

Synthesis of Photoreactive Imidazole Derivatives and Thermal Curing Reaction of Epoxy Resins Catalyzed by Photo-Generated Imidazole

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ABSTRACT: Photoreactive blocked imidazoles such as *N*-(2-nitrobenzyloxycarbonyl)imidazole (2-NBCI), *N*-(3-nitrobenzyloxycarbonyl)imidazole (3-NBCI), *N*-(4-nitrobenzyloxycarbonyl)imidazole (4-NBCI), *N*-(4-chloro-2-nitrobenzyloxycarbonyl)imidazole (CNBCI), *N*-(5-methyl-2-nitrobenzyloxycarbonyl)imidazole (MNBCI), and *N*-(4,5-dimethoxy-2-nitrobenzyloxycarbonyl)imidazole (DNBCI) were synthesized in good yields by reactions of *N,N'*-carbonyldiimidazole (CDI) with corresponding benzyl alcohols. The prepared 2-NBCI decomposed smoothly to produce imidazole by UV-irradiation in tetrahydrofuran (THF) solution or poly(methyl methacrylate) (PMMA) film. Rates of photolysis of DNBCI, MNBCI and CNBCI were higher than that of 2-NBCI in PMMA film, although the rates of 3-NBCI and 4-NBCI were slower than that of 2-NBCI in PMMA film under the same conditions. Thermal curing reactions of epoxy resins and poly(glycidyl methacrylate-co-methyl methacrylate) [P(GMA₅₅-MMA₄₅)] using photo-generated imidazole were examined at 100–160°C. The ring opening reaction of epoxide groups, confirmed by IR spectra, in epoxy resins and P(GMA₅₅-MMA₄₅) proceeded smoothly by catalysis of the photo-generated imidazole.

KEY WORDS Synthesis of Blocked Imidazole / Photo-Generation / Imidazole / Thermal Curing Reaction / Epoxy Resin / Poly(glycidyl methacrylate-co-methyl methacrylate) /

Epoxy resins are typical thermo-setting resins, and widely used for coatings, paints, adhesives, composite, for sealing, packaging, and so on in industry. Thermal curing reactions of epoxy resins are normally performed with hardeners^{1,2} such as polyfunctional amines, carboxylic acids, carboxylic acid anhydrides, phenols, thiols, and active esters. Thermal crosslinking reactions of epoxy resins were also carried out with appropriate acidic catalysts or basic catalysts such as imidazole compounds. However, storage stability of the mixtures of epoxy resins with hardeners or catalysts has not been satisfactory at room temperature. To solve the above problem in the epoxy resin mixtures, many technical methods have been investigated to increase the storage stability of epoxy resins containing hardeners or catalysts. Pappas and his co-workers propose³ some benzylium salts as acidic thermal latent catalysts, which decompose to produce the corresponding benzyl cations⁴ by heating and enhanced the thermal crosslinking reaction of epoxy resins at elevated temperatures. Endo *et al.* reported that benzylpyridinium salts,⁵ benzylphosphonium salts,⁶ and hydrazinium salts⁷ can be used as thermal latent catalysts for the polymerization of epoxy compounds as did as benzylium salts. Crivello *et al.*^{8,9} reported that certain triarylsulfonium salts and diaryliodonium salts containing BF₄, PF₆, AsF₆, and SbF₆ as counter anions are used as photo-initiating cationic catalyst for the crosslinking reactions of polyfunctional epoxy compounds, because these triarylsulfonium salts and diaryliodonium salts decompose to produce corresponding Brønsted acids upon UV-irradiation.

Winkle *et al.* reported¹⁰ the photo-generation of free amines from 2-nitrobenzyl carbamates upon irradiation with UV-light. Kutal *et al.* examined¹¹ photo-generation of ammonia by the reaction of a cobalt-amine complex.

Tsunooka *et al.*¹² reported the photo-generation of free amines from the reactions of *O*-acyloxyamines. Cameron *et al.*¹³ reported the photo-generation of polyfunctional free amines such as hexamethylenediamine (HMDA) by the photochemical reaction of certain blocked polyfunctional amines.

The authors recently reported¹⁴ the photo-generation of various polyfunctional free amines from certain blocked polyfunctional amine compounds followed by novel thermal curing reactions of epoxy resins and polyurethane oligomers. The authors also reported¹⁵ the photo-generation of polyfunctional free thiols from blocked polyfunctional thiol compounds and thermal crosslinking reactions of epoxy resins with photo-generated polyfunctional thiols. However, equimolar amounts of the reagents were needed ordinarily when the thermal crosslinking reactions of epoxy resins with photo-generated hardeners were carried out. Therefore, the photo-generation of base catalyst from the blocked compounds upon UV-irradiation and application to the curative formulation of epoxy resins represent key advances in photopolymer chemistry. This paper reports the synthesis of blocked imidazole compounds, photo-generation of free imidazole, and thermal curing reaction of epoxy resins catalyzed by the produced imidazole.

EXPERIMENTAL

Materials

Organic solvents were dried using P₂O₅, CaH₂, or Na metal wire and purified by the usual method before use. Commercial epoxy resins such as Epicoat 828 (epoxide equivalent: 190) and DEN 438 (epoxide equivalent: 181) were used without further purification. Reagent grade *N,N'*-carbonyldiimidazole (CDI), 2-nitrobenzyl alcohol, 3-nitrobenzyl alcohol, 4-nitrobenzyl alcohol, 4-chloro-2-nitrobenzyl alcohol, 5-methyl-2-nitrobenzyl alcohol, and 4,5-dimethoxy-2-nitrobenzyl alcohol were used without

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further purification. Poly(methyl methacrylate) (PMMA) ($M_n = 64300$, $M_w/M_n = 1.29$) was donated from Professor Nakamura's Laboratory, Kanagawa University, and was used without further purification. Poly(glycidyl methacrylate-co-methyl methacrylate) containing a pendant epoxide group (epoxide equivalent: 223) [P(GMA₅₅MMA₄₅)] ($M_n = 43700$, $M_w/M_n = 1.56$) was synthesized by the radical copolymerization of glycidyl methacrylate (50 mol%) and methyl methacrylate (50 mol%) using azobisisobutyronitrile (AIBN) as an initiator in dimethylformamide (DMF) at 60°C for 12 h according to the reported method.¹⁶

Measurement

Infrared (IR) spectra were measured on a JASCO model IR-700 spectrometer. ¹H NMR spectra were recorded on a JEOL model JNM FX-200 (200 MHz) using deuterated solvents and Me₄Si (tetramethylsilane, TMS) as the internal standard. UV spectra were obtained on a Shimadzu model UV-2100S UV-VIS spectrophotometer. Molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of a model LC-909 GPC (Japan Analytical Industry Co., Ltd.) equipped with a refractive index detector using JAIGEL-1HA-F and JAIGEL-1H-A gel columns (eluent: tetrahydrofuran (THF), calibrated with narrow molecular weight polystyrene standards). Thermal analysis was performed on a Seiko Electronic model TG/GTA 200 at a heating rate 10°C min⁻¹ for thermogravimetric analysis (TGA) under nitrogen atmosphere.

Synthesis of *N*-(2-Nitrobenzyloxycarbonyl)imidazole (2-NBCI)

N-(2-Nitrobenzyloxycarbonyl)imidazole (2-NBCI) (mp 143–144°C) [UV (in THF): 241 nm ($\epsilon = 8500$)] was synthesized in 74% yield by the reaction of 2-nitrobenzyl alcohol with CDI in acetonitrile according to the reported method.¹⁵

Synthesis of *N*-(3-Nitrobenzyloxycarbonyl)imidazole (3-NBCI)

CDI (0.973 g; 6 mmol) was dissolved in acetonitrile (15 mL), and a solution of 3-nitrobenzyl alcohol (0.766 g; 5 mmol) in acetonitrile (5 mL) was added to this solution at room temperature for 1 h under stirring. The solution was stirred at room temperature for 4 h, and the solvent was evaporated *in vacuo*. The crude product was dissolved in chloroform, washed with water, dried with anhydrous magnesium sulfate for overnight, and the chloroform was evaporated. The product thus obtained was recrystallized from ethyl acetate. The yield of 3-NBCI was 0.964 g (78%). mp 106–107°C. IR (KBr): 1770 (C=O), 1528 and 1346 (–NO₂), and 1181 cm⁻¹ (C–O–C). UV (in THF): 252 nm ($\epsilon = 7430$). ¹H NMR (200 MHz, CDCl₃, TMS): $\delta = 5.5$ (s, 2H, CH₂), 7.1 (s, 1H, C=CH), 7.4–7.5, (m, 1H, CH=C), and 7.6–8.4 ppm (m, 5H, N=CH and aromatic protons).

Anal. Calcd for C₁₁H₉N₃O₄: C, 53.44%; H, 3.67%; N, 17.00%. Found: C, 53.64%; H, 3.97%; N, 16.70%.

Synthesis of *N*-(4-Nitrobenzyloxycarbonyl)imidazole (4-NBCI)

The reaction of CDI (0.811 g; 5 mmol) with 4-nitro-

benzyl alcohol (0.766 g; 5 mmol) was carried out in acetonitrile (20 mL) at room temperature for 24 h, and the crude product obtained by the same method was recrystallized from ethyl acetate. The yield of 4-NBCI was 0.911 g (74%). mp 128–129°C. IR (KBr): 1756 (C=O), 1512 and 1350 (–NO₂), and 1181 cm⁻¹ (C–O–C). UV (in THF): 263 nm ($\epsilon = 13650$). ¹H NMR (200 MHz, CDCl₃, TMS): $\delta = 5.5$ (s, 2H, CH₂), 7.1 (s, 1H, CH=C), 7.4–7.5, (m, 1H, CH=C), and 7.6–8.3 ppm (m, 5H, N=CH and aromatic proton).

Anal. Calcd for C₁₁H₉N₃O₄: C, 53.44%; H, 3.67%; N, 17.00%. Found: C, 53.16%; H, 3.64%; N, 17.23%.

Synthesis of *N*-(4-Chloro-2-nitrobenzyloxycarbonyl)imidazole (CNBCI)

CNBCI was synthesized by reaction of CDI (0.811 g; 5 mmol) with 4-chloro-2-nitrobenzyl alcohol (0.938 g; 5 mmol) in acetonitrile (15 mL) at room temperature for 24 h under stirring, and the crude product was recrystallized from ethyl acetate. The yield of CNBCI was 1.12 g (79%). mp 140–141°C. IR (KBr): 1762 (C=O), 1525 and 1362 (–NO₂), and 1181 cm⁻¹ (C–O–C). UV (in THF): 243 ($\epsilon = 7900$) and 303 ($\epsilon = 1800$) nm. ¹H NMR (200 MHz, CDCl₃, TMS): $\delta = 5.8$ (s, 2H, CH₂), 7.1 (s, 1H, CH=C), 7.4–7.5, (m, 1H, CH=C), and 7.6–8.3 ppm (m, 4H, N=CH and aromatic proton).

Anal. Calcd for C₁₁H₈N₃O₄Cl: C, 46.91%; H, 2.86%; N, 14.92%. Found: C, 47.08%; H, 2.81%; N, 14.90%.

Synthesis of *N*-(5-Methyl-2-nitrobenzyloxycarbonyl)imidazole (MNBCI)

The reaction of 0.973 g (6 mmol) of CDI with 0.836 g (5 mmol) of 5-methyl-2-nitrobenzyl alcohol was performed in THF (25 mL) at room temperature for 24 h under nitrogen, and THF was evaporated *in vacuo*. The mixture was diluted with chloroform, washed several times with water, and dried with anhydrous magnesium sulfate for overnight. Chloroform was evaporated from the solution and the product was recrystallized from methanol. The yield of MNBCI was 1.18 g (94%). mp 81–82°C. IR (KBr): 1762 (C=O), 1514 and 1336 (–NO₂), and 1175 cm⁻¹ (C–O–C). UV (in THF): 274 nm ($\epsilon = 3100$). ¹H NMR (200 MHz, CDCl₃, TMS): $\delta = 2.5$ (s, 3H, CH₃), 5.8 (s, 2H, CH₂), 7.1 (s, 1H, CH=C), 7.3–7.6, (m, 3H, CH=C and aromatic protons), and 8.1–8.2 ppm (m, 2H, N=CH and aromatic proton).

Anal. Calcd for C₁₂H₁₁N₃O₄: C, 55.17%; H, 4.24%. Found: C, 55.27%; H, 4.29%.

Synthesis of *N*-(4,5-Dimethoxy-2-nitrobenzyloxycarbonyl)imidazole (DNBCI)

CDI (0.973 g; 6 mmol) was made to react with 4,5-dimethoxy-2-nitrobenzyl alcohol (0.639 g; 3 mmol) in THF (40 mL) at 0°C for 6 h, and the solvent was evaporated *in vacuo*. The obtained crude product by the same method was recrystallized twice from ethyl acetate. The yield of DNBCI was 0.664 g (72%). mp 135–137°C. IR (KBr): 1766 (C=O), 1525 and 1332 (–NO₂), and 1178 cm⁻¹ (C–O–C). UV (in THF): 342 nm ($\epsilon = 2460$). ¹H NMR (200 MHz, CDCl₃, TMS): $\delta = 4.0$ (s, 6H, O-CH₃), 5.8 (s, 2H, CH₂), 7.0 (s, 1H, aromatic proton), 7.1 (s, 1H, CH=C), 7.5, (s, H, CH=C), 7.8 (s, 1H, aromatic proton), and 8.2 ppm (m, 1H, N=CH).

Anal. Calcd for $C_{13}H_{13}N_3O_6$: C, 50.82%; H, 4.26%. Found: C, 51.09%; H, 4.20%.

Typical Procedure for Photolysis of Blocked Imidazole in Solution

An 2-NBCI solution (0.371 g; 1.5 mmol) in THF (0.05 mol L^{-1} ; 30 mL) was charged into a small cylindrical quartz reactor with a water jacket and a thermometer. Gaseous nitrogen was bubbled through the solution for 30 min before UV irradiation. Photolysis of the 2-NBCI was carried out using a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) with thermal-ray filter (HA-50) under nitrogen atmosphere at 30°C for 6 h. During photo-irradiation, the intensity of incident light was kept always at $1.92\text{--}1.98 \text{ mW cm}^{-2}$ (at 310 nm). THF was evaporated *in vacuo*. The ^1H NMR spectrum (in CDCl_3) of the reaction mixture showed decrease of methylene protons of 2-NBCI at $\delta = 5.8$ ppm, and conversion was calculated from the intensity of methylene protons at $\delta = 5.8$ ppm and methine proton at $\delta = 7.1$ ppm due to the imidazole ring.

Typical Procedure for Photolysis of Blocked Imidazole in PMMA Film

PMMA (0.3 g) and 2-NBCI (0.025 g; 1 mmol) were dissolved in THF (5 mL). The solution was cast on a KBr plate and dried to make a polymer film. The film was irradiated by a 250-W high-pressure mercury lamp (Ushio Electric Co., USH-250D) without a filter. The intensity of the light was kept at 10.0 mW cm^{-2} (at 310 nm). Decreasing rate of the NO_2 group of 2-NBCI at 1523 cm^{-1} was measured by IR spectroscopy.

Typical Procedure for Photolysis of Blocked Imidazole in Epoxy Resin and Thermal Curing Reaction of Epoxy Resin with Photo-Generated Imidazole

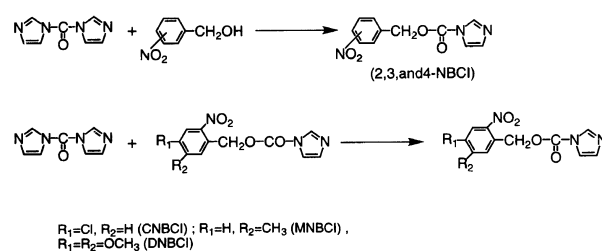
The rate of the thermal curing reaction of epoxy resin was measured as follows. Epicoat 828 (0.380 g; 2 mmol as epoxy group) and 2-NBCI (0.049 g; 0.2 mmol) were mixed in an agate mortar and the paste mixture was cast on a KBr plate. The mixture on the plate was irradiated by a 250-W high-pressure mercury lamp (Ushio Electric Co., USH-250D) without a filter under nitrogen atmosphere. The intensity of the light was kept at 10.8 mW cm^{-2} (at 310 nm). The rate of decrease of the cyclic C–O–C group of the epoxy resin at 910 cm^{-1} in the mixture with photo-generated imidazole by heating at 120°C was measured by IR spectroscopy.

Typical Procedure for Thermal Curing Reaction of P(GMA₅₅-MMA₄₅) using Photo-Generated Imidazole
P(GMA₅₅-MMA₄₅) (0.555 g; 2.5 mmol as epoxide group) and 2-NBCI (0.031 g; 0.125 mmol) were dissolved in THF (5 mL). The solution was cast on a KBr plate and dried to make a polymer film on the plate. The film was irradiated under the same conditions as for the reaction of epoxy resin with 2-NBCI, and the polymer film irradiated for 10 min was heated at 120°C . Decreasing rate of the cyclic C–O–C group at 910 cm^{-1} was recorded by the IR spectroscopy.

RESULTS AND DISCUSSION

Synthesis of Blocked Imidazole

Photoreactive various blocked imidazole derivatives were synthesized by reactions of CDI with certain nitrobenzyl alcohols in acetonitrile or THF. The reaction conditions and results are summarized in Table I. Reactions of CDI with 3-nitrobenzyl alcohol, 4-nitrobenzyl alcohol and 4-chloro-2-nitrobenzyl alcohol proceeded very smoothly in acetonitrile at room temperature, and the corresponding blocked imidazoles such as 3-NBCI, 4-NBCI, and CNBCI were obtained in 78, 74, and 79% yields, respectively (Scheme 1). When the reaction of CDI with 5-methyl-2-nitrobenzyl alcohol was performed under the same conditions, the production of small amounts of MNBCI and large amounts of by-products was confirmed by thin layer chromatography. MNBCI was synthesized in high yield (94%) when the reaction was carried out with 1.2 times CDI in THF at room temperature. DNBCI was yielded in 72% by the reaction of 2.0 times CDI with 4,5-dimethoxy-2-nitrobenzyl alcohol in THF at 0°C , although a by-product, di(4,5-dimethoxy-2-nitrobenzyl)carbonate, was obtained by equimolar reaction at room temperature. These results indicate that blocked imidazole compounds such as 2-NBCI, 3-NBCI, 4-NBCI, and CNBCI are readily obtained by reactions of CDI and nitrobenzyl



Scheme 1.

Table I. Synthesis and properties of blocked imidazole derivatives

Run no	Blocked imidazole	Reaction solvent	Temp.	Time	Yield	Mp	T_d^a	λ_{max}^b
			$^\circ\text{C}$	h	%	$^\circ\text{C}$	$^\circ\text{C}$	nm
1	2-NBCI	Acetonitrile	Room temp.	24	74	143	182	241 (8500) ^c
2	3-NBCI	Acetonitrile	Room temp.	5	78	106	149	252 (7430) ^c
3	4-NBCI	Acetonitrile	Room temp.	24	74	128	157	263 (13650) ^c
4	CNBCI	Acetonitrile	Room temp.	24	79	140	172	243 (7900) ^c 303 (1800) ^c
5	MNBCI	THF	Room temp.	24	94	81	154	274 (3100) ^c
6	DNBCI	THF	0	6	72	135	158	342 (2460) ^c

^a T_d , temperature of initial weight loss. ^b Measured in THF. ^c ϵ , the absorption maximum.

Table II. Solubility of blocked imidazole derivatives^a

Solvent	2-NBCI	3-NBCI	4-NBCI	CNBCI	MNBCI	DNBCI
<i>n</i> -Hexane	—	—	—	—	+	—
Diethyl ether	—	—	+	—	+	—
Methanol	+	+	+	+	+	+
Ethyl acetate	+	+	+	+	++	+
Acetone	++	++	++	++	++	++
Acetonitrile	+	++	++	+	++	+
Chloroform	++	++	++	++	++	++
THF	++	++	++	++	++	+

^a ++, soluble at room temperature; +, soluble by heating; —, insoluble.

alcohols with low nucleophilicity in acetonitrile at room temperature, and the imidazole compounds such as MNBCI and DNBCI can be obtained by reactions of 1.2–2.0 times CDI and nitrobenzyl alcohols with high nucleophilicity in THF at low temperature.

Decomposition temperatures of the synthesized imidazole derivatives were measured by TGA under nitrogen atmosphere. As summarized in Table I, 3-NBCI had the lowest decomposition temperature at 149°C, while 2-NBCI showed the highest decomposition temperature at 182°C. This is an important feature of the blocked imidazole derivatives for practical use as the catalyst for epoxy resins.

Absorption maxima (λ_{\max}) of blocked imidazole compounds are important for photo-generation of free imidazole by UV-irradiation, and were measured in THF solution by UV spectra. As shown in Table I, λ_{\max} of 2-NBCI, 3-NBCI, 4-NBCI, CNBCI, MNBCI, and DNBCI are 241, 252, 263, 243 and 303, 274, and 342 nm, respectively. This means that the introduction of 4-chloro, 5-methyl, or 4,5-dimethoxy group into 2-nitrobenzyloxy moiety red-shifted effectively the absorption of the blocked imidazole.

The solubility of the blocked imidazoles 2-NBCI, 3-NBCI, 4-NBCI, MNBCI, and DNBCI was examined. As summarized in Table II, although all blocked imidazoles were insoluble in *n*-hexane and diethyl ether at room temperature, MNBCI was soluble in the both solvents by heating and 4-NBCI was soluble in diethyl ether by heating. All blocked imidazoles were soluble in methanol, ethyl acetate, acetone, acetonitrile, chloroform, or THF. This means that these blocked imidazole compounds have ordinarily good solubility in common organic solvents.

Photolysis of Blocked Imidazoles in THF Solution and in PMMA Film

Photolysis of 2-NBCI was carried out in THF solution in a cylindrical quartz reactor under UV-irradiation using a 500-W high-pressure mercury lamp. As shown in Figure 1, 2-NBCI decomposed gradually under UV-irradiation. The reaction proceeded with 70% conversion, as determined by the intensity of proton signals at 5.8 ppm due to methylene protons vs. at 7.1 ppm due to methine proton of the imidazole ring, after 5 h irradiation under nitrogen atmosphere (Figure 1). After irradiation, the ¹H NMR spectrum showed signal of CHO proton at $\delta=9.8$ ppm due to (2-nitroso)benzaldehyde. This shows that photo-deprotection of 2-NBCI to produce free imidazole occurs in solution under UV-irradiation

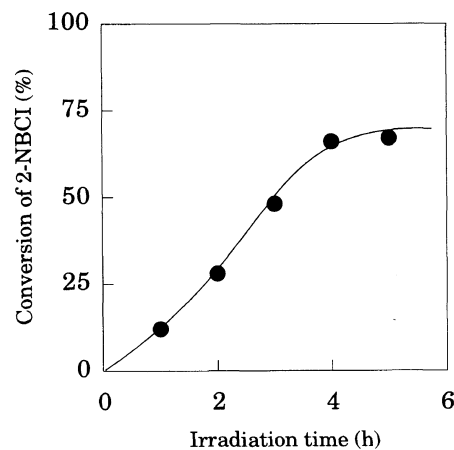
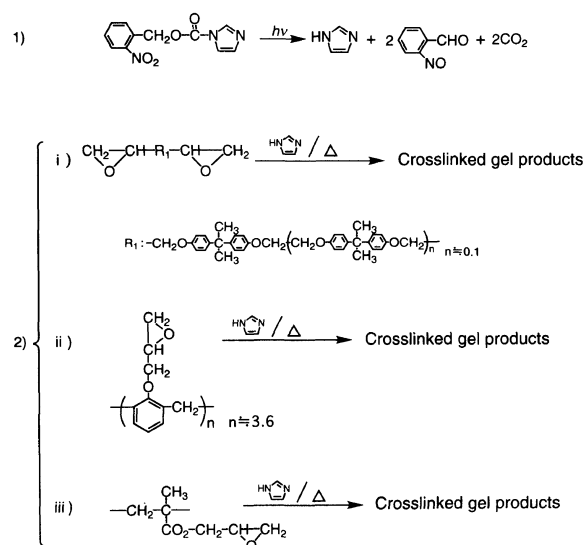


Figure 1. Time-conversion curve of photolysis of 2-NBCI in THF solution.



Scheme 2.

(Scheme 2).

The photolysis of 2-NBCI in PMMA film was examined on a KBr plate. The rate of disappearance of 2-NBCI was measured by monitoring the NO₂ group at 1523 cm⁻¹ in the IR spectroscopy. Almost 100% 2-NBCI decomposed to produce free imidazole in PMMA film after UV-irradiation for 60 min (Figure 2). 3-NBCI and 4-NBCI also decomposed upon irradiation; however, the rates of photolysis of 3-NBCI and 4-NBCI were slower than that of 2-NBCI under the same conditions. This indicates that 2-nitrobenzyloxycarbonyl group is a better protecting group than 3-nitrobenzyloxycarbonyl or 4-

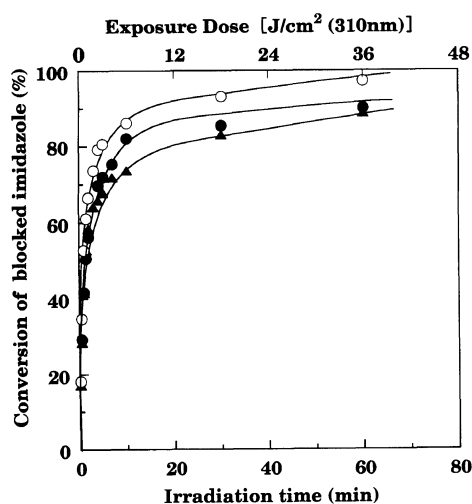


Figure 2. Time-conversion curve of photolysis of blocked imidazoles in PMMA film. (○) 2-NBCI; (●) 3-NBCI; (▲) 4-NBCI.

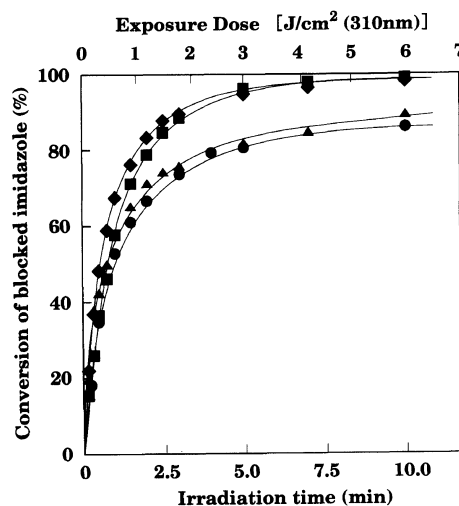


Figure 3. Rates of photolysis of blocked imidazoles in PMMA film. (◆) DNBCI; (■) MNBCI; (▲) CNBCI; (●) 2-NBCI.

nitrobenzyloxycarbonyl groups for the photo-production of free imidazole. Similar results have been found¹⁷ on the photo-decomposition of poly(2-nitrobenzyl methacrylate), poly(3-nitrobenzyl methacrylate), and poly(4-nitrobenzyl methacrylate).

As shown in Figure 3, almost all DNBCI and MNBCI decomposed upon UV-irradiation for only 10 min, although conversions of 2-NBCI and CNBCI were about 85 and 90%, respectively, under the same irradiation conditions. This means that the introduction of a suitable chromophore such as 4,5-dimethoxy or 5-methyl group into the 2-nitrobenzyloxy moiety enhances strongly the rates of photo-decomposition of the blocked imidazole compounds due to the electronic effect of the substituent on the benzene ring. The introduction of chloro group into the 2-nitrobenzyloxy moiety increased the photo-decomposition of the blocked imidazole compound, CNBCI. It seems that the red-shift of the UV absorptions of CNBCI, MNBCI, and DNBCI also may enhance each rate of photolysis.

Photolysis of Blocked Imidazole in Epoxy Resin and Thermal Curing Reaction of Epoxy Resins Catalyzed by Photo-Generated Imidazole

The photolysis of 2-NBCI (10 mol% to epoxide group) in bisphenol-type epoxy resin (Epicoat 828) for 60 min (39 J cm^{-2}) and 90 min (58 J cm^{-2}), respectively, followed by the thermal curing reaction of the epoxy resin at 120°C were performed on a KBr plate. The thermal curing reaction of the epoxy resin containing 10 mol% of imidazole was examined under the same conditions as for the reference reaction. The rates of ring-opening of epoxide groups in the resin were measured from decrease in absorption peaks due to cyclic C–O–C stretching at 910 cm^{-1} using IR spectroscopy. As shown in Figure 4, the rate of conversion of epoxide group of the mixture of the resin with 10 mol% of imidazole was faster than those of the photo-irradiated mixtures of the resin with 10 mol% of 2-NBCI, and the conversion of epoxide group of the former mixture reached nearly 90% by heating at 120°C for 30 min. The conversions of epoxide groups of the photo-irradiated mixtures for 60 and 90 min were 42 and 68%, respectively, by heating

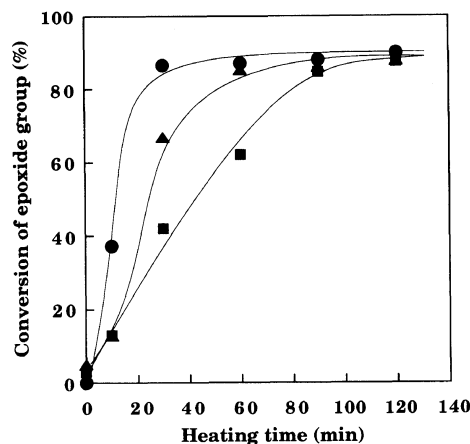


Figure 4. Rates of ring-opening of epoxy group in a mixture of bisphenol-type epoxy resin with 2-NBCI (10 mol% to epoxide group) or imidazole (10 mol% to epoxide group) by heating at 120°C . (●) with imidazole; (▲) after UV-irradiation for 90 min with 2-NBCI; (■) after UV-irradiation for 60 min with 2-NBCI.

under the same conditions for 30 min. These conversions reached nearly 90% by heating for 120 min, and the cured mixtures became insoluble in THF and chloroform. This means that photo-generation of free imidazole in the epoxy resin mixture increases with irradiation time, and the photo-generated imidazole from 2-NBCI promotes effectively the thermal curing reaction of the epoxy resin (Scheme 2).

A mixture of the same epoxy resin with 2-NBCI (10 mol% to the epoxide group) was irradiated with UV-light for 60 min, and the mixture was heated at various temperatures. As shown in Figure 5, conversion of epoxide groups of the resin mixtures was about 5% after UV-irradiation for 60 min at room temperature, which was confirmed from decrease of absorption peak of cyclic ether at 910 cm^{-1} by the IR spectrum. This indicates that the ring-opening reaction of epoxide group in the resin may be partially catalyzed by photo-generated free imidazole during UV-irradiation. The conversion of epoxide group in the mixture increased with heating time and temperature, and reached 77, 88, and 98%, respectively, after thermal treatment at 100, 120, and 140°C for 120 min. Each cured mixture after heating for

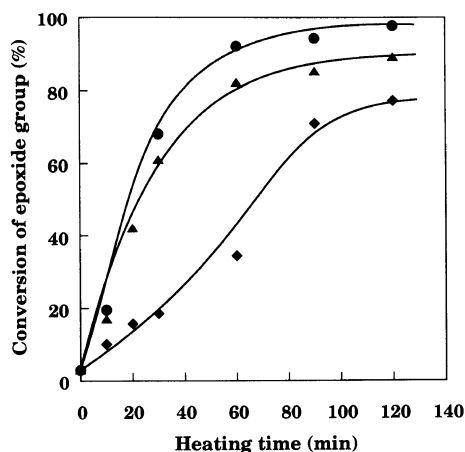


Figure 5. Rates of ring-opening of epoxy group in a mixture of bisphenol-type epoxy resin with 2-NBCI (10 mol% to epoxy group) after UV-irradiation for 60 min followed by heating. (◆) at 100°C; (▲) at 120°C; (●) at 140°C.

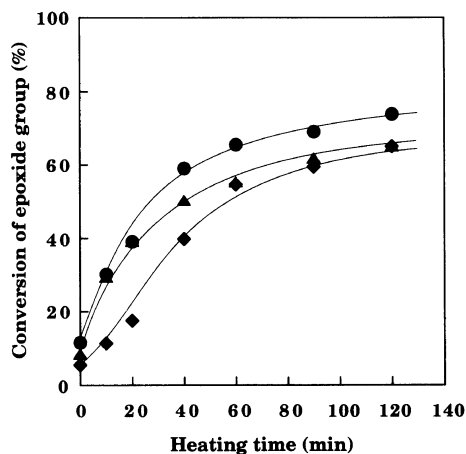


Figure 6. Rates of ring-opening of epoxy group in a mixture of novolac-type epoxy resin with 2-NBCI (10 mol% to epoxy group) after UV-irradiation for 60 min followed by heating. (◆) at 120°C; (▲) at 140°C; (●) at 160°C.

120 min became insoluble in THF and chloroform. This means that the thermal curing reaction of the epoxy resin catalyzed by photo-generated free imidazole is strongly affected by reaction temperature.

The photo-initiating thermal curing reaction of novolac-type epoxy resin (DEN 438) containing three or more epoxy groups in a molecule with 2-NBCI (10 mol% to epoxide group) was also performed under the same conditions. As shown in Figure 6, conversion of epoxide groups of the resin mixtures was about 5–10% after UV-irradiation for 60 min at room temperature. The conversion of epoxide group in the mixture increased with heating time and temperature, and reached 65, 65, and 73%, respectively, after thermal treatment at 120, 140, and 160°C for 120 min. Each cured mixture of the novolac-type epoxy resin with 2-NBCI was insoluble in THF and chloroform after UV-irradiation for 60 min followed by heating for 120 min. These results indicate that thermal curing reaction of novolac-type epoxy resin with the photo-generated imidazole occurs as shown in Scheme 2, where n is the degree of polymerization, although the rate of ring opening of epoxide group of novolac-type epoxy resin was slower than that of epox-

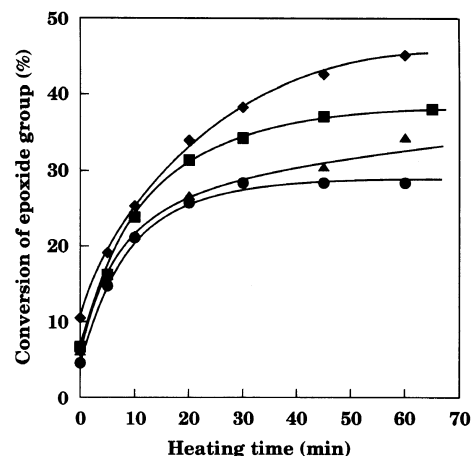


Figure 7. Rates of ring-opening of epoxy group in mixtures of P(GMA₅₅-MMA₄₅) and various amounts of 2-NBCI after UV-irradiation for 10 min followed by heating at 120°C. (●) with 1 mol% of 2-NBCI; (▲) with 3 mol% of 2-NBCI; (■) with 5 mol% of 2-NBCI; (◆) with 10 mol% of 2-NBCI.

ide group of bisphenol-type epoxy resin due to their structures.

The photo-initiating thermal curing reaction of P(GMA₅₅-MMA₄₅) film containing 1, 3, 5, and 10 mol% of 2-NBCI was carried out on KBr plates. Since about 80 mol% of 2-NBCI decomposed by UV-irradiation for 10 min (6 J cm^{-2}) in PMMA film as shown in Figure 3, the photo-irradiation toward this system was performed only for 10 min, and the thermal curing reaction at 120°C. As shown in Figure 7, conversion of pendant epoxide groups in P(GMA₅₅-MMA₄₅) films containing 1, 3, 5, and 10 mol% of 2-NBCI increased with time, reaching 28, 33, 38, and 45%, respectively, by heating for 60 min. All polymer films composed of P(GMA₅₅-MMA₄₅) and 2-NBCI became insoluble in THF and chloroform after UV-irradiation for 10 min followed by heating at 120°C for 60 min (Scheme 2). This shows that the photo-initiating thermal curing reaction of P(GMA₅₅-MMA₄₅) film is possible by the addition of a small amount of blocked imidazole compound and short time UV-irradiation.

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