Photo-initiated and thermal curing of epoxides by the use of photo-base generators bearing acyloxyimino groups

Ken-ichi Ito, Yoshitaka Shigeru, Yu-uichi Kawata, Katsuhiko Ito, and Masahiro Tsunooka

Abstract: The formation of amines by the photolysis of *O*-acyloximes derived from acetophenone oxime, benzophenone oxime, fluorenone oxime, and 2-acetonaphthone oxime and the curing of epoxides by the resulting amines were investigated. The quantum yields of their photolysis at 366 nm in polystyrene films depend on their structures, and those for bifunctional ones bearing phenyl or naphthyl moieties were found to be very high, at 0.88 and 0.76, respectively. The yields of the resulting amines in polymer matrices were higher than those in solution. The yields for *O*-acyloximes bearing a naphthyl moiety were ca. 90% and higher than for those bearing a phenyl moiety. Although the resulting amines were efficient photo-cross-linkers for poly(glycidyl methacrylate), they were not effective for curing of epoxy resins (oligomers). On the other hand, polymer amines with a glass transition temperature lower than room temperature, which were obtained by the photolysis of copolymers bearing acyloxyimino groups, were found to be effective photo-cross-linkers for the epoxy resins.

Key words: photo-base generator, acyloxyimino group, photo-initiated and thermal curing, poly(glycidyl methacrylate), epoxy resin.

Résumé : On a étudié la formation d'amines par la photolyse d'*O*-acyloximes dérivées des oximes de l'acétophénone, de la benzophénone, de la fluorénone et de l'acéto-2-naphtone et la réaction des amines qui en résultent avec les époxydes. Les rendements quantiques de leurs photolyses à 366 nm, dans des films de polystyrène, dépendent de leurs structures; on a trouvé que ceux des composés bifonctionnels avec des portions phényle ou naphtyle sont très élevés, soit respectivement 0,88 et 0,76. Les rendements des amines qui en résultent dans les matrices de polymère sont plus elevés que ceux en solution. Les rendements pour les *O*-acyloximes portant un groupe naphtyle sont plus élevés (environ 90%) que ceux des acyloximes portant un groupe phényle. Même si les amines qui en résultent sont des photoréticuleurs efficaces pour le poly(méthacrylate de glycidyle), ils ne sont pas efficaces pour la cuisson des résines époxy (oligomères). Par ailleurs, on a trouvé que les amines polymériques, qui se forment par photolyse de copolymères portant des groupes acyloxyimino et qui présentent une température de transition vitreuse inférieure à la température ambiante, sont des photoréticuleurs efficaces pour les résines époxy.

Mots clés : générateur de photobase, groupe acyloxyimino, photoinitiation et cuisson thermique, poly(méthacrylate de glycidyle), résine époxy.

[Traduit par la rédaction]

Introduction

A large number of photo-acid generators such as aromatic diazonium salts and aromatic iodonium salts have been developed and their wide use in the fields of photo-curable coatings (1) and chemically amplified photo-resists (2) investigated. Similarly, although photo-base generators are expected to be promising as photo-cross-linkers for epoxides, used without worrying about corrosive trouble derived from photo-generated acids, only a few articles were published before 1990 concerning photo-base generators and their applications. Kutal and Willson reported that the photolysis of a cobalt–ammine complex led to the formation of ammonia, which induced the cross-linking of a glycidyl methacrylate – ethyl acrylate copolymer upon heating (3). Winkle and Graziano utilized an amine generated by photolysis of an *o*-nitrobenzyl carbamate in a positive photoresist (4). We had also reported that in the photolysis of copolymers of *O*-acryloyl acetophenone oxime (AAPO) with styrene, pendant acyloxyimino (AOI) groups led to pendant amino groups in a good yield (5). Recently, studies on photo-base generators such as *o*-nitrobenzyl carbamates (6) and α,α-dimethyl-3,5-dimethoxybenzyl carbam-

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Fig. 1. Structures and abbreviations of *O*-acyloximes.

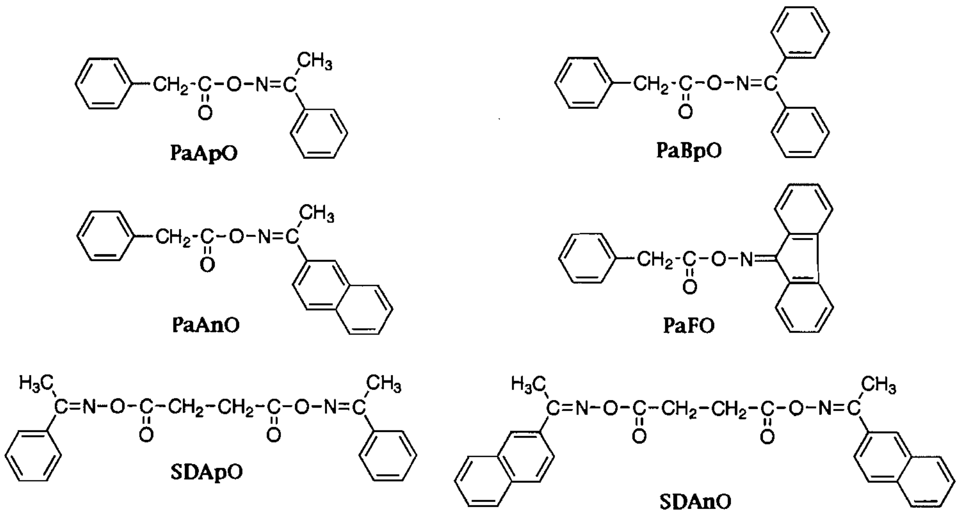
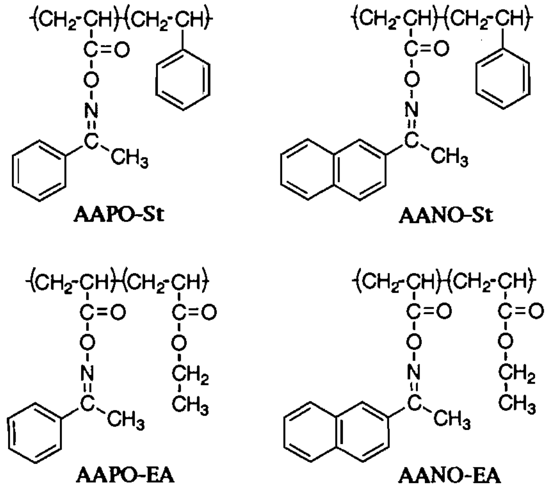


Fig. 2. Structures and abbreviations of copolymers bearing AOI groups.



ates (7) have been reported and their utility is gradually being recognized. In particular, applications to microlithography, that is, chemically amplified photo-resists using photo-base generators, have been developed in analogy with those using photo-acid generators. For example, Leung et al. reported the decarboxylation of pendant carboxylic acid groups using photo-generated amines as catalysts (8), and Fréchet et al. (9) and Mckean et al. (10) also used photo-generated amines as catalysts for imidization of polyamic esters. In addition, for application to UV curing, Nishikubo and co-workers (11) utilized amines generated by the photolysis of blocked amines as cross-linkers of epoxy resins or polyurethane oligomers.

In previous articles, we reported that the yields of amines formed by the photolysis of some *O*-acyloximes in polystyrene (PSt) films depended on their structures (12), and these amines were efficient cross-linkers for poly(glycidyl methacrylate) (PGMA) films, but not for epoxy resins (13). In this article, we report various features of *O*-acyloximes as photobase generators and their applications to photo-initiated and thermal curing of epoxides.

Experimental

Materials

Monofunctional *O*-acyloximes, i.e., *O*-phenylacetyl acetophenone oxime (PaApO), *O*-phenylacetyl 2-acetonaphthone oxime (PaAnO), *O*-phenylacetyl benzophenone oxime (PaBpO), and *O*-phenylacetyl fluorenone oxime (PaFO), and bifunctional *O*-acyloximes, i.e., *O,O′*-succinyl diacetophenone oxime (SDApO) and *O,O′*-succinyl di-2-acetonaphthone oxime (SDAnO), were prepared by a method similar to that described in a previous article (12). Their structures and characteristics are shown in Fig. 1 and Table 1, respectively.

O-Acryloyl acetophenone oxime (AAPO) and *O*-acryloyl 2-acetonaphthone oxime (AANO) were prepared by reaction of the corresponding oximes with acryloyl chloride by a method similar to that described in a previous article (14). Styrene (St) and ethyl acrylate (EA) were purified by distillation under reduced pressure. Copolymers of AAPO or AANO with St or EA were prepared by radical copolymerization in benzene using α,α′-azobisisobutyronitrile (AIBN) as initiator under vacuum at 60°C (5). In the case of the copolymer of molecular weight below 10 000, 0.2 mol% lauryl mercaptan as chain transfer agent was added in the benzene solution. The structures and abbreviations of the copolymers are shown in Fig. 2. The contents of monomeric AAPO and AANO in the copolymers were determined by their elemental analysis carried out on a Yanaco MT-3 CHN corder. Their molecular weights were determined by using GPC (JASCO) in comparison with those of polystyrene standards. Their glass transition temperatures (T_g's) were determined by using DSC (Rigaku DSC 8230). Table 2 shows the polymerization conditions and the characteristics of the copolymers.

Poly(glycidyl methacrylate) ($\overline{M}_n$ = 117 000) was prepared by solution polymerization in benzene using AIBN as initiator under vacuum at 60°C and was purified by reprecipitation of PGMA in tetrahydrofuran (THF) with methanol. Commercial epoxy resins, EPOLIGHT 100MF (trimethylol propane triglycidyl ether, epoxy equivalent: 140) (TMPGE) and EOCN 104S (*o*-cresol novolac epoxy resin, epoxy equivalent: 215) (EOCN) were provided by Kyoueisha Yusi Kagaku Kogyo

Table 1. Preparation and characteristics of *O*-acyloximes.

O-Acyloxime	Yield (%)	Melting point (°C)	IR[a] (cm^{-1})	UV[d] λ_{max} (nm)	UV[d] ε (L mol^{-1} cm^{-1})	Elemental analysis (%)
PaApO ($C_{16}H_{15}O_2N$)	36.0	42–43.5	1770[b]	245	14 200	Found: C 76.13, H 6.02, N 5.60 Calcd: C 75.87, H 5.97, N 5.53
PaAnO ($C_{20}H_{17}O_2N$)	57.8	85–87	1770[b]	247	22 500	Found: C 79.19, H 5.65, N 4.62 Calcd: C 79.54, H 5.64, N 4.56
PaBpO ($C_{21}H_{17}O_2N$)	68.0	81–82	1770[b]	253	16 600	Found: C 80.50, H 5.40, N 4.40 Calcd: C 80.00, H 5.43, N 4.44
PaFO ($C_{20}H_{17}O_2N$)	85.2	128–132	1775[b]	255	59 400	Found: C 81.02, H 4.63, N 4.43 Calcd: C 80.50, H 4.82, N 4.47
SDApO ($C_{20}H_{20}O_4N_2$)	79.1	155–158	1760[c]	245	27 900	Found: C 67.92, H 5.64, N 8.01 Calcd: C 68.17, H 5.72, N 7.95
SDAnO ($C_{28}H_{24}O_4N_2$)	72.0	208–210	1760[c]	247	40 000	Found: C 74.02, H 5.34, N 6.07 Calcd: C 74.34, H 5.31, N 6.19

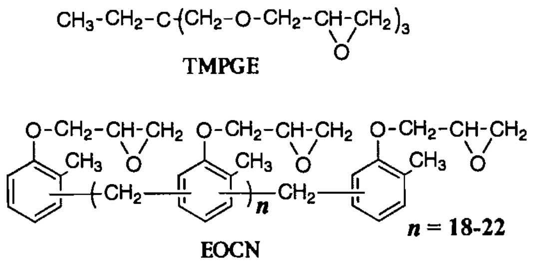
[a] Absorbance due to carbonyl group.
[b] In CCl_4.
[c] In $CHCl_3$.
[d] In tetrahydrofuran.

Table 2. Preparation[a] and characteristics of copolymers bearing AOI groups.

Copolymer	Content of AAPO[b] or AANO[c] (mol%) In feed	In copolymer	P.T.[d] (h)	Conversion (%)	$M_n/10^4$	M_w/M_n	T_g (°C)
AAPO(33)–EA[e]	30	33	2.0	26.1	9.2	1.80	5.1
AAPO(26)–EA	25	28	7.0	29.6	0.52	1.88	0.8
AANO(32)–EA	30	32	13.5	45.1	9.0	2.17	37.4
AAPO(34)–St[f]	33	34	7.5	40.2	8.5	1.96	93.3
AAPO(29)–St	33	29	14.0	37.7	0.33	2.44	70.2

[a] Initiator: 0.4 wt.% α,α′-azobisisobutyronitrile to monomer; polymerization temperature: 60°C.
[b] *O*-Acryloyl acetophenone oxime.
[c] *O*-Acryloyl 2-acetonaphthone oxime.
[d] Polymerization time.
[e] Ethyl acrylate.
[f] Styrene.

Fig. 3. Structures and abbreviations of epoxy resins.



Co. Ltd. The structures and the degree of polymerization of epoxy resins are shown in Fig. 3.

Reagent grade benzophenone (BP) was recrystallized from ethanol. Tetrahydrofuran (Reagent grade) was distilled prior to use. 3,5-Dinitrobenzoyl chloride (Tokyo Kasei Co., HPLC labeling grade, mp 67–69°C) (DNBC) was used without further purification. Polystyrene (Katayama Kagaku Kogyo Co., $\overline{M}_n$ = 113 000) was purified by reprecipitation of PSt in THF with methanol. Poly(methyl acrylate) ($\overline{M}_n$ = 129 000) (PMA) was prepared and purified in a similar manner to PGMA.

Photo-irradiation and quantitative analysis of amines or amino groups

The determination of the yield of amines for *O*-acyloximes in polymer films was carried out by a method similar to that described in a previous article (12). That is, polymer films (35–45 μm thick) with 5 wt.% *O*-acyloxime and 10 wt.% BP as sensitizer to the polymer were prepared by casting THF solutions of the polymer and additives on a Petri dish. In the case of PSt films, they were taken out of the Petri dish after standing overnight in the dark at room temperature and dried under reduced pressure (3 Torr; 1 Torr = 133.3 Pa) overnight at room temperature. These films were irradiated with a high-pressure mercury lamp (Sen Tokusyu Kogen, HL-100, 100 W) without a filter at a distance of 10 cm at room temperature under N_2 for 1 h to photolyze the *O*-acyloximes completely. On the other hand, PMA films were irradiated on a Petri dish in a similar manner as described above because they were too soft to take out of the Petri dish, their T_g being below room temperature. The intensity of the incident light was 4.10 mW/cm^2 at 366 nm. A water-vapor treatment was carried out to completely hydrolyze the photolysates formed by the photolysis of *O*-acyloximes in the irradiated film. That is, the irradiated film was allowed to stand for 10 min in a glass chamber with saturated water vapour at 25°C. Then the polymer films (40–50 mg) were dissolved in THF (2 mL). After the amines in the solution were converted into *N*-3,5-dinitrobenzoylamines (DNBAs) by the reaction with DNBC, the amount of DNBAs in the solution was determined on a HPLC equipped with a UV detector (JASCO 970-UV).

Quantitative analysis of the amines formed in solution was carried out as follows. A benzene solution (3 mL) of an *O*-acyloxime (0.1 mol/L) containing BP (0.1 mol/L) in a quartz cell (1 × 1 × 5 cm) was irradiated under N_2 for 1 h, in a similar manner as described above. After the irradiated benzene solution (0.5 mL) was diluted with THF (19.5 mL), DNBC (ca. 20 mg) was added to a portion (2 mL) of the solution. The very small amount of water in the THF was enough to hydrolyze the photolysates formed by the photolysis of *O*-acyloximes. The amount of amines in the solution was determined on the HPLC in a manner similar to that described above.

Determination of the yield of amino groups for copolymers bearing AOI groups was carried out by a method similar to that described in a previous article (5). That is, the films of copolymers with 10 wt.% BP (ca. 20 μm thick) were irradiated without a filter, in a manner similar to that described above, to photolyze the AOI groups completely; this was confirmed by the disappearance of the absorption of AOI groups at 1760 cm^{-1} in the IR spectrum. After the water-vapour treatment, the irradiated film was dissolved in THF, and the resulting polymer in THF was purified by reprecipitation with methanol 3 times. Then the polymer was dried under reduced pressure (3 Torr) overnight at room temperature. The nitrogen content of the polymer was determined by elemental analysis. The yield of amino groups was calculated from the nitrogen content.

Quantum yield of photolysis of *O*-acyloximes in a polymer matrix

The PSt films (ca. 45 μm thick) containing 5 wt.% *O*-acyloximes and a given amount of BP were irradiated with 366 nm light by use of the high-pressure mercury lamp combined with a filter (Toshiba UV-D1B) at room temperature in air in a similar manner to that described above. The degree of decomposition of the *O*-acyloximes was determined by following the changes in absorbance, at about 1750 cm^{-1}, due to the AOI groups in their IR spectra, which were measured on a IR spectrometer (JASCO IR-810). The quantum yield of photolysis of *O*-acyloximes in PSt films with 366 nm light (ϕ_{366}) was determined as moles of decomposed *O*-acyloximes divided by einsteins of light absorbed by the film (eq. [1]).

$$[1] \quad \phi_{366} = \Delta m/\Delta I_{\mathrm{abs}} = \Delta m/[I_0(1-10^{-A})tS]$$

where Δm: moles of decomposed *O*-acyloximes (mol); ΔI_{abs}: einsteins of light absorbed by the film (einstein); I_0: intensity of light at 366 nm (einstein cm^{-2} s^{-1}); A: absorbance of the film at 366 nm; S: irradiated area of the film (cm^2); and t: irradiation time (s).

The intensity of the irradiating light was determined by potassium ferrioxalate actinometry (15).

Photo-chemical insolubilization of PGMA films with *O*-acyloximes

The PGMA films (ca. 35 μm thick) with a given mol% *O*-acyloxime and 10 wt.% BP prepared by the casting method were irradiated in a similar manner as that described above, in air for 1 h, followed by the water-vapor treatment. Then the films were heated at 80°C for 1 h on a hot plate. The films (ca. 0.05 g) were immersed in THF (5 mL) for 1 d at room temperature; then the insoluble fractions were separated by centrifugation. The supernatant liquid was next removed and THF (5 mL) was added for washing the insoluble fraction, and the insoluble fraction was again separated by centrifugation. This series of washing operations with THF was repeated 3 times, the supernatants were removed, and then methanol (5 mL) was added for washing the insoluble fraction. This insoluble fraction was separated by centrifugation. After most of the solvent was removed by an aspirator, the insoluble fraction was dried under reduced pressure (3 Torr) at room temperature overnight, and its dry weight determined (13).

Photo-chemical insolubilization of the films composed of copolymers bearing AOI groups and epoxy resins

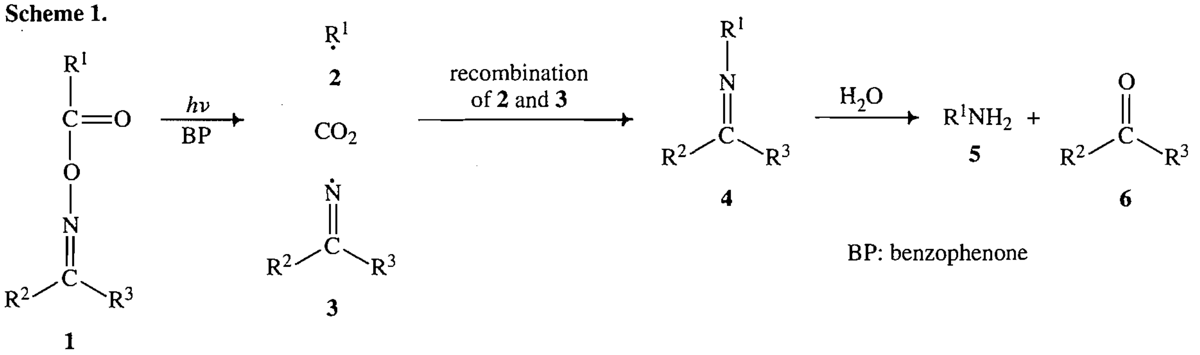
Thin films (ca. 0.15 μm thick) containing a given amount of copolymers bearing AOI groups an epoxy resin, and BP were prepared by casting their THF solutions onto a quartz plate. Each film was irradiated on the quartz plate with the high-pressure mercury lamp at a distance of 7 cm, at room temperature in air, for a given time. Then the irradiated film was heated at a given temperature for a given time. In this case, the water-vapor treatment was not carried out because the insoluble fraction of the film was not changed by this treatment. After the film was immersed in THF for 10 min at room temperature, it was dried under hot air for a few minutes. The insoluble fractions were determined from the difference in thickness of the films before and after the immersion. The thickness of the films was determined by two-beam interferometry with an interference microscope (Nikon OPTIPHOT).

Results and Discussion

Amine formation by the photolysis of *O*-acyloximes

In a previous article (12), we reported that amines are formed in the photolysis of *O*-acyloximes in PSt films as shown in Scheme 1. That is, benzophenone (BP) absorbs UV light and the energy of the excited BP is transferred to the *O*-acyloximes. The decomposition of the excited *O*-acyloxime (**1**) leads to the formation of an alkyl radical (**2**), an imino radical (**3**), and carbon dioxide. Then an azomethine (**4**) is formed by the recombination of 2 and 3, and finally an amine (**5**) and a

Scheme 1.



ketone (**6**) are generated by the hydrolysis of **4**. Most of the intermediary azomethines are considered to be easily hydrolyzed by water vapor in air during irradiation since PGMA films (even ca. 35 μm thick) containing *O*-acyloximes and BP were insolubilized appreciably by heating after irradiation under air without a water-vapor treatment (16). Besides, although imines and azines are obtained from **3** as described in the previous article (12), the yield of the azines was very low and the yield of the imines depended on the structure of the *O*-acyloximes.

Table 3 gives quantum yields of photolysis at 366 nm (ϕ_{366}) for *O*-acyloximes in the presence of 10 wt.% BP. The ϕ_{366} for PaAnO was highest among the monofunctional *O*-acyloximes, at 0.58, and that for PaFO was lowest, at 0.06. Although the triplet energies of the *O*-acyloximes are deduced to be close to triplet energies of the original ketones (17), it is difficult to clarify the relation between the triplet energies and the ϕ_{366} values for each at present. The ϕ_{366} for PaAnO was hardly altered by the change in amount of BP as sensitizer in the range of 5–15 wt.%. This result shows that the decomposition rate is proportional to the amount of BP over this range, and that the efficiency of decomposition based on absorbed light intensity is the same. Interestingly, the ϕ_{366} for the bifunctional *O*-acyloximes, i.e., SDApO and SDAnO, was higher than for the monofunctional *O*-acyloximes. Similar results were observed for the ϕ_{366} of pendant acyloxyimino (AOI) groups in polymers (Table 3).

Table 3. Apparent quantum yields of photolysis at 366 nm (ϕ_{366}) for *O*-acyloximes in polystyrene films.

Compound	BP content (wt.%)	ϕ_{366}
PaApO	10	0.41
PaAnO	5	0.59
	10	0.58
	15	0.54
PaBpO	10	0.35
PaFO	10	0.06
SDApO	10	0.88
SDAnO	10	0.76
AAPO(26.3)–St	10	0.70

Table 4 shows the yields of amines based on decomposed *O*-acyloximes. The yields of amines for PaApO and PaAnO in the PSt films were 72% and 89%, respectively, which were ca. 30% higher than those in benzene solutions. This result shows that the recombination of imino and alkyl radicals occurs more effectively in a polymer matrix than in solution. As described in a previous article (12), it is deduced that the movement of *O*-acyloximes is restricted by the PSt main chains since the glass transition temperature (T_g) of PSt containing 5 wt.% *O*-acyloximes and 10 wt.% BP is 54°C, and higher than room temperature. This result suggests that the increase in the yield is due to a cage effect of the polymer matrix.

On the other hand, the yields for PaApO and PaAnO in PMA films were lower than those in PSt films. Since the segment motions in the main chains in the PMA (T_g = 7°C) occur at room temperature, it is deduced that the PMA matrix is not effective for the formation of amine precursors.

The yields of amines for PaAnO and SDAnO in PSt films were ca. 20% higher than those for PaApO and SDApO, respectively. This result suggests that the bulkiness of a naphthyl moiety in PaAnO and SDAnO was advantageous to the formation of amine precursors. Similarly, the yield of amine for PaBpO was high, as well as that for PaAnO or SDAnO. This seems to be due to the bulkiness of AOI groups bearing two phenyl moieties. These results suggest that the bulkiness of the AOI group is important for efficient formation of the amine precursors.

Table 4. Yields of amines in photolysis of *O*-acyloximes under N_2.

		Yield (%)		
		Solid phase		
O-Acyloxime	Resulting amine	PSt	PMA	Liquid phase
PaApO	Benzylamine	72	40	43
PaAnO	Benzylamine	89	73	57
PaBpO	Benzylamine	89	—	—
SDApO	Ethylenediamine	68	—	—
SDAnO	Ethylenediamine	90	—	—

The formation of polymer amines was also similarly investigated. Figure 4 shows the relationship between the yield of amino groups and the content of AAPO or AANO in the copolymers. The results for AAPO copolymers are taken from a previous article (5). In Fig. 4, yields of amino groups for AANO–St's were almost the same as those for AAPO–St's at any content of AANO. This result was different from the result for *O*-acyloximes described above. It seems that, judging from the T_g's of the copolymers, the motions of pendant AOI groups are restricted more strongly by the main chains of the copolymers at room temperature, and that the yields for the two copolymers are almost the same. Here, since an increase in the contents of AANO in the copolymers leads to an

Fig. 4. Relationship between contents of AAPO or AANO in copolymers and yields of amino groups: (○, ●) AAPO–St, (△, ▲) AANO–St.

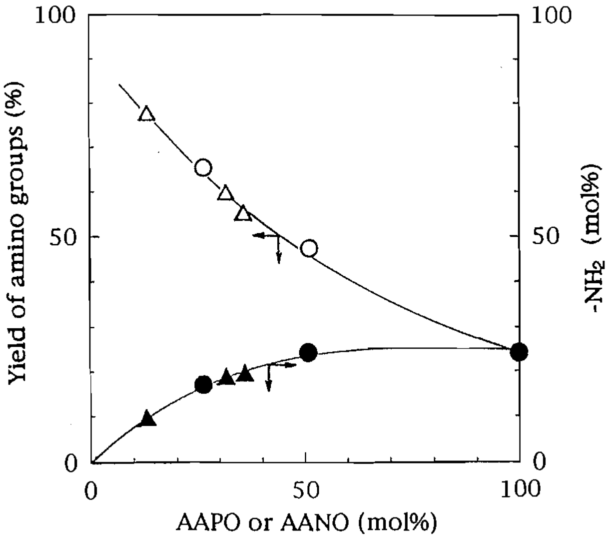


Table 5. Insolubilization[a] of PGMA films with *O*-acyloximes and BP by UV irradiation.

O-Acyloxime	Content (mol%)	Insoluble fraction (%)
PaApO	0.3	41
	0.6	62
PaAnO	0.3	49
	0.6	70
SDApO	0.15	75
	0.3	85
SDAnO	0.15	79
	0.3	96

[a] Irradiated for 1 h and then heated at 80°C for 1 h after water-vapor treatment at 25°C for 10 min.

increase in their T_g's, the effect of T_g on the yield was not considered.

Photo-chemical insolubilization of PGMA film with *O*-acyloximes

Table 5 shows the results of insolubilization of PGMA films containing *O*-acyloximes and BP by UV irradiation. The films were irradiated for 1 h in air and then heated at 80°C for 1 h after water-vapor treatment. No insolubilization of the films occurred by the water-vapor treatment and (or) by heating without irradiation. From the results for insoluble fractions of the films, PaAnO was more active than PaApO and a similar relation was observed for bifunctional *O*-acyloximes. However, the bifunctional *O*-acyloximes, SDApO and SDAnO, were more active than the monofunctional ones, PaApO and PaAnO. In Table 4, the yield of benzylamine for PaAnO is higher than that for PaApO. Thus, the order of activity of the monfunctional *O*-acyloximes as photo-cross-linkers is understood to be due to the difference in the yields of amines. Although there is no difference in the yields of amines between monofunctional and bifunctional oximes with the same AOI groups, bifunctional oximes were much more active as photo-cross-linkers than the monfunctional ones. Ethylenediamine and benzylamine are obtained in the photolysis of bi- and monofunctional *O*-acyloximes, respectively. Although the difference in their basicity should be considered, bifunctionality of the resulting amine is thought to be beneficial for cross-linking.

While these results show that the *O*-acyloximes acted as photo-cross-linkers of PGMA, these amines were not efficient cross-linkers for trifunctional epoxy resins such as TMPGE, as described in a previous article (13). We later investigated thermal curing of epoxy resins by polymer amines formed by the photolysis of copolymers bearing AOI groups.

Photo-chemical insolubilization of AAPO copolymer films with TMPGE as a cross-linker

Figure 5 shows the effect of irradiation time and heating temperature on photo-cross-linking of AAPO(34)–St or AAPO(33)–EA films. On heating at 150°C after irradiation, both films were insolubilized rapidly at almost the same rate With lowering of the heating temperature, the insolubilization rate of AAPO(34)–St films fell significantly, while that of AAPO(33)–EA films did so only slightly. To clarify the difference in the photo-cross-linking behavior of these copolymers, effects of miscibility of TMPGE and BP with the copolymers and of the T_g's of the copolymers on the photo-cross-linking were investigated. The miscibility of the copolymers with TMPGE and BP was satisfactory, because only one T_g was observed for each film composed of AAPO–St or AAPO–EA, BP, and TMPGE. The T_g's of AAPO(34)–St and AAPO(33)–EA with 10 wt.% TMPGE and 10 wt.% BP were 68.3 and –11.8°C, respectively.

Figure 6 shows Arrhenius plots of the photo-cross-linking of AAPO(34)–St and AAPO(33)–EA films. The photo-cross-linking rate (κ) was determined as a reciprocal of the time required for insolubilization of 50% of the copolymer film in Fig. 5. The apparent activation energies (E_{act}) of insolubilization for AAPO(34)–St and AAPO(33)–EA films that were calculated from the plot were 64.3 and 21.3 kJ/mol, respectively. The cause of the lowering in E_{act} for AAPO(33)–EA is thought to be due to the difference in energy required for the segmental motion of AAPO(33)–EA, because miscibility of TMPGE with both polymers was good and the T_g of AAPO(33)–EA was considerably lower than that of AAPO(34)–St.

Figure 7 shows the effects of the molecular weights of AAPO copolymer and the heating temperature after irradiation on insoluble fractions of AAPO copolymer films. The films were heated at a given temperature for 10 min after irradiation for 10 min in air.

All AAPO films were cross-linked effectively by TMPGE on heating at 150°C after irradiation, while the proportion of the insoluble fractions was very different at lower temperatures. Insolubilization of AAPO(33)–EA (T_g = 5.1°C, $\overline{M}_n$ = 92 000) films occurred at room temperature and the insoluble fraction of the film reached ca. 50%, while heating at temperatures over 70°C was required for insolubilization of AAPO(34)–St (T_g = 93.3°C, $\overline{M}_n$ = 85 000) films. Since the T_g of AAPO(33)–EA is lower than room temperature, it is deduced that the reaction of amino groups in the copolymer with epoxy groups occurs efficiently at room temperature. Although the T_g's of AAPO(26)–EA (T_g = 0.8°C, $\overline{M}_n$ = 5200)

Fig. 5. Effect of irradiation time and heating temperature on photo-cross-linking[a] of AAPO(34)–St films (*a*) and AAPO(33)–EA films (*b*) with 10 wt.% BP and 10 wt.% TMPGE (ca. 0.15 μm thick): (■) 60°C, (□) 80°C, (●) 100°C, (○) 150°C.

[a] After irradiation in air, heated for 5 min.

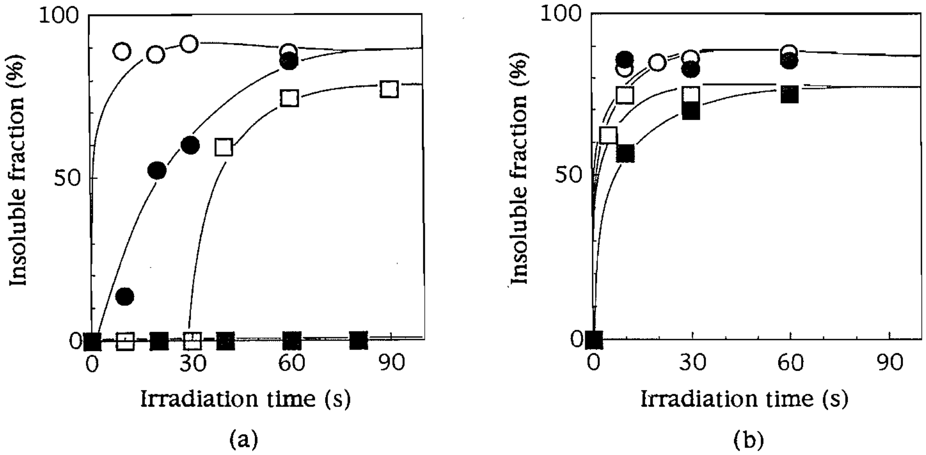
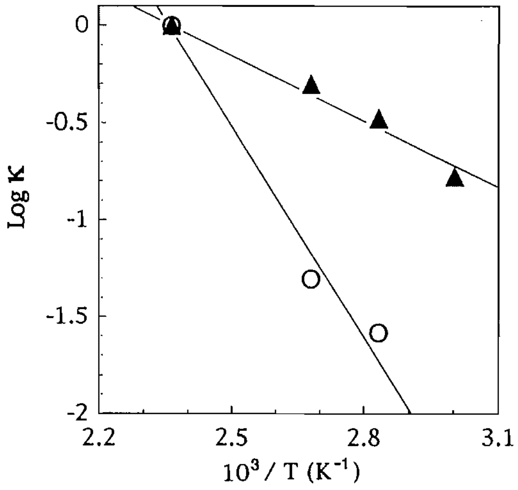


Fig. 6. Arrhenius plot of photo-cross-linking of copolymer films (ca. 0.15 μm thick) with 10 wt.% BP and 10 wt.% TMPGE: (○) AAPO(34)–St, (▲) AAPO(33)–EA. κ: Photo-cross-linking rate at 50% of insoluble fraction of copolymer films.



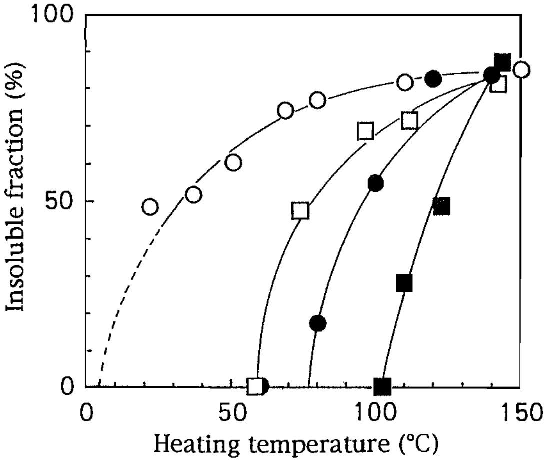
and AAPO(29)–St (T_g = 70.2°C, $\overline{M}_n$ = 3300) were lower than those of the corresponding copolymers, which had higher molecular weights, the higher temperature for insolubilization of the former two copolymers was needed. It is deduced that the lowering of molecular weights of the copolymers affects the insolubilization more strongly than the lowering of T_g.

Photo-chemical insolubilization of epoxy resin films by use of AAPO or AANO copolymers as photo-cross-linkers

Table 6 shows relations between the ratio of TMPGE and AAPO copolymers in the films and the insoluble fractions. The films were heated at 100°C for 5 min after irradiation for 10 min in air. The insoluble fractions for any copolymer except AAPO(29)–St were highest at 10 wt.% TMPGE. At this wt.%, insoluble fractions for both AAPO(33)–EA and AAPO(34)–St, which had higher molecular weights, were ca. 90%.

Fig. 7. Effects of molecular weights of AAPO copolymers and heating temperature on insoluble fraction[a] of AAPO copolymer films (ca. 0.15 μm thick): with 10 wt.% BP and 10 wt.% TMPGE: (○) AAPO(33)–EA (M_n = 92 000, T_g = 5.1°C), (●) AAPO(26)–EA (M_n = 5200, T_g = 0.8°C), (□) AAPO(34)–St (M_n = 85 000, T_g = 93.3°C), (■) AAPO(29)–St (M_n = 3300, T_g = 70.2°C).

[a] After irradiation for 10 min in air, heated for 10 min.



The insoluble fractions were lowered with an increase in content of TMPGE. In the case of AAPO copolymers, which had lower molecular weights, the insoluble fractions were lower than those for the copolymers that had higher molecular weights. Especially, AAPO(29)–St films were not insolubilized at any ratio. These results show that AAPO copolymers do not work as photo-cross-linkers for TMPGE at low content.

Table 7 shows the effect on the insoluble fractions of the weight ratio of an epoxy resin with a higher molecular weight, EOCN, to the copolymers. Since only one T_g was observed in any ratio of EOCN and copolymer and the T_g varied with the ratio as shown in Table 8, it is thought that the miscibilities of EOCN with the copolymers were also good. The films were heated at 100°C for 5 min after irradiation for 10 min in air. The insoluble fractions for AAPO(33)–EA and AANO(32)–EA were ca. 80% at any ratio except AANO(32)–EA with 80 wt.% EOCN. This result was very different from the results in

Table 6. Effect on the insoluble fractions of the ratio of TMPGE and AAPO copolymer in films with 10 wt.% BP.[a]

	Insoluble fraction (%)			
Epoxide/copolymer (wt%)	AAPO(33)–EA ($\bar{M}_{\rm n}$ = 92 000) ($T_{\rm g}$ = 5.1°C)	AAPO(26)–EA ($\bar{M}_{\rm n}$ = 5200) ($T_{\rm g}$ = 0.8°C)	AAPO(34)–St ($\bar{M}_{\rm n}$ = 85 000) ($T_{\rm g}$ = 93.3°C)	AAPO(29)–St ($\bar{M}_{\rm n}$ = 3300) ($T_{\rm g}$ = 70.2°C)
0/100	0	0	0	0
10/90	89	65	88	0
20/80	79	56	74	0
30/70	71	49	53	0
40/60	54	32	29	0
50/50	41	0	0	0
60/40	36	0	0	0
70/30	29	0	0	0
80/20	0	0	0	0
90/10	0	0	0	0
100/0	0	0	0	0

[a] After irradiation for 10 min in air, heated at 100°C for 5 min.

Table 7. Effect on the insoluble fractions of the ratio of EOCN and copolymer bearing AOI groups in films with 10 wt.% BP.[a]

	Insoluble fraction (%)		
Epoxide/copolymer (wt%)	AAPO(33)–EA ($\bar{M}_{\rm n}$ = 92 000) ($T_{\rm g}$ = 5.1°C)	AANO(32)–EA ($\bar{M}_{\rm n}$ = 90 000) ($T_{\rm g}$ = 37.4°C)	AAPO(34)–St ($\bar{M}_{\rm n}$ = 85 000) ($T_{\rm g}$ = 93.3°C)
20/80	82	82	75
40/60	84	81	—
50/50	82	79	62
60/40	83	—	60
80/20	80	69	53

[a] After irradiation for 10 min in air, heated at 100°C for 5 min.

Table 8. Effect on the $T_{\rm g}$ of the ratio of EOCN and copolymer bearing AOI groups.

	$T_{\rm g}$ (°C)		
Epoxide/copolymer (wt.%)	AAPO(33)–EA	AANO(32)–EA	AAPO(34)–St
0/100	5.1	37.4	93.3
20/80	2.1	13.2	39.8
50/50	–3.3	5.1	19.0
80/20	–8.2	–3.0	6.9
100/0	–9.6	–9.6	–9.6

Table 6. Although the films of AAPO(34)–St were also insolubilized even at lower content of the copolymer, the proportion of insoluble fractions of AAPO(34)–St was lower than that of AAPO(33)–EA or AANO(32)–EA. It is thought that the $T_{\rm g}$'s of their copolymers played an important role in the insolubilization. These results suggest that copolymers bearing AOI groups can be used as effective photo-cross-linkers for epoxy resins by choosing an appropriate combination of epoxy resin and copolymers.

Conclusions

1. The use of *O*-acyloximes and copolymers bearing AOI

groups as photo-base generators was verified. This could be applied to photo-initiated curing of epoxides.

2. The yields of amine for *O*-acyloximes bearing a bulky moiety such as a naphthyl group were found to reach ca. 90% in PSt films under N_2.

3. It was found that the T_g of copolymers bearing AOI groups played a very important role in the curing of epoxides when the copolymers were used as photo-cross-linkers.

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