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A New Photobase Generator Containing Oxime-urethane Group and Its Application

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SUMMARY: Photochemical base formation from oxime-urethane derivatives was observed via pH changes, GC and HPLC analysis, and laser flash photolysis study. Photolysis of these derivatives results in the formation of amines which induce cross-linking of poly(glycidyl methacrylate) (PGMA) upon heating. Photocross-linking reaction of the copolymers, containing epoxy and oxime-urethane groups, were studied by measuring the insoluble fraction of copolymer films under various reaction conditions. Thermal cross-linking reaction of the copolymer was catalysed by the photogenerated pendant amines. The copolymer containing oxime-urethane groups which photogenerate aromatic amines can be utilized as an image recording material.

Introduction

Photoinitiators can be classified as radical or ionic photoinitiators based on their reaction mechanism. Although most of the industrially used photoinitiators are radical initiators, ionic ones have also become increasingly important in microlithography, photoresists, and coatings application. The advantages of ionic photoinitiators over radical ones are their ability to introduce ring opening polymerization, and lack of volume contraction and oxygen inhibition. Cationic photoinitiators have been studied extensively1), and utilized to develop several new and commercially important technologies. Anionic photoinitiators have also been developed in similar ways as cationic photoinitiators. However, despite numerous studies of cationic photoinitiators, only a few have been reported on the photo-induced base formation2).

The first example of a photobase generating compound was reported by Willson et al.3) in 1987. The photochemical formation of free amines from chemical systems such as cobalt-amine complex3), benzoyl formic acid amine salt4), urethane5), o-nitrobenzoyl carbamate6), oxime-ester7), blocked aniline8), and benzoin carbamate9) derivatives has been reported. The photobase generators have been applied to photoresists10-11), cross-linking reagents for epoxy resins7, 12), imidation catalysts13-14), and surface modification15).

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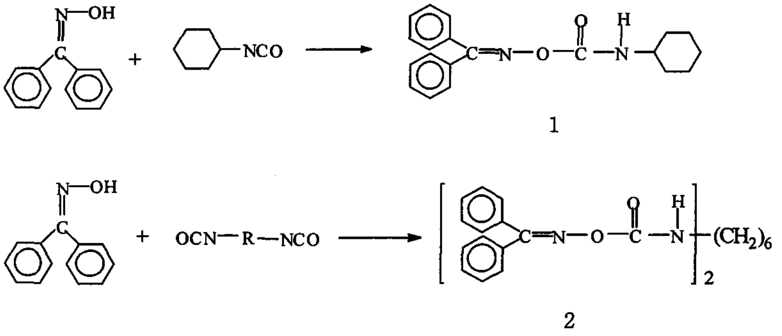
Scheme 1:



Oxime-urethane groups have been used as precursors to isocyanate groups[16)]. We found that the photolysis of oxime-urethane derivatives led to the formation of amines which induce cross-linking reaction of epoxy resins upon heating. In this paper we describe the photochemical base formation from oxime-urethane derivatives and its application to some polymeric systems.

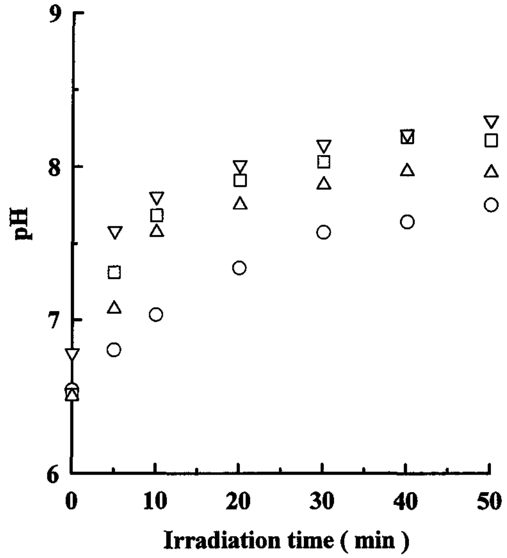


Fig. 1. pH changes of oxime-urethane derivatives as a function of irradiation time in acetonitrile-water solution: (O) compound **1**; (Δ) compound **1** with benzophenone; (□) compound **2**; (∇) compound **2** with benzophenone.

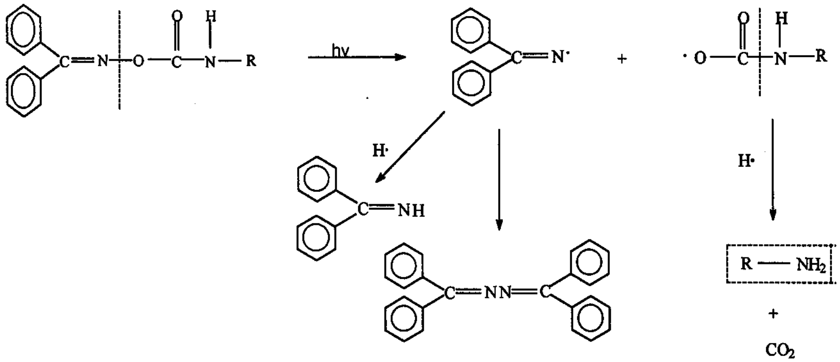
Photogeneration of amine from oxime-urethane derivatives[17)]

Oxime-urethane derivatives were prepared from the reaction of cyclohexyl isocyanate or hexamethylenediisocyanate with benzophenone oxime, as shown in Scheme 1.

Photoinduced amine formation from oxime-urethane derivatives was confirmed by GC, HPLC, and pH changes. Fig. 1 shows pH changes of oxime-urethane derivatives in acetonitrile-water solution. The pH changed from 6.5 to 8.2 upon irradiation with 254 nm UV light. The addition of benzophenone augmented the pH changes, which implies that this photochemical reaction may take place in its excited triplet state. The photobase generation efficiency for bifunctional oxime-urethane derivative **2** was greater than that of mono-functional derivative **1**.

Scheme 2 shows a possible reaction mechanism for the photogeneration of amine from oxime-urethane derivatives. It is expected that photolysis of oxime-urethane derivatives would lead to the homolytic cleavage of N-O bond, resulting in an iminyl radical and carbonate radical pair. The iminyl radical can undergo hydrogen abstraction to form an imine, or dimerization to form an azine. The carbonate radical can undergo decarboxylation followed by hydrogen abstraction to form an amine.

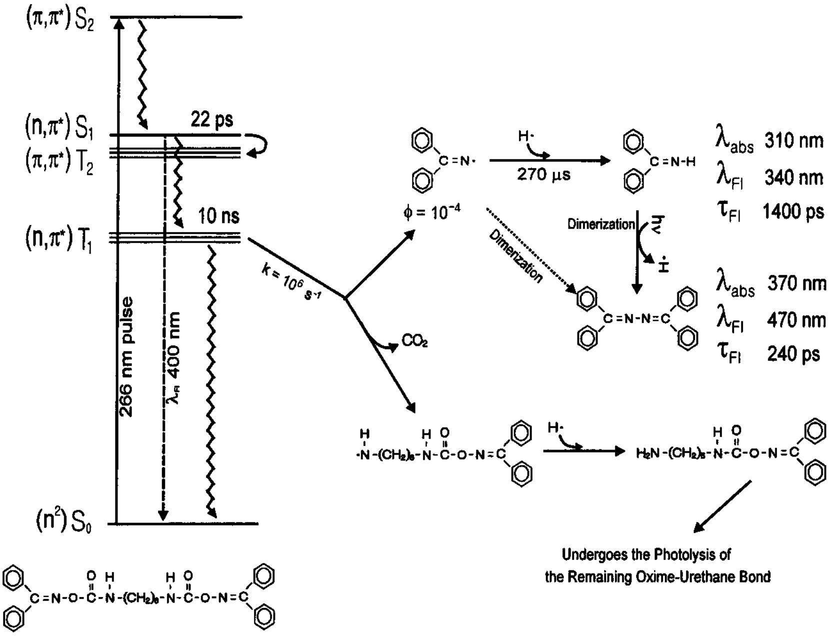
Scheme 2:



Laser flash photolysis study[18)]

The photochemical and photophysical phenomena of compound **2** was investigated with laser flash photolysis to understand its photodecomposition mechanism in anionic polymerization reactions. Scheme 3 shows the summary of our laser flash photolysis study of compound **2**. Irradiation of 266 nm laser pulse to compound **2** results in the transition from ground state

Scheme 3:



to the (π, π*) S_2 state, followed by a fast internal conversion to the (n, π*) S_1 state. In 22 ps the population of the S_1 state undergoes a rapid intersystem crossing to the (π, π*) T_2 state that happens to lie near the S_1 state in energy. The (n, π*) T_1 state, populates immediately via internal conversion from T_2 state, is then depopulates in the time scale of 10 ns via intersystem crossing to the S_0 ground state.

About 2 % of the T_1 state population tend to undergo decarboxylation within its decay time, generating dehydrogenated iminyl radical and aminyl radical. Abstracting a hydrogen atom within the time frame of 270 μs, the iminyl radical converts mainly into diphenyl-1-imine which, upon irradiation, dehydrogenates and dimerizes to yield benzophenone azine. Meanwhile, the aminyl radicals abstract H to generate benzophenoneoxime-urethanyl hexamethyleneamine, which raises solution pH or initiates thermal curing reaction of epoxy resin as a photobse.

Cross-linking reaction of epoxy resin photoinduced by oxime-urethane derivatives[17]

Amines are very important reagents for thermal cross-linking reaction of epoxy resins in adhesives, paints, and coatings industry. However, a mixture of epoxy resins with aliphatic amines is very unstable due to the high reactivity of aliphatic amines. Therefore, light induced amine formation from blocked amine groups is a very useful technique for the formulations of epoxy resins which can lead to a new industrial technology.

The thermal cross-linking reaction of poly(glycidyl methacrylate) (PGMA) films containing compound **1** as a function of heating temperature showed that the PGMA films without the addition of compound **1** were not cross-linked upto 120 °C, for heating time of 10 min. However, the insoluble fraction increased with heating temperature and irradiation time in the presence of compound **1**. Slight thermal cross-linking behavior was observed for non-irradiated PGMA films containing compound **1**. This may be due to the oxime-urethane groups which produce isocyanate groups upon heating, that can react with epoxy groups in PGMA to form cross-links.

Fig. 2 shows the effect of heating time on the thermal cross-linking reaction of irradiated PGMA films containing 5 wt.-% of compound **1** at 100 °C. The insoluble fraction of non-irradiated PGMA films increased slightly with heating time. However, the insoluble fraction

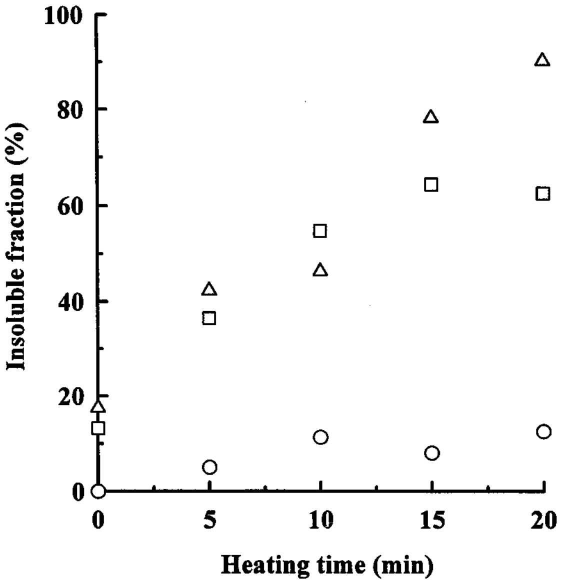
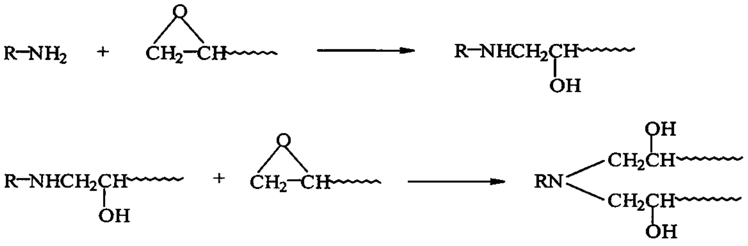


Fig. 2. Effects of heating time on thermal cross-linking reaction of irradiated PGMA films containing 5 wt.-% of compound 1: (o) no irradiation; (□) irradiated for 5 min; (Δ) irradiated for 10 min. Heating temperature, 100 °C.

Scheme 4:

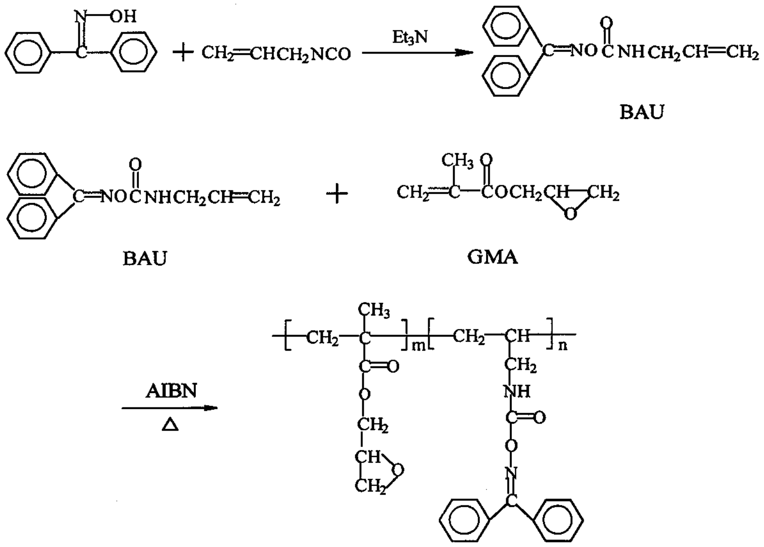


of PGMA films after irradiation increased with heating and irradiation time. After 20 min of heating, an appreciable increase in the insoluble fraction, upto 90%, was observed for the PGMA films irradiated for 10 min. This indicates that thermal cross-linking of PGMA films was induced by the amines which were produced by the photolysed oxime-urethane derivatives.

The insoluble fraction of PGMA films containing two different oxime-urethane derivatives as a function of irradiation time showed that bifunctional derivative **2** was more efficient than monofunctional derivative **1** in inducing thermal cross-linking of PGMA films.

Amine-induced cross-linking mechanism of PGMA is shown in Scheme 4. Photochemically produced amines from oxime-urethane derivatives attack epoxy groups of PGMA to form secondary amines, which in turn, react with other epoxy groups to form cross-links.

Scheme 5:



Photoinduced cross-linking reaction of epoxy resin containing oxime-urethane groups[19)]

The idea of the photobase generation from oxime-urethane derivatives was extended to the thermal cross-linking reaction of epoxy resins containing oxime-urethane groups. The synthetic route for the preparation of glycidyl methacrylate copolymers containing oxime-urethane groups is shown in Scheme 5. Benzophenoneoxime allyl urethane (BAU), a monomer containing oxime-urethane group, was prepared from benzophenoneoxime and allyl isocyanate. Copolymers containing oxime-urethane groups was prepared by the copolymerization of BAU and GMA.

Table 1 shows the physical properties of the copolymers which were prepared by varying the molar ratio of BAU from 9 to 33%. The content of BAU units in the copolymer was in the range of 0.7 – 3.0 %. Intrinsic viscosity of the copolymers was in the range of 0.23 – 0.32. Molecular weight and intrinsic viscosity decreased with the amount of BAU units in the copolymer. Tg of these copolymers ranged between 85 –90 °C, with Tm of approximately 280 °C.

Table 1. Physical properties of the copolymers

Copolymer[a]	Mole % of BAU in feed	Mole % of BAU in copolymer[b]	Yield (%)	Intrinsic viscosity	Tg [c] (°C)	Molecular weight Mn	Molecular weight Mw	Molecular weight Dispersity
I	9.1	0.7	55	0.32	87	138,000	166,000	1.20
II	16.7	1.2	60	0.26	90	129,000	162,000	1.26
III	33.3	3.1	59	0.23	85	124,000	162,000	1.31

[a] Polymerization was carried out with 1 wt% of AIBN in 3 ml of THF at 60 °C for 24 hours.
[b] The content of BAU units in the copolymer was determined from 300 MHz NMR spectra.
[c] Obtained from DSC thermogram under N_2 atmosphere with scan speed of 10 °C/min.

The photo-crosslinking reaction of the copolymers containing epoxy and oxime-urethane groups was studied by measuring the insoluble fraction of the copolymer films under various reaction conditions.

Fig. 3 shows the effect of heating temperature on the insoluble fraction of PGMA and copolymer I films in THF before and after irradiation. The PGMA films thermally cross-linked up to 37 % at 140 °C. The insoluble fraction of non-irradiated copolymer I film containing 0.7 % of BAU units increased about twice that of PGMA. The insoluble fraction of the copolymer film after irradiation was 25-30 % higher than that of non-irradiated

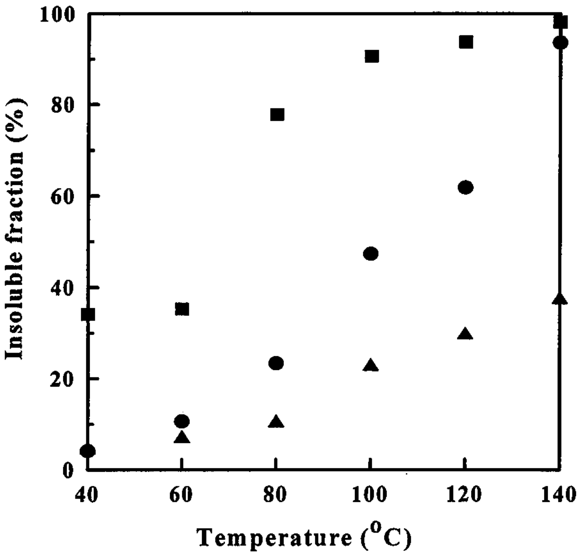


Fig. 3. Effect of heating temperature on the insoluble fraction of PGMA (▲) and copolymer I film in THF before (●) and after (■) irradiation for 40 min with heating time for 40 min.

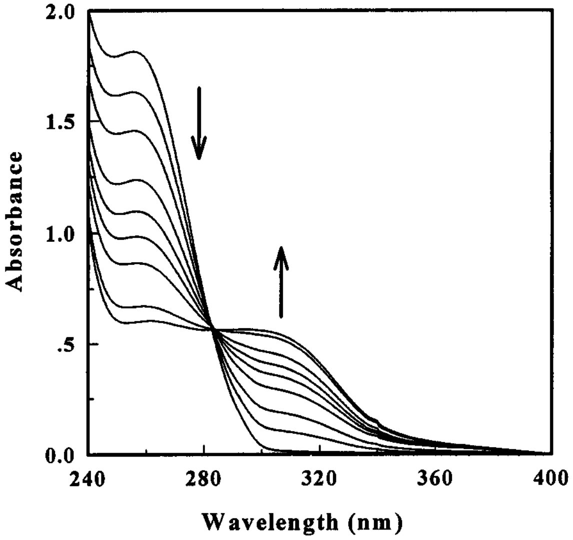


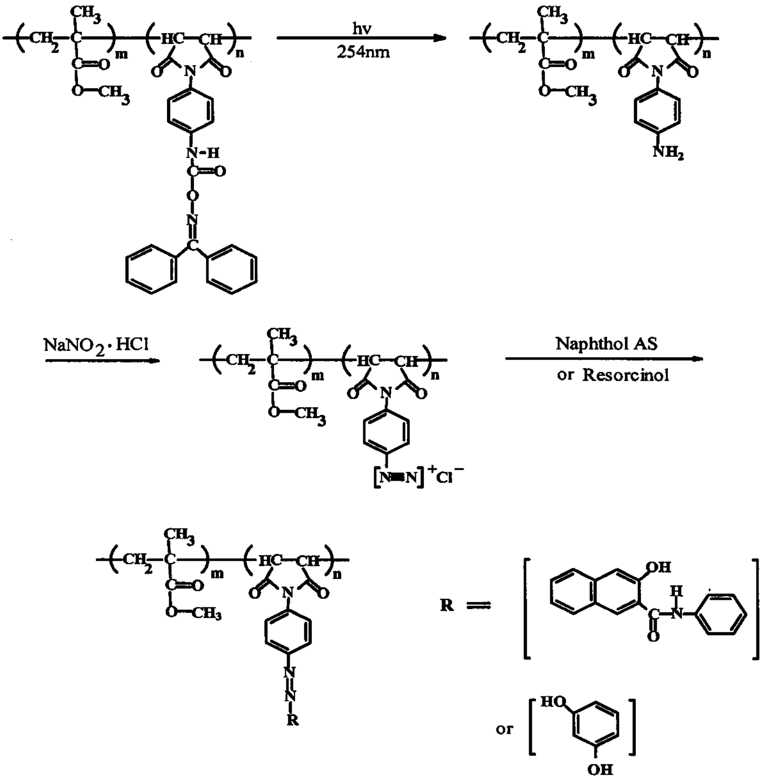
Fig. 4. UV absorption spectral changes of copolymer I in THF with irradiation time.

copolymer film at 40 – 60 °C. However, the difference in the insoluble fraction of irradiated and non- irradiated copolymer films increased up to 55 % at 80 °C. Thus, the higher insoluble fraction observed for the irradiated copolymer films can be attributed to the thermal cross-linking reaction of copolymers catalyzed by the amines produced from photolysed oxime-urethane groups.

The insoluble fraction of copolymer films in THF as a function of irradiation time at different heating temperatures was studied. The insoluble fraction increased with irradiation time, heating temperature and the content of BAU units in the copolymer. The maximum insoluble fraction of copolymer I film was 35 %, below 60 °C, but it increased up to 95 % above 80 °C at the irradiation time of 40 min. Thus there was a large difference in the insoluble fraction of copolymer films between 60 – 80 °C. This can be explained by the mobility difference of photogenerated amino groups in the polymer chain at the temperatures below and above Tg.

UV absorption spectral changes with irradiation was observed in order to study the photochemical reaction of copolymers. Fig. 4 shows UV absorption spectral changes of

Scheme 6:



copolymer I film upon irradiation with UV light of 254 nm for various irradiation time. An isosbestic point appeared at 283 nm. The absorption band at wavelengths shorter than the isosbestic point decreased, while that at wavelengths longer than the isosbestic point increased. The decrease in absorbance at wavelengths shorter than 283 nm is due to the photodecomposition of oxime-urethane groups while the increase at wavelengths longer than 283 nm is due to the formation of azine type compounds.

UV and IR absorption spectral studies indicate that oxime-urethane groups in the polymer chain photodecomposed to form pendant amines, which in turn effectively catalysed the thermal cross-linking reaction of epoxy groups in the copolymer chain.

Applications in image recording material

Scheme 6 shows a chemical reaction which displays a possible application of the photobase generating polymer as an image recording material. The irradiation of the MMA copolymer containing oxime-urethane groups leads to the formation of aromatic pendant amines in the irradiated parts. Further reactions with sodium nitrite generate diazonium salts, which are treated with phenol derivatives such as resorcinol or naphthol AS, resulting in the formation of diazo groups. Various colors were developed depending on the phenolic compounds.

Fig. 5 shows an example of image recording using this polymer. The images in this figure represent a raven with three legs, symbolizing 'the sun' in Koguruh dynasty about 1000 years ago in Korea. The color red was developed from treatment with naphthol AS while yellow was developed from treatment with resorcinol.

Fig. 5. An example of image recording. The color red was developed in the irradiated parts after diazotization followed by treatment with naphthol AS on the polymer surface.

Conclusion

The photolysis of oxime-urethane derivatives leads to the formation of amine which induces cross-linking reaction of epoxy resin upon heating. Epoxy copolymers containing oxime-urethane groups effectively cross-linked, induced by the photogenerated pendant amine. Thus, polymers which can generate photochemical aromatic amines can be utilized as an image recording material.

Acknowledgement

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