dissolved in PGMEA, filtered with 0.45 μm pore size PTFE disposable filters, and spin-coated on silicone or quartz plates. The films were heated at 80 °C for 2 min on the hot plate to remove the PGMEA and were then irradiated with the low-pressure mercury lamp with a light intensity of 1.0 mW/cm^2 at 254 nm. IR and UV spectral changes of the films were obtained after repeating irradiation and spectral measurement.

After irradiation, the films were post-exposure baked at 140 °C on the hot plate and soaked in THF for 10 min at room temperature. The insoluble fractions were obtained from the thickness ratio before and after soaking.

3. Results and discussion

PaVO-co-GMA was obtained via conventional free-radical polymerization. According to the ^{1}H NMR spectrum of this copolymer in Fig. 1, the molar ratio of PaVO and GMA was estimated to be 21: 79 with a feed ratio of 10: 90. The thermal stability of PaVO-co-GMA was high, as demonstrated by its T_d at 234 °C.

Fig. 2 shows the IR spectral changes of the PaVO-co-GMA and PaApO-blended PGMA (PGMA/PaApO) films upon irradiation at 254 nm in ambient air. In both cases, a peak at approximately 1765 cm^{-1} due to the C=O stretching of the *O*-acyloxime moiety decreased upon irradiation. Based on the changes of peak intensity at approximately 1765 cm^{-1}, the degree of *O*-acyloxime photolysis is plotted in Fig. 3. The photoreactivity of the *O*-acyloxime unit in both films was nearly identical.

For the PaVO-co-GMA films, a peak appeared upon irradiation at 1680 cm^{-1}, which is assigned to an aromatic ketone group in Scheme 1. This signal indicates that the hydrolysis in Scheme 1 immediately proceeded with water, which was involved in the polymer matrix or supplied from moisture. Contrastingly, the PGMA/PaApO film showed little change near this region. This result suggests that the photo-generated acetophenone vaporized from the thin film during irradiation.

Fig. 4 presents the UV spectral changes of the PaVO-co-GMA and PaApO/PGMA films upon irradiation at 254 nm in ambient air. A peak at 258 nm for the PaVO-co-GMA film decreased slowly with a small blue shift. This result is consistent with the formation of benzylamine and a pendant acetophenone unit because benzylamine and 4-methylacetophenone demonstrate maximum peaks at 259 nm (in ethanol, ε: 232) [16] and 251 nm (in methanol, ε: 12,670) [17], respectively. In contrast, a peak at 247 nm for the PGMA/PaApO film almost disappeared after irradiation ⩾600 mJ/cm^2, suggesting vaporization of the generated acetophenone from the irradiated films. The thickness changes of the PaVO-co-GMA

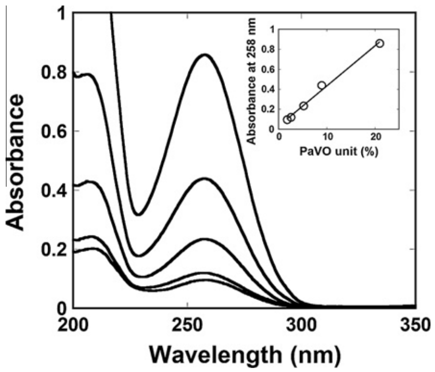
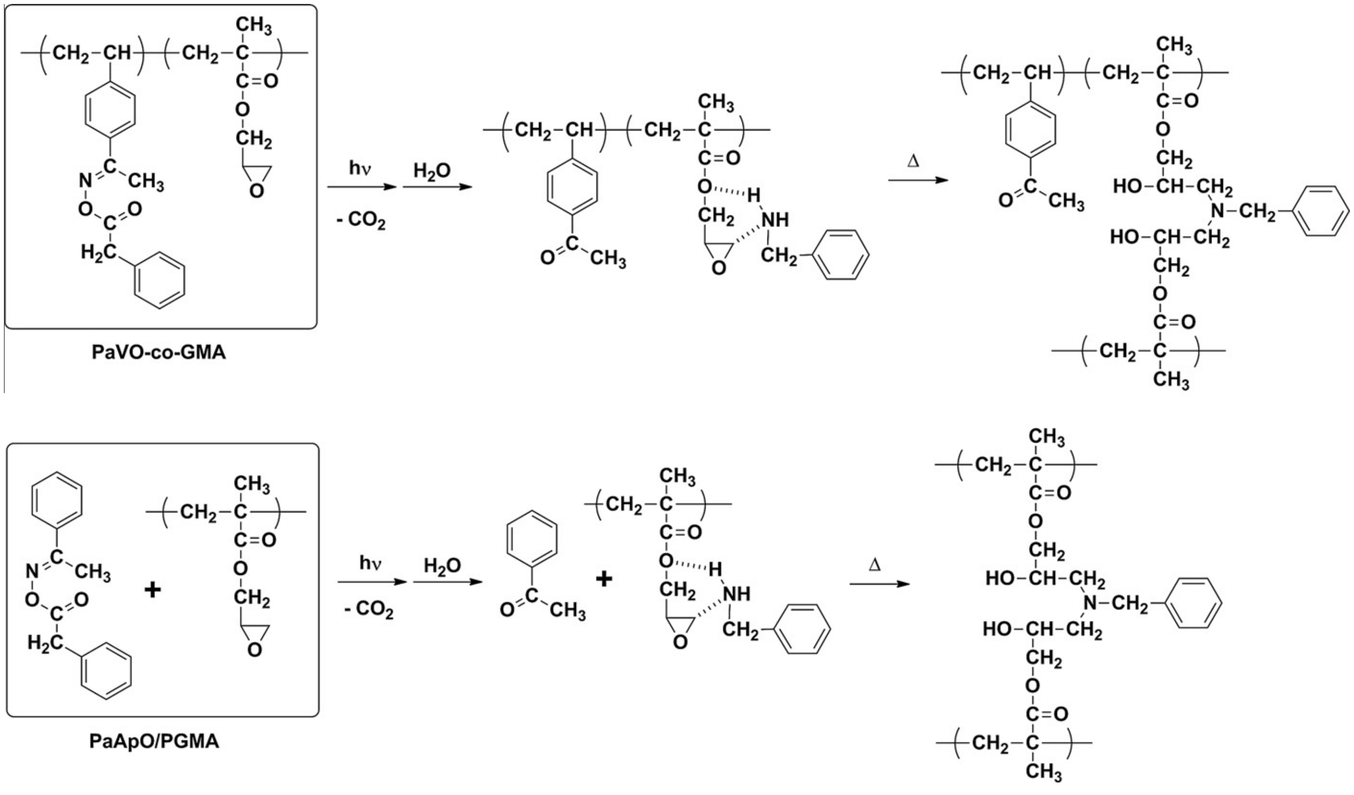


Fig. 6. The UV spectra of PaVO-co-GMA blended PGMA films. Film thickness: 0.4 μm. The inset shows the absorbances at 258 nm plotted against the PaVO molar ratio in the films.



Scheme 2. The photo-induced crosslinking of PaVO-co-GMA and PaApO/PGMA.

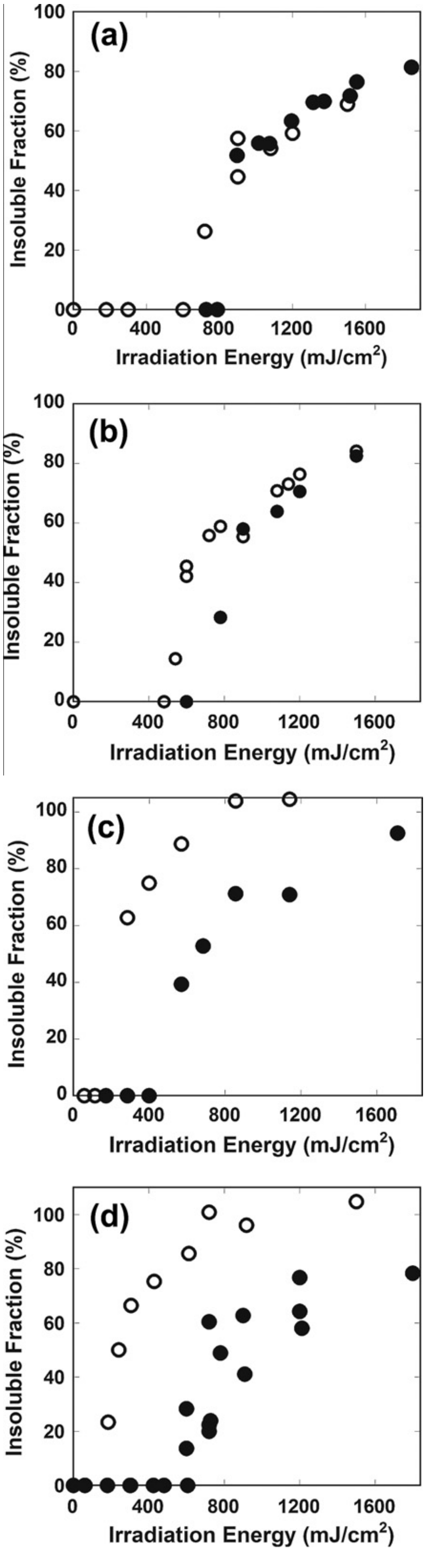


Fig. 7. The insolubilization of PaVO-co-GMA blended with PGMA (open) and PaApO/PGMA (solid symbols) films upon irradiation, followed by heating at 140 °C for 10 min and soaking in THF for 10 min. *O*-acyloxime unit/epoxy unit = (a) 1.8/98.2, (b) 2.6/97.4, (c) 10.5/89.5, and (d) 21/79 (mol/mol).

and PGMA/PaApO films during irradiation, heating, and soaking processes were monitored. As shown in Fig. 5a, the film thickness of PaVO-co-GMA was almost constant even after irradiation (○) and heating at 140 °C (△). This result indicates that the generated benzylamine and ketone units remained in the polymer matrix, despite that the boiling point of benzylamine is 185 °C and lower than that of acetophenone (202 °C). For the reaction mechanism of epoxy-amine curing, the possibility of epoxy and amine complex formation [18] and the catalytic role of added water [19] have been recently reported. In the present study, such complex formation or addition reaction between epoxy and amino groups likely prevented the vaporization of the generated benzylamine. After soaking in THF (×), the films were soluble in THF at low irradiation energy, showing insufficient network formation. As the irradiation energy increased, the remaining film thicknesses increased due to crosslinking between the generated benzylamine and pendant epoxy groups.

The PGMA/PaApO films in Fig. 5b demonstrated a difference in behavior of thickness changes. The film thicknesses decreased upon irradiation (○) with increasing irradiation energy, suggesting the removal of the volatile acetophenone formed on irradiation. The film thicknesses reduced upon heating at 140 °C (△), although they slightly increased with increasing irradiation energy. This trend suggests that PaApO sublimed upon this heating condition, and the generated benzylamine stayed in the PGMA matrix as discussed above. The irradiated and heated films (×) became insoluble in THF when the irradiation energy was >700 mJ/cm^2. However, the remaining films were thinner when compared to those of PaVO-co-GMA.

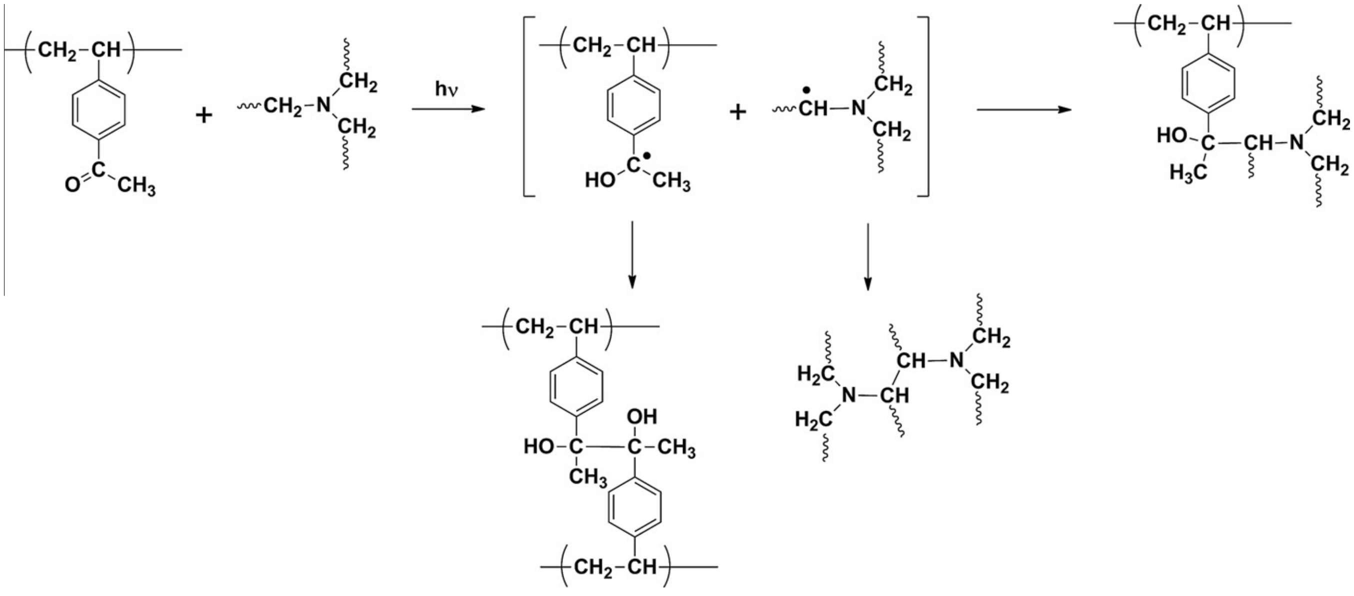
From the above results, the photo- and crosslinking reactions of both systems are proposed in Scheme 2. Although we could not obtain spectral evidence, a linkage is likely generated between the benzylamine and two epoxy groups due to its high reactivity. For example, a near IR measurement clarified the formation of a tertiary amino group after heating the mixture of 3-(aminomethyl)benzylamine and diglycidyl ether of bisphenol A for 10 min even at 80 °C [20].

The photo-induced crosslinking of the films containing different feed ratios of *O*-acyloxime units was also investigated. The molar ratios were controlled via blending PaVO-co-GMA and PGMA. No haze was observed for all of the blended films, and the UV spectra of the films indicate that the absorbance at 258 nm is proportional to the PaVO molar ratio, as shown in Fig. 6. These results suggest the absence of PaVO-co-GMA aggregation in the PGMA matrix. Fig. 7 shows the changes of the insoluble fractions of the PGMA films containing PaVO-co-GMA and PaApO with the same *O*-acyloxime unit. When the films contained 1.8% *O*-acyloxime unit (Fig. 7a), similar solubility curves were obtained. With increasing the molar ratio of the *O*-acyloxime unit (Fig. 7b–d), less irradiation energy was required to induce crosslinking due to the increased crosslinking points. However, the crosslinking of films containing PaVO-co-GMA was initiated at lower irradiation energy.

The higher ability of PaVO-co-GMA/PGMA crosslinking can be explained by the possibility of secondary photoreactions of photoproducts which were incorporated in the polymers. It is well known that free radicals are produced via α-hydrogen abstraction of the amino groups by the photogenerated ketone [21]. The resulting radicals can couples together to form crosslinking points, as shown in Scheme 3.

4. Conclusions

We have prepared copolymer PaVO-co-GMA from a new monomeric PBG and compared its behavior to that of PGMA/PaApO films. The photoreactivity and thermal stability were similar for both films. Removal of the acetophenone by-product from the irradiated PaApO/PGMA films was confirmed in terms of spectral and film thickness changes, although such removal was not observed for PaVO-co-GMA. Both films became insoluble in THF upon



Scheme 3. Plausible secondary photoreactions.

irradiation, followed by heating due to crosslinking, and PaVO-co-GMA films showed a higher photocrosslinking efficiency when compared to that of PaApO/PGMA films.

References

[1] M. Nechifor, React. Funct. Polym. 69 (2009) 27–35.
[2] C.W. Lee, J.W. Kim, J.-H. Lee, K.-D. Ahn, React. Funct. Polym. 69 (2009) 737–742.
[3] H. Okamura, E. Yamauchi, M. Shirai, React. Funct. Polym. 71 (2011) 480–488.
[4] V. Gaud, F. Rougé, Y. Gnanou, J.-P. Desvergne, React. Funct. Polym. 72 (2012) 521–532.
[5] E. Velickova, P. Petrov, C. Tsvetanov, S. Kuzmanova, M. Cvetkovska, E. Winkelhausen, React. Funct. Polym. 70 (2010) 908–915.
[6] K. Dietliker, Photobase generators, in: G. Bradley (Ed.), Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, second ed., John Wiley & Sons, Chichester, England, 1998 (Chapter 4).
[7] K. Dietliker, R. Husler, J.L. Birbaum, I.S. Misteli, S. Villeneuve, K. Studer, T. Jung, J. Benkhoff, H. Kura, A. Matsumoto, H. Oka, Prog. Org. Coat. 58 (2007) 146–157.
[8] K. Suyama, M. Shirai, Prog. Polym. Sci. 34 (2009) 194–209.
[9] K. Ito, Y. Shigeru, Y. Kawata, K. Ito, M. Tsunooka, Can. J. Chem. 73 (1995) 1924–1932.
[10] J. Lalevée, X. Allonas, J.P. Fouassier, H. Tachi, A. Izumitani, M. Shirai, M. Tsunooka, J. Photochem. Photobiol. A: Chem. 151 (2002) 27–37.
[11] K. Suyama, T. Inoue, S. Ogata, M. Shirai, Chem. Lett. 39 (2010) 362–363.
[12] K. Suyama, S. Ogata, T. Inoue, M. Shirai, J. Photopolym. Sci. Technol. 23 (2010) 439–446.
[13] R. Burrows, R.S. Davidson, D.R. Illsley, Surf. Coat. Int. Part B: Coat. Trans. 87 (2004) 127–135.
[14] A. Hirao, K. Kato, S. Nakahama, Macromolecules 25 (1992) 535–540.
[15] S.E. Denmark, C.R. Butler, Org. Lett. 8 (2006) 63–66.
[16] H. Shizuka, M. Nakamura, T. Morita, J. Phys. Chem. 83 (1979) 2019–2024.
[17] J. Kulhánek, S. Böhm, K. PalátJr, O. Exner, J. Phys. Org. Chem. 17 (2004) 686–693.
[18] J.E. Ehlers, N.G. Rondan, L.K. Huynh, H. Pham, M. Marks, T.N. Truong, Macromolecules 40 (2007) 4370–4377.
[19] S. Choi, A.P. Janisse, C. Liu, E.P. Douglas, J. Polym. Sci. Part A: Polym. Chem. 49 (2011) 4650–4659.
[20] S. Paz-Abuin, A. Lopez-Quintela, M. Varela, M. Pazos-Pellin, P. Prendes, Polymer 38 (1997) 3117–3120.
[21] Y. Yagci, S. Jockusch, N.J. Turro, Macromolecules 43 (2010) 6245–6260.