

SYNTHESIS OF PHOTOBASE GENERATORS AND THEIR USE FOR DESIGN OF POLYMERIC PHOTOSENSITIVE SYSTEMS

MASAHIRO TSUNOOKA, HIDEKI TACHI, KAORI ASAKINO AND KANJI SUYAMA

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Osaka 599-8531, Japan

(Received 28 June 1999; accepted 30 July 1999)

Abstract—The use of O-carbamoyloximes as photobase generators was investigated. α -Methylbenzilydeneamino phenylcarbamate (**2a**) and α -methyl benzilydeneamino cyclohexylcarbamate (**2b**) were prepared by the reaction of phenyl or cyclohexyl isocyanates with acetophenone oxime, respectively. Aniline, phenylhydrazine and N,N'-diphenylhydrazine were detected in the photolysis of **2a** and cyclohexylamine and cyclohexylhydrazine in the photolysis of **2b**. A monomer having pendant carbamoyloxyimino groups (BGM) was prepared by the reaction of methacryloyloxyethyl isocyanate with acetophenone oxime, and copolymerized with styrene. The BGM copolymer films turned insoluble on UV irradiation, and the degree of insolubilization was increased by post-baking. The photocrosslinking was thought to be due to coupling of resulting pendant aminyl radicals, and the thermal crosslinking was due to association of resulting amino and hydrazino groups by hydrogen bonding. The introduction of epoxy groups into polymer increased the degree of thermal crosslinking by post-baking.

INTRODUCTION

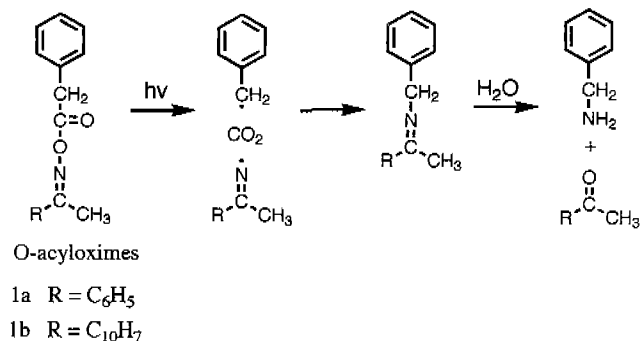
Photosensitive polymers whose physical properties are modified by UV irradiation are key materials not only as UV curing materials in the surface finishing¹ and photoresists used for fabrication of Large Scale Integrated circuits,² but also as those for fabrication of biomolecular devices such as biosensors.³ Photocrosslinking of polymers is one of most useful reactions for the design of photosensitive polymers. The use of photoacid and photobase generators in the photocrosslinking systems has recently attracted considerable attention for attainment of high sensitivity by chemical amplification.^{4,5}

In our laboratory, we have investigated the use of O-acyloximes as photobase generators.⁶⁻¹¹ O-acyloximes are transformed into amines photochemically (Scheme 1),⁶ and the resulting amines are used as thermal crosslinkers of poly(glycidyl methacrylate) (PGMA).⁷ We have also found that acetophenone O-acryloyloxime (AAPO)-styrene (St) copolymers acted as polymeric pho-

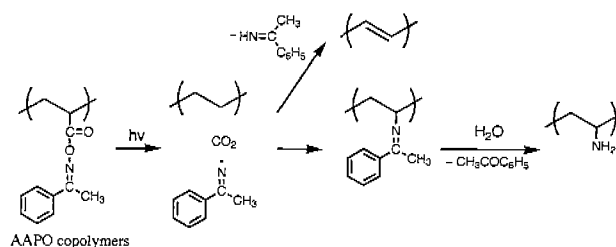
tobase generators (Scheme 2),⁸ and that resulting amino groups in the copolymers were utilized as thermal crosslinkers of epoxy compounds or functional groups for polarity alternation of the films.⁹

In addition, we have found that AAPO-methyl methacrylate (MMA) copolymer films with quinones were insolubilized photochemically, and enhanced thermal treatment after the irradiation.¹⁰ In this system, the quinones act not only as the photosensitizer for photolysis of acyloxyimino (AOI) groups in AAPO but also as scavengers of resulting radicals and amino groups, which leads to the insolubilization of the copolymers.

Recently, the use of several O-carbamoyloximes as photobase generators has been reported. Bucher et al. have reported the mechanism of amines generation from O-carbamoyloximes by laser flash photolysis,¹² and Chae *et al.* reported thermal



Scheme 1. Photolysis of O-acyloximes.



Scheme 2. Photolysis of AAPO copolymers.

crosslinking of PGMA films by cyclohexylamine generated in the photolysis of benzophenone O-cyclohexylcarbamoyloxime¹³ and of irradiated glycidyl methacrylate copolymers bearing carbamoyloxyimino (COI) groups.¹⁴

We have been interested in the features of O-acyloximes and O-carbamoyloximes as photobase generators. In the course of

study on the photocrosslinking of copolymers bearing COI groups, we have found that their photocrosslinking behavior is very different from that of copolymers bearing AOI groups, which was explained by the difference in processes of the generation of bases in their photolysis.

In this paper, we report the feature of photocrosslinking of copolymers bearing COI groups in comparison with those bearing AOI groups.

MATERIALS AND METHODS

Materials Dibutyltin(IV) dilaurate (Wako Chemical (chemical grade)), cyclohexyl isocyanate (Wako (special grade)), phenyl isocyanate (Tokyo Chemical Industry) and methacryloyloxyethyl isocyanate (Showa Denko) were used as received. Solvents and monomers (styrene (St) and glycidyl methacrylate (GMA)) were distilled before use. 2,2'-Azoisobutyronitrile (AIBN) was recrystallized from ethanol. The structures of compounds having COI groups used in this paper are shown in Fig. 1.

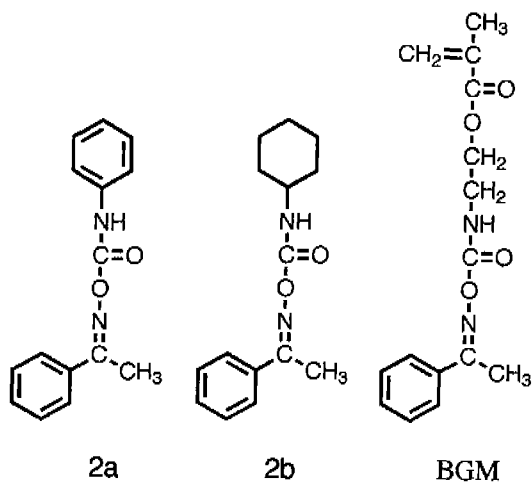


Figure 1. Structures of COI compounds having COI groups.

Measurements FT-IR spectra were obtained using JASCO FT-IR 7300. Shimadzu UV-2400PC was used to obtain UV spectra. Elemental analyses were performed by Yanaco MT-3 CHN coder. ^1H NMR spectra was recorded in CDCl_3 on a JEOL GX-270 using trimethylsilane as standard. Gel permeation chromatography (GPC) was carried out on a JASCO GPC system (pump: JASCO PU-980, columns: Shodex KF-806M, detector: JASCO RI-910, integrator: JASCO 807-IT, eluent: tetrahydrofuran (THF)) using polystyrene standard. Glass transition temperature was measured on a Rigaku DSC 8320. Product analysis was carried out by HPLC on JASCO high performance liquid chromatography (HPLC) systems (pump: JASCO BIP-1, columns: CHEMCOSORB 10-ODS-L, detector: JASCO UV-970) and by gas chromatography (GC) on Shimadzu GC-8A with a detector using thermal conductivity and a column packed with Apiezone-L (10 %). A mixture of water and methanol (6 : 4 by volume) was used as an eluent for HPLC and He gas as a carrier gas for GC.

Preparation of α -methylbenzilydeneamino phenylcarbamate (2a) Acetophenone oxime (1.35 g, 0.01 mol) and a small amount of dibutyltin(IV) dilaurate were dissolved in 5ml of methylene chloride. Phenyl isocyanate (1.28 ml, 0.01 mol) was added dropwise to the solution with stirring. After completion of the addition of phenyl isocyanate, the solution was further stirred for 48 h at room temperature. Then, the removal of methylene chloride of the solution gave a white solid. The solid was recrystallized from ethyl acetate to afford 1.80 g of crystals (70.9 %). mp 65.0-65.5 °C. IR(KBr): 1710 (C=O), 1520 (NHC=O) cm^{-1} . UV(MeOH): $\epsilon_{245}=25000$. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2$: C, 70.87; H, 5.71; N, 11.32. Found: C, 70.99; H, 5.60; N, 11.57. ^1H NMR(CDCl_3): δ 8.38 (br, 1H), 7.73-7.68 (m, 2H), 7.53-7.41 (m, 5H), 7.37-7.31 (m, 2H), 7.15-7.08 (t, 1H), 2.48 (s, 3H), 2.26-2.02 (m, 2H), 1.76-1.15 ppm (m, 8H).

Preparation of α -methylbenzilydeneamino cyclohexylcarbamate (2b) 2b was prepared in a similar manner as 2a using cyclohexyl isocyanate instead of phenyl isocyanate. Yield: 72.3 %. mp 132.5-133.0 °C. IR(KBr): 1710 (C=O), 1520 (NHC=O) cm^{-1} . UV(MeOH): $\epsilon_{245}=13000$. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$: C, 69.23; H, 7.69; N, 10.77. Found: C, 69.48; H, 7.71; N, 10.82. ^1H NMR(CDCl_3): δ 7.66-7.62 (m, 2H), 7.48-7.38 (m, 3H), 6.30 (br, 1H), 3.67 (br, 1H), 2.41 (s, 3H), 2.02 (m, 2H), 1.75-1.15 ppm (m, 8H).

Preparation of base generating monomer (BGM): It was prepared by the reaction of acetophenone oxime (2.70 g, 0.02 mol) and methacryloyloxyethyl isocyanate (3.11 g, 0.02 mol) in a similar manner as 2a. Yield: 95.6 %. mp 52.0-53.0 °C. IR(KBr): 3350 (NH), 1760 (C=O), 1692 (C=O), 1627 (C=N), 1525 (NHC=O) cm^{-1} . UV(MeOH): $\epsilon_{244}=16000$. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4$: C, 69.23; H, 7.69; N, 10.77. Found: C, 69.48; H, 7.71; N, 10.82. ^1H NMR(CDCl_3): δ 7.69-7.65 (m, 2H), 7.48-7.36 (m, 3H), 6.80 (br, 1H), 6.12 (s, 1H), 5.57 (s, 1H), 4.31 (t, 2H), 3.81 (t, 2H), 2.66 (s, 3H), 1.94 ppm (s, 3H).

Copolymerization of BGM and St: BGM (1.15 g, 0.004 mol), St (1.66 g, 0.016 mol) and AIBN (0.028 g, 1 wt% against monomers) was dissolved in dry dimethylformamide (3 ml) in a polymerization tube. The tube was degassed by freeze-pump-thaw cycles. The polymerization was carried out at 60 °C for 4.5 h. The polymer solution was poured into a large amount of methanol. Resulting polymers were reprecipitated with THF-methanol. The composition of resulting copolymers was determined by elemental analysis. The polymers containing glycidyl methacrylate were also prepared similarly. Polymerization conditions and physical properties of copolymers are shown in Table 1.

Preparation of polymer films and UV irradiation: The films (ca. 0.3 μm) were prepared by casting a THF solution of BGM copolymers onto a glass plates. UV irradiation was carried out by a low-pressure mercury lamp (USHIO ULO-6DQ) or a high-pressure mercury lamp (USHIO UM-102). The irradiated films were baked at a given temperature on a hot plate. The films were developed with THF for 10 min at room temperature. The insoluble fraction was determined by the ratio of film thickness before and after the development by two-beam interferometry with an interference microscope (Nikon OPTIPHOT).

Photolysis of O-carbamoyloximes in a film: Poly(methyl methacrylate) (PMMA) films (ca. 40 μm) were prepared by cast-

Table 1. Polymerization Conditions and Physical Properties of Polymers

Polymer	in feed (mol %)			in polymer (mol %)			P.T (h)	Conv. (%)	\overline{M}_n ($\times 10^{-4}$)	$\overline{M}_w / \overline{M}_n$	T_g ($^{\circ}\text{C}$)
	BGM	GMA	St	BGM	GMA	St					
BGM(25)-St	25	-	75	27	-	72	4.5	35.2	4.3	1.91	84.2
BGM(20)-GMA(27)-St	16	16	68	20	27	53	2.5	22.1	4.6	1.87	74.9

Initiator: AIBN. Solvent: dimethylformamide. Polymerization temperature: 60 $^{\circ}\text{C}$ P.T.: Polymerization time.

ing a THF solution of PMMA and 15 wt% of O-carbamoyloximes based on PMMA in a Petri dish. The films were mounted on plastic frames with window (3.5 \times 3.5 cm) and irradiated in air or under nitrogen. The irradiated films were dissolved in 1 ml of THF, and the PMMA was reprecipitated by adding of 5 ml of methanol. The precipitated PMMA was separated from the solution by centrifugation, and the resulting solution was used for an analyses of N,N'-diphenylhydrazine (**6a**), acetophenone phenylhydrazine (**7a**), acetophenone (**9a**), acetophenone azine (**10a**), **2a** and **2b** by HPLC. Aniline (**5a**) and phenylhydrazine (**8a**) formed in the photolysis of **2b** were quantitatively analyzed by GC as their derivatives by the use of trifluoroacetic anhydride. Analyses of resulting cyclohexylamine and cyclohexylhydrazine were carried out by HPLC as their derivatives by the use of 3,5-dinitrobenzoyl chloride or salicylaldehyde, respectively.

RESULTS AND DISCUSSION

Photochemical behavior of O-acyloximes and copolymers bearing AOI groups: In previous papers,⁶⁻⁸ we have reported the photochemical generation of amines from O-acyloximes. Scheme 1 shows the photolysis of O-acyloximes. The photolysis of O-acyloximes results in the formation of two kinds of radicals which recombine to form an N-benzylimine. The hydrolysis of the imine leads to the formation of benzylamine. Table 2 shows the yields of resulting amines and quantum yields in the photolysis of O-acyloximes. The yields of benzylamine in PSt films were higher than those in solution, and yields of **1b** were higher than **1a**. Quantum yields of photolysis at 366 nm of **1a** and **1b** were 0.41 and 0.58, respectively.

We have also reported that pendant AOI groups in acetophenone O-acryloyloxime (AAPO) copolymers are photochemically transformed into pendant amino groups as shown in Scheme 2.

When AAPO(30)-St copolymer films with benzophenone as a photosensitizer were irradiated, the efficiency of recombination of resulting polymer radicals and iminyl radicals in the copolymer was 70%, and the yield of double bonds in polymer main-chains derived from polymer radicals was 30%. The irradiated copolymer films were still soluble in THF, but turned insoluble by post-baking.¹¹ The insolubilization by the post-baking is thought to be due to association of resulting pendant amino groups by hydrogen bonding.

Photochemical behavior of O-carbamoyloximes and copolymers bearing carbamoyloxyimino (COI) groups: BGM having a COI group was prepared by addition reaction of methacryloyloxyethyl isocyanate with acetophenone oxime, and copolymerized with St or/and GMA.

Photolysis of **2a** in PMMA films was investigated. The proposed mechanism is shown in Scheme 3. Aminyl radicals (**3a**) and iminyl radicals (**4a**) are formed in the photolysis of **2a**. **3a** forms aniline (**5a**) by hydrogen abstraction from RH (ex. polymers or residual solvents). N,N'-diphenylhydrazine (**6a**) is formed by radical coupling between two **3a**s and the recombination of **3a** and **4a** leads to the formation of acetophenone phenylhydrazone (**7a**), which is then hydrolyzed or photolyzed to phenylhydrazine (**8a**) and acetophenone (**9a**). Acetophenone azine (**10a**) is formed by the dimerization of **4a**s.

Table 3 shows the yields of the products in air or under N₂. Total yields of products based on **3a** in air and under N₂ were 72 and 64 %, respectively. In the photolysis of **2a** under N₂, the total yield of **6a**, **7a** and **8a** was higher than that of **5a**. These results suggest that radical coupling between **3a** and **3a** or **4a** was easier than hydrogen abstraction of **3a**. The presence of O₂ decreased the yield of **7a** and increased those of **5a** and **6a**. This result was thought to be due to capture of **4a** by O₂ as seen in the increase in the yield of **9a**.

In the photolysis of **2b** in the PMMA films under N₂, the yields of cyclohexylamine and cyclohexylhydrazine were 15 and 10 %, respectively, and the presence of O₂ did not affect the results.

Fig. 2 shows UV spectral changes of BGM(25)-St copolymer films irradiated at 254 nm. An absorption band at 250 nm due to π - π^* transition decreased on irradiation. This spectral change was almost the same as that of low molecular-weight model compounds (**2a** or **2b**) in PSt films.

Fig. 3 shows IR spectral changes of BGM(25)-St copoly-

Table 2. Yields of Benzylamine in the Photolysis of O-acyloximes and Quantum Yields of Photolysis of O-acyloximes

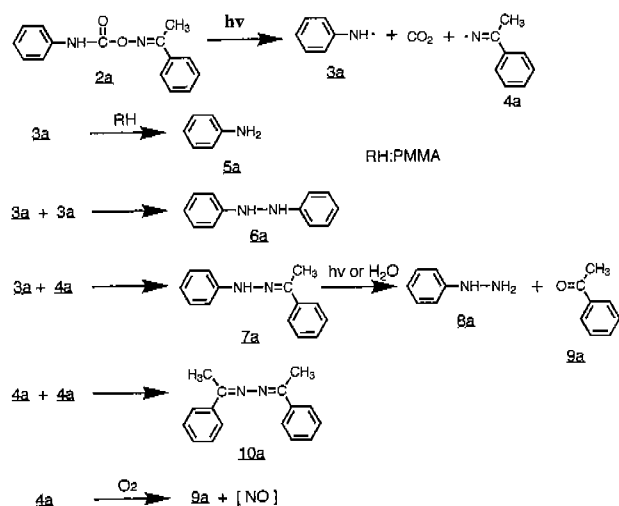
	Benzylamine(%)		Quantum yield at 366 nm ^a	
	1a	1b	1a	1b
in PSt film	70	90	0.41	0.58
in benzene	43	57	_b	_b

a) with benzophenone⁸, b) no data.

Table 3. Yields of Products in the Photolysis of **2a** in PMMA Films in Air or under N₂

Irradiation time (min)	Conversion (%)	Products (%)					
		5a	6a	7a	8a	9a	10a
30	20 (23)	12 (7)	15 (11)	9 (17)	21 (18)	52 (31)	0 (7)
80	35 (42)	13 (7)	14 (10)	9 (13)	22 (20)	56 (29)	0 (8)

The values in parentheses show amounts of products under N₂.

Scheme 3. Photolysis of **2a**

mer films irradiated at 254 nm. Absorption bands at 1710 cm⁻¹ due to carbonyl units and 1510 cm⁻¹ due to urethane units in COI groups decreased gradually on UV irradiation.

Solubility changes of copolymers bearing COI groups on UV irradiation were investigated. Fig. 4 shows the effect of photo-irradiation and PEB (post exposure bake) on their insolubilization. The insolubilization of BGM(25)-St copolymer films was observed on UV irradiation, and PEB increased the degree of the insolubilization. Based on products in Table 3, we have deduced that photo-insolubilization is due to coupling of pendant aminyl radicals formed by the pho-

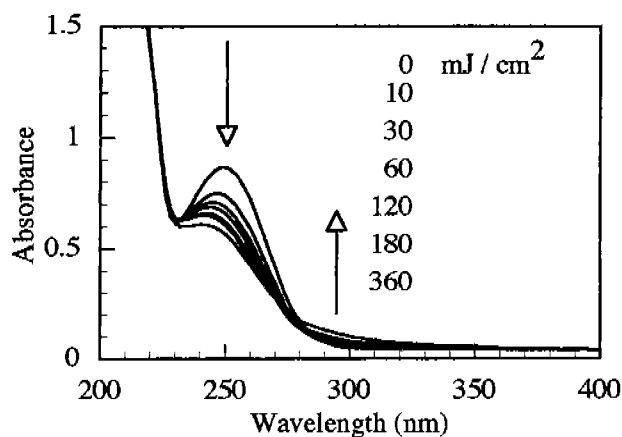


Figure 2. UV spectral changes of BGM(25)-St copolymer films irradiated at 254 nm: 0, 10, 30, 60, 120, 180 and 360 mJ/cm².

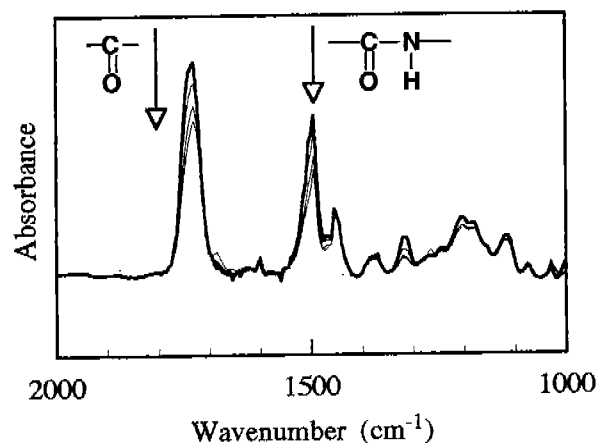


Figure 3. IR spectral changes of BGM(25)-St copolymer films irradiated at 254 nm: 0, 300, 600, 1800 mJ/cm².

tolysis of COI groups. In fact, the degree of insolubilization of the films irradiated under N₂ was higher than that in air as shown in Fig. 5, which suggests that photo-insolubilization was due to radical reactions. This photo-insolubilization behavior was very different from that of AAPO copolymers,

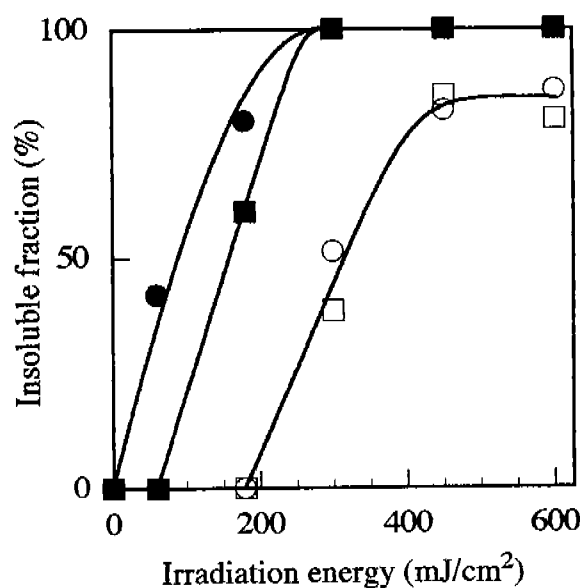


Figure 4. Photo-initiated thermal crosslinking of BGM copolymer films: (□, ■) BGM(25)-St, (○, ●) BGM(20)-GMA(27)-St. Open symbols: irradiation at 254 nm, Closed symbols: baking at 100 °C for 3 min.

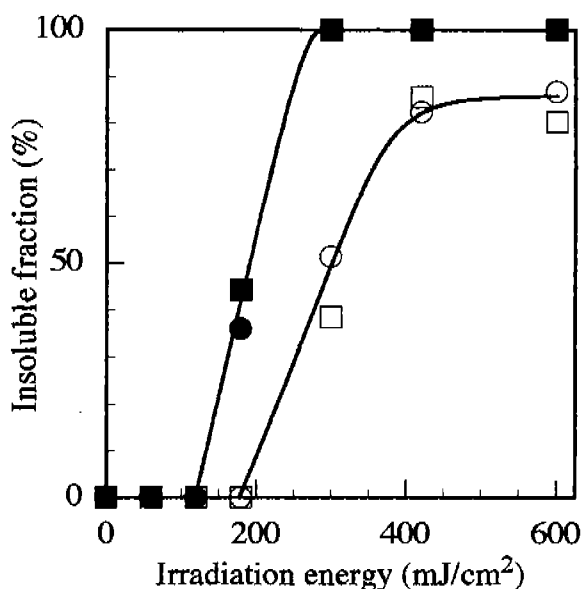


Figure 5. Effect of atmosphere on photo-insolubilization of BGM copolymer films: (□, ■) BGM(25)-St, (○, ●) BGM(20)-GMA(27)-St. Open symbols: irradiation in air, Closed symbols: irradiation under N₂.

because AAPO copolymers are soluble in solvents after the exposure to UV light. In the Fig. 4, the presence of epoxy groups in BGM(20)-GMA(27)-St copolymer films was not effective for the photo-insolubilization, but remarkably effective for thermal insolubilization by PEB.

We have already reported that the irradiated AAPO(30)-St copolymer films turned insoluble with PEB at temperatures higher than its T_g, and this result was explained by the association of resulting amino groups using hydrogen bond-

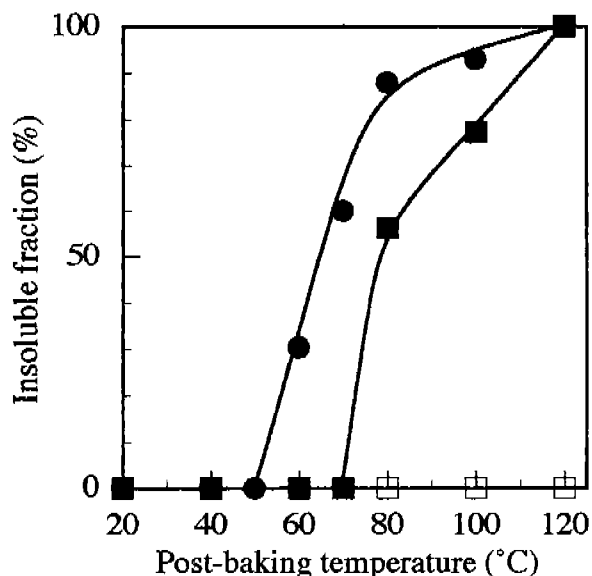
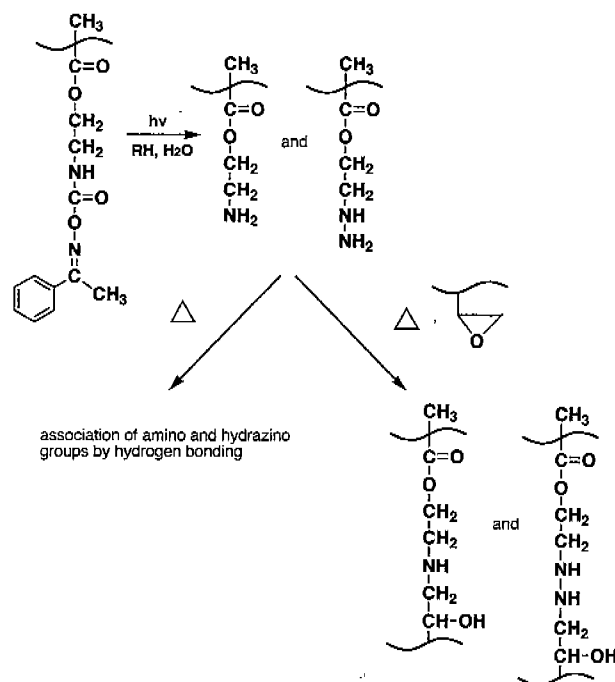


Figure 6. Effect of post-baking temperature on thermal insolubilization of BGM copolymer films after irradiation: (■, □) BGM(25)-St (T_g: 84.2 °C), (●, ○) BGM(20)-GMA(27)-St (T_g: 74.9 °C), Closed symbols: baking for 10 min after irradiation at 254 nm with 180 mJ/cm², Open symbols: without irradiation.

ing.¹¹ Thermal insolubilization of BGM copolymer films after irradiation was also expected, because they have resulting amino and hydrazino groups. Fig. 6 shows the effect of PEB temperature on thermal insolubilization after the irradiation. PEB of irradiated BGM(25)-St and BGM(20)-GMA(27)-St copolymers films, which have no insoluble fraction before the PEB, was carried out at given temperatures for 10 min. The insolubilization degree of the BGM(25)-St copolymer films was increased by baking at about 80 °C which is a little lower than its T_g. They could not turn insoluble without the irradiation, even if they were baked at 150 °C for 10 min. These behavior is very similar to that of AAPO copolymers, which suggests that the association of amino and hydrazino groups were effect for thermal insolubilization of BGM copolymers. In the case of BGM(20)-GMA(27)-St copolymer films, the insolubilization occurred by baking at 60 °C below its T_g, which suggests that thermal insolubilization of irradiated BGM(20)-GMA(27)-St copolymer was not only due to the association of resulting amino and hydrazino groups, but also the reaction of epoxy groups with resulting amino or hydrazino groups (Scheme 4).



Scheme 4. Thermal crosslinking mechanism of BGM copolymers bearing GMA groups.

From the viewpoint of UV curing, the efficient use of UV light at 313 nm and 366 nm emitted from the light source is very important. BGM(25)-St copolymer films containing benzophenone (BP) was irradiated at $\lambda > 290$ nm using a medium-pressure mercury lamp with a UV-31 cut filter (Fig. 7). Photo-insolubilization of the films was observed, and post-baking increased the degree of the insolubilization. As BGM copolymers have no absorption band at wavelengths longer than 290 nm, it is apparent that the photolysis of COI groups, and the insolubilization of BGM copolymers were induced

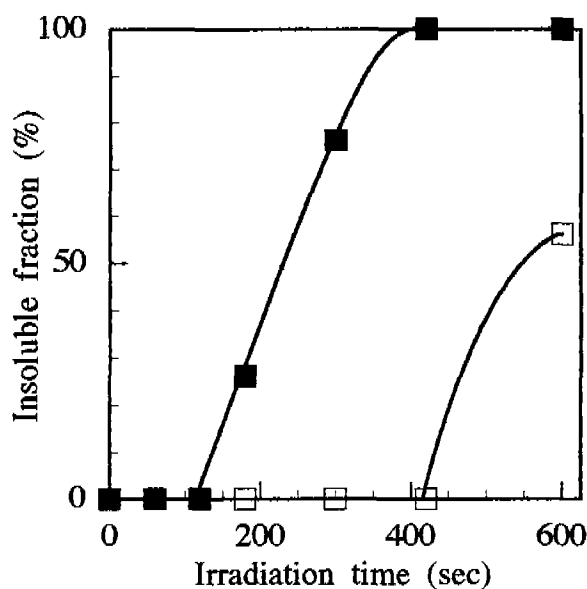


Figure 7. Photo-initiated thermal insolubilization of BGM(25)-St with benzophenone*: (□) irradiation: $\lambda > 290$ nm. (■) baking at 80 °C for 10 min after irradiation.

* The amount of benzophenone is equal to the molar amount of BGM.

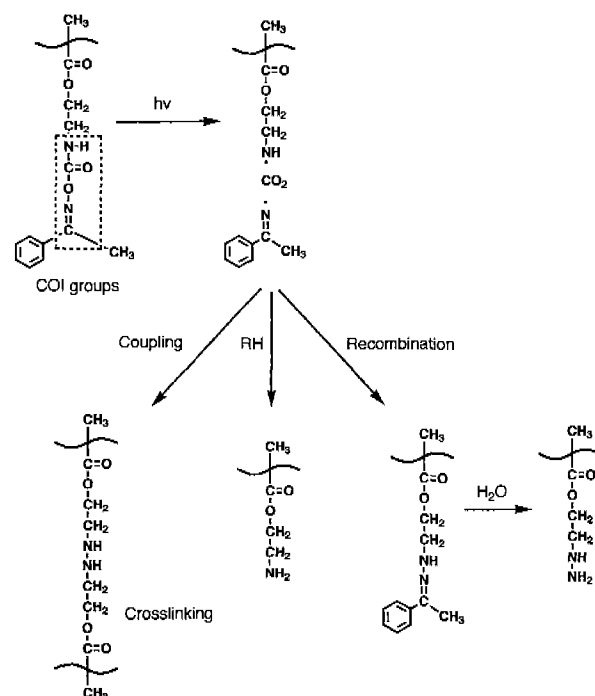
by the sensitization of BP.

The mechanism of photo-initiated thermal insolubilization of BGM copolymer films was shown in Scheme 5. Pendant COI groups in BGM copolymers decompose on UV irradiation at 254 nm or at wavelengths longer than 290 nm when BP is present to form pendant aminyl radicals and iminyl radicals. Photo-insolubilization is thought due to the coupling between aminyl radicals. Amino groups are formed from aminyl radicals by hydrogen abstraction from hydrogen donors (polymers or residual solvents). Hydrazino groups are formed by the recombination of aminyl and iminyl radicals, followed by hydrolysis or photolysis.

Thermal insolubilization of the films after irradiation is thought to be due to association of resulting amino and hydrazino groups by baking at temperatures higher than their T_g .

CONCLUSION

Photochemical behavior of copolymers bearing COI groups as polymeric photobase generators was investigated. In this photolysis the transformation of COI groups into amino and hydrazino groups was proved by the use of low molecular-weight model compounds. The copolymer films turned insoluble photochemically, and PEB increased the degree of the insolubilization further. The result that BGM copolymer films turned insoluble by only UV irradiation was very different from that of AAPO copolymer films. Their photo-insolubilization was thought to be due to coupling of aminyl radicals formed by the photolysis of COI groups, and thermal insolubilization due to association of resulting basic groups. The degree of thermal insolubilization of BGM copolymers



Scheme 5. Photochemical reactions of copolymers bearing pendant COI groups.

was increased by the introduction of epoxy groups.

Acknowledgment—This work was supported in part by a Grant-in-Aid for Scientific Research (C) No. 10650870 from the Japan Society for the promotion of Science and by a grant from Shorai Foundation for Science and Technology. Methacryloyloxyethyl isocyanate was kindly supplied by Showa Denko.

REFERENCES

1. Fouassier, J. P. (1995) Photoinitiation, photopolymerization and photocuring fundamentals and applications, Hanser Publishers, Munich.
2. Thompson, L. F., C. G. Willson and M. J. Bowden (1994) Introduction to microlithography, 2nd Ed., American Chemical Society, Washington D.C.
3. Nicolau, D. V., T. Taguchi, H. Taniguchi and S. Yoshikawa (1996) Bio-microlithography: UV- and E-beam patterning of bioactive molecules. *J. Photopolym. Sci. Technol.* **9**, 645-652.
4. Shirai, M. and M. Tsunooka (1996) Photoacid and photobase generators: chemistry and applications to polymeric materials. *Prog. Polym. Sci.* **21**, 1-45.
5. Shirai, M. and M. Tsunooka (1998) Photoacid and photobase generators: prospects and their use in the development of polymeric photosensitive systems. *Bull. Chem. Soc. Jpn.* **71**, 2483-2507.
6. Ito, K., M. Nishimura, M. Sashio and M. Tsunooka (1994) Photo-initiated base formation in a polymer matrix. *J. Polym.*

- Sci., Part A : Polym. Chem.* **32**, 2177-2185.
7. Ito, K., M. Nishimura, M. Sashio and M. Tsunooka (1994) Thermal crosslinking of poly(glycidyl methacrylate) films and epoxy resin films using amines formed by photolysis of O-acyloximes. *J. Polym. Sci., Part A : Polym. Chem.* **32**, 1793-1796.
 8. Ito, K., Y. Shigeru, Y. Kawata, K. Ito and M. Tsunooka (1995) Photo-initiated and thermal curing of epoxides by the use of photo-base generators bearing acyloxyimino groups. *Can. J. Chem.* **73**, 1924-1932.
 9. Song, K. H., S. Tonogai, M. Tsunooka and M. Tanaka (1989) A positive-type photoresist utilizing photoinitiated introduction of pendant amino groups. *J. Photochem. Photobiol. A : Chem.* **49**, 269-272.
 10. Ito, K., Y. Shigeru and M. Tsunooka (1996) Novel photocrosslinking of polymers bearing pendant acyloxyimino groups in the presence of *p*-benzoquinone. *Macromol. Rapid Commun.* **17**, 203-207.
 11. Tsunooka, M., T. Matsuoka Y. Miyamoto and K. Suyama (1998) Photo- and thermo- chemical behavior of polymeric photobase generators bearing pendant sensitizing groups. *J. Photopolym. Sci. Technol.* **11**, 123-124.
 12. Bucher, G., J. C. Scaiano, R. Sinta, G. Barclay and J. Cameron (1995) Laser flash photolysis of carbamates derived from 9-fluorenone oxime. *J. Am. Chem. Soc.* **117**, 3848-3855.
 13. Chae, K. H. (1998) Thermal curing reaction of poly(glycidyl methacrylate) using photogenerated amines from oxime-urethane derivatives. *Macromol. Rapid. Commun.* **19**, 1-4.
 14. Chae, K.H., and H. B. Song (1998) Crosslinking reaction of glycidyl methacrylate copolymers containing oxime-urethane groups using photogenerated pendant amines. *Polym. Bull.* **40**, 667-674.