Thermally Stable Carbamates as Novel Photobase Generator

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Six carbamates were prepared as novel photobase generators (PBGs), and their photo-reactivity and thermal stability were investigated. The introduction of an alkyl substituent into NH moiety in O-carbamoyloximes and/or the use of naphthalimide moieties instead of oxime moieties gave higher temperature of thermal decomposition (T_d). These carbamates were photo-decomposed on irradiation at 254 nm, and the photolysis rates of oxime carbamates were higher than those of naphthalimide carbamates. The generation of amines from naphthalimide carbamates was confirmed by HPLC analysis of irradiated solutions. Although corresponding amines were not detected from oxime carbamates, the formation of 2-acetanaphthalone was observed, suggesting the formation of the other type of basic compounds after photolysis. Films of poly(glycidyl methacrylate) containing oxime carbamates or naphthalimide carbamates became insoluble on irradiation followed by post-exposure bake.

Keywords: photobase generator, carbamate, thermal stability, post-exposure bake, crosslink, epoxide

1. Introduction

Photobase generators (PBGs) are materials that release basic species on irradiation. Because of its potential availability as a catalyst for polymerization and crosslinking of polymeric materials as well as photoacid generators, PBG is one of promising materials.[1,2]

Among PBGs, carbamates are representative photo-labile precursors of amines, and O-carbamoyloximes have higher photo-reactivity to generate basic compounds as shown in Scheme 1(i, ii).[3-6] Several papers describe their utility as a catalyst of crosslinking epoxy polymers and oligomers.[7-10] However, O-carbamoyloximes turn to oximes and isocyanates on heating at relatively lower temperature as shown in Scheme 1 (iii).[11,12] Although this characteristics is advantageous in curing systems using both photochemical and thermal reactions[13-16], the utilization in processes at higher temperature range is limited.

In this article, we have newly prepared six carbamates listed in Fig. 1 as novel PBGs. In order to improve the thermally stability, an alkyl group was introduced into carbamoyl moieties to avoid thermal deblocking into oximes and isocyanates (1a and 1b). Another attempt is the introduction of N-hydroxynaphthalimide moiety instead of oxime group (2). 3a and 3b involves both, and 4 was O-carbamoyloxime corresponding to 1b. The photochemical and thermal properties of these carbamates are investigated as well as

![Scheme 1. Photo- and thermal reactions of O-carbamoyloximes.](image-url)
their ability to crosslink poly(glycidyl methacrylate) (PGMA).

2. Experimental

2.1 Apparatus

Melting points were measured by a Yanako MT-3S micro melting point meter. IR, UV, and NMR spectral measurements were performed using Jasco FTIR410, Shimadzu 2400PC, and Jeol JNM-GX270 (270 MHz) spectrometers, respectively. Molecular weights were measured by size exclusion chromatography (SEC) with polystyrenes as standards and tetrahydrofuran (THF) as eluent. Thermogravimetric analysis (TGA) was carried out by a Shimadzu TGA50 thermogravimetric analyzer with a heating rate of 10 K/min under N₂. Light intensity was measured by an Ore UV-M02 illuminometer. Thickness of films on silicon plates was measured by a Nanometrics Nanospec / AFT M3000 interferometer. Normal phase high performance liquid chromatography (HPLC) was carried out with a system consisting of a Jasco PU2980 pump, a Jasco UV2070 detector, and a Chromatocience CSPAQ SIL column. Reversed phase HPLC was performed by a system composed of a Jasco PU980 pump, a Jasco UV980 detector, and a Chromatocience CSPAQ C18 column, or that composed of a Varian Prostar pump, a C18 CSpAke column, and a Varian PDA330 detector.

2.2 Materials

Glycidyl methacrylate (GMA), methacrylonitrile (MAN), N,N-dimethylformamide (DMF), cyclohexanone, and tetrahydrofuran (THF) were distilled before use. Diethylamine (Nacalai Tesque), N,N-dibuthylcarbamoyl chloride (Aldrich), N,N-diethylcarbamoyl chloride (Tokyo Kasei), butylisocyanate (Tokyo Kasei), dibutyltin dilaurate (Wako Chemical), 2-acetonaphthone (Wako Chemical), and 2,4-dinitrofluorobenzene (Wako Chemical) were used as received.

N-Hydroxynaphthalimide [17] was prepared from 1,8-naphthalic anhydride and hydroxylamine hydrochloride; yellow crystals, mp: 278–281 °C. 2,4-Dinitro-N,N-diethylaniline, 2,4-dinitro-N,N-dibutylaniline, and 2,4-dinitro-N-buthylaniline were prepared from 2,4-dinitrofluorobenzene (DNFB) and corresponding amines as yellow needles (mp: 79–80 °C, lit[18]: 80 °C), reddish tar, and yellowish needles (mp: 85–87 °C, lit[19]: 89–90 °C), respectively.

PGMA was prepared by heating degassed solution of GMA: α,α′-azobisobutyronitrile: toluene: 1-dodecylmercaptan = 100:1:100:5 (wt/wt) at 60 °C for 5 h followed by repeated reprecipitations from THF–methanol system; yield 70 %, Mn: 10,500, Mw/Mn: 1.57, Tg: 60.2 °C. Poly(methacrylonitrile) (PMAN) was obtained by heating degassed solution of MAN: AIBN: 2-butane = 100:1:50 (wt/wt) at 55 °C for 48 h followed by repeated reprecipitations from acetone–methanol system; yield 15 %, Tg: 304 °C. 2.3 Preparation of PBGs

2.3.1 2-Acetonaphthone N,N-diethylcarbamoyloxime (1a)

In a 100 ml of flask, 3.33 g (18 mmol) of 2-acetonaphthone oxime was dissolved in 25 ml of dry pyridine. To this solution, 2.74 ml (21.6 mmol) of N,N-diethylcarbamoyl chloride and 2 drops of dibutyltin dilaurate were added with stirring. After refluxing for 2 h, the solution was cooled to room temperature, and added dil. HCl solution till the pH of the solution became 7–8. The mixture was extracted by chloroform three times, and the combined organic layer (total 250 ml) was washed with sat. NaHCO₃ and sat. NaCl solutions. After drying with magnesium sulfate and evaporation of the solution, resulting solid (2.2 g) was purified by silica gel column chromatography (eluent: ethyl acetate/hexane = 1/1(v/v)) and recrystallization from cyclohexane to afford 2.04 g (yield 40 %) of yellow crystals. IR (KBr): 1725 cm⁻¹ (C=O). ¹H NMR (CDCl₃): δ = 1.25 (6H, t, CH₃), 2.48 (3H, s, N=CH₂), 3.41 (4H, q, CH₂), 7.47–8.16 (7H, m, aromatic). Caled for C₂₄H₂₈N₂O₂: C 71.81, H 7.09, N 9.85. Found: C 71.92, H 7.29, N 9.96.

2.3.2 2-Acetonaphthone N,N-dibuthylcarbamoyl-
oxime (1b)

1b was obtained as white solid in 25% yield from 2-acetonaphthone oxime and N,N-dibutylcarbamoyl chloride by a similar method described for 1a: IR (KBr): 1735 cm⁻¹ (ester C=O). ¹H NMR (CDCl₃): δ = 0.97 (6H, t, CH₃), 1.28–1.45 (4H, m, CH₂), 1.58–1.69 (4H, m, CH₂), 2.47 (3H, s, N=C=CH₂), 3.34 (4H, t, NCH₂), 7.48–8.16 (7H, m, aromatic). Calculated for C₃₂H₂₆N₂O₈: C 74.08, H 8.29, N 8.23. Found: C 74.00, H 8.60, N 8.05.

2.3.3 N-Butylcarbamoyloxynaphthalimide (2)

In a flask equipped with a CaCl₂ tube and a septum, 0.53 g (2.5 mmol) of N-hydroxynaphthalimide, a few drops of dibutyltin dilaurate, several pieces of molecular sives, and 8 ml of DMF were placed. To the mixture, 0.33 ml (3.0 mmol) of butyldisocyanate was added dropwise through the septum. After stirring for 24 h at room temperature, most of DMF was removed by evaporation. The concentrated liquid was poured in an excessive hexane, and the resulting solid was recrystallized from acetonitrile to afford 0.34 g (yield 43%) of colorless crystals: IR (KBr): 3312 cm⁻¹ (NH), 1754 cm⁻¹ (ester C=O), 1722 and 1700 cm⁻¹ (imide C=O), 1546 cm⁻¹ (N-H). ¹H NMR (CDCl₃): δ = 0.88–1.03 (3H, m, CH₃), 1.35–1.66 (6H, m, CH₂), 3.33 (2H, m, CH₂), 5.34 (1H, broad s, NH), 7.68–8.69 (6H, m, aromatic). Calculated for C₁₃H₁₆N₂O₈: C 65.38, H 5.16, N 8.97. Found: C 65.29, H 5.11, N 9.35.

2.3.4 N,N-Diethylcarbamoyloxynaphthalimide (3a)

To the flask were added 2.13 g (10 mmol) of N-hydroxynaphthalimide, 40 ml of dried pyridine, and 1.28 ml (10 mmol) of N,N-diethylcarbamoyl chloride. After stirring for 1.5 h at room temperature, dil. HCl solution was added to the mixture till pH becomes 7–8 with stirring. Percolated yellow solid was washed with water and recrystallized from ethyl acetate: hexane = 3:2 (v/v) to afford 1.05 g (yield: 34%) of yellow crystals: IR (KBr): 1758 cm⁻¹ (ester C=O), 1717 and 1696 cm⁻¹ (imide C=O). ¹H NMR (CDCl₃): δ = 1.26 (3H, t, CH₃), 1.42 (3H, t, CH₃), 3.44 (2H, q, CH₂), 3.58 (2H, q, CH₂), 7.71–8.62 (6H, m, aromatic). Calculated for C₁₅H₁₈N₂O₈: C 65.38, H 5.16, N 8.97. Found: C 65.48, H 4.86, N 8.85.

2.3.5 N,N-Dibutylcarbamoyloxynaphthalimide (3b)

3b was obtained as yellow crystals in 89% yield from N-hydroxynaphthalimide and N,N-dibutylcarbamoyl chloride by a similar method described for 3a: IR (KBr): 1756 cm⁻¹ (ester C=O), 1719 and 1692 cm⁻¹ (imide C=O). ¹H NMR (CDCl₃): δ = 0.84–1.01 (6H, m, CH₃), 1.24–1.83 (8H, m, CH₂), 3.31–3.50 (4H, m, CH₂), 7.72–8.62 (6H, m, aromatic). Calculated for C₂₃H₂₄N₂O₈: C 68.46, H 6.57, N 7.60. Found: C 68.33, H 6.62, N 7.67.

2.3.6 2-Acetonaphthone N-buthylcarbamoyloxime (4)

4 was obtained as yellow crystals in 12% yield from 2-acetonaphthone oxime and butylisocyanate by a similar method described for 2: IR (KBr): 3373 cm⁻¹ (N-H) 1716 cm⁻¹ (ester C=O) 1487 cm⁻¹ (N-H). ¹H NMR (CDCl₃): δ = 0.96 (3H, t, CH₃), 1.34–1.66 (4H, m, CH₂), 2.57 (3H, s, N=C-CH₃), 3.36 (2H, m, NCH₂), 6.50 (1H, broad s, CH), 7.53–8.09 (7H, m, aromatic). Calculated for C₁₃H₂₀N₂O₈: C 71.81, H 7.09, N 9.85. Found: C 71.69, H 7.21, N 10.13.

2.4 Irradiation

Solutions were put in a tube bearing 1 x 1 cm quartz cuvette, degassed by freeze-pump-thaw cycles, and irradiated in the cuvette with an Ushio ULO-6DQ low-pressure mercury lamp (6 W). The light intensity at 254 nm was 1.0 mW/cm².

PMAN films were obtained by spin coating on silicon wafers or quartz plates from cyclohexanone solutions of PMAN: PBG = 100:5 (wt/wt) and prebaked at 90 °C for 25 min on a Koike HM-15G Hotplate. For PGMA films, GMA units: PBG = 100:1 (mol/mol), and the films were prebaked at 80 °C for 2 min. Thickness of all films was 0.6 μm.

Films were irradiated with the Ushio ULO-6DQ lamp in air. Post-exposure bake (PEB) was carried out on the hot plate.

Insoluble fraction of the films was obtained from ratios of thickness before and after soaking the films in THF for 5 min at room temperature.

For IR spectral changes of PBGs in PMAN, films were coated and pre-baked as above and heated for 1 h at 60 °C under reduced pressure. After irradiation, the films were removed from the silicon plates, mixed in KBr to form 3 mm³ disks, and measured their IR spectra.

2.5 HPLC studies

For monitoring the photolysis of PBGs in ethanol, irradiated solutions were evaporated and dried using a vacuum pump. The residue was dissolved in a mixed solution of chloroform: hexane = 7:3 (v/v), passed through a pipette holding small amount of silica gel, and evaporated again. The residue was dissolved in 4 ml of
chloroform–hexane mixture containing 1.16 x 10⁻⁴ M benzoin as standard, filtered with a disposable PTFE membrane filter, and applied to normal phase HPLC with chloroform : hexane = 7 : 3 (v/v) as mobile phase and UV detection at 290 nm.

Generating amines were derived to 2,4-dinitroanilines as shown in Scheme 2[20], and the derivatives were analyzed by HPLC. Irradiated solution was mixed with ethanol solution of DNFB (x 5 mol against PBG) and potassium carbonate (x 15 mol) and refluxed for 1 h. The solution was passed through a short silica gel column and evaporated. 5 ml of mobile phase was added to the flask. Derivatives of amines from 1a, 1b, and 4 were analyzed by normal phase HPLC with detection at 400 nm and chloroform : hexane = 7 : 3 (v/v) as mobile phase. 2, 3a, and 3b were analyzed by reversed phase HPLC with methanol : water = 7 : 3 or 5 : 5 (v/v) as mobile phase and UV detection at 245 nm.

Irradiated solutions of 1b were concentrated to ca. 1/3 by evaporation and analyzed by a Varian reversed phase HPLC system with UV detection at 284 nm and a gradient mobile phase starting from 1% acetic acid in water : methanol = 90 : 10 to 1 : 99 (v/v) during 60 min.

3. Results and Discussion
3.1 Synthesis and physical properties of PBGs

Oxime carbamates were prepared from acid chlorides and 2-acetonaphthone oxime, and the yields of 1a and 1b were low due to low reactivity of N,N-dialkylcarbamoyl chlorides with 2-acetonaphthone oxime. However, the addition of dibutyltin dilaurate improved the yield compared to the reaction without the catalyst.

Table 1 shows physical properties of PBGs. Naphthalimide and 2-acetonaphthone oxime moieties are chromophores having maximum wavelengths around 332 and 283 nm, respectively. At 254 nm, molar extinction coefficients (ε) of oxime carbamates (1a, 1b and 4) were about 20 times greater than those of naphthalimide carbamates (2, 3a, and 3b).

<table>
<thead>
<tr>
<th>PBG</th>
<th>mp (°C)</th>
<th>Td (°C)</th>
<th>λmax (nm)</th>
<th>ε (L·mol⁻¹·cm⁻¹) at λmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>77-77.5</td>
<td>240</td>
<td>283</td>
<td>12,900 27,500</td>
</tr>
<tr>
<td>1b</td>
<td>40-41</td>
<td>252</td>
<td>283</td>
<td>13,700 31,700</td>
</tr>
<tr>
<td>2</td>
<td>188</td>
<td>333</td>
<td>11,400</td>
<td>1,500</td>
</tr>
<tr>
<td>3a</td>
<td>228-229</td>
<td>281</td>
<td>322</td>
<td>13,000 1,600</td>
</tr>
<tr>
<td>3b</td>
<td>85-86</td>
<td>288</td>
<td>322</td>
<td>10,100 1,400</td>
</tr>
<tr>
<td>4</td>
<td>53-55</td>
<td>173</td>
<td>283</td>
<td>14,900 34,800</td>
</tr>
</tbody>
</table>

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Table 1. Physical properties of PBGs.

a) Onset temperature from TGA under N₂.
b) In ethanol for 1a, in acetonitrile for others.
c) Clear melting point was not obtained.

Both melting points and T_{d}s of 2, 3a, and 3b were higher than those of 4, 1a, and 1b, showing that the introduction of naphthalimide moiety contributed to higher thermal stability than oxime moiety. 1b and 3b having butyl groups showed higher T_{d} than 1a and 3a having ethyl group.

2 showed two-stage decomposition in Fig. 2 because of thermal decomposition as shown in Scheme 1(iii). The first weight loss was 35 wt% which was in good agreement with weight fraction (34.9 wt%) of butylisocyanate in 2. The TGA profile in second weight loss region fit well to that of N-hydroxynaphthalimide. 4 did not give the two-stage decomposition because of low sublimation temperature of 2-acetonaphthone oxime.

![Fig. 2. TGA profiles of PBGs under N₂.](image)
3.2 Spectral Changes of PBGs on Irradiation

Figure 3 shows UV spectral changes of 1b and 3b on irradiation in ethanol. Peaks at 283 nm for 1b and 332 nm for 3b decreased on irradiation with an increase in a region of 300–360 nm and 350–500 nm, respectively. The change for 1b was much faster than 3b. Similar results were obtained for all carbamates both in ethanol and in PMAN.

Figure 4 shows typical IR spectral changes of 1b and 3b in PMAN on irradiation. In Fig. 4a, the decrease of the peak at 1735 cm$^{-1}$ due to ester C=O stretching band in 1b was clearly observed in difference spectra (iii). The decrease of C=O stretching bands in carbonyl, imide and imide moieties at 1757, 1719, and 1692 cm$^{-1}$, respectively, are also observed for 3b in Fig. 4b. In both cases, uncharacterized peaks appeared around at 1670 cm$^{-1}$.

3.3 Photo-Reactivity of PBGs

Figure 5 shows the degree of photolysis of PBGs in ethanol as a function of logarithm of irradiation energy. The photolysis rates of oxime carbamates were faster than those of naphthalimide carbamates. For example, irradiation energies required for 50% photolysis of 1a and 3a were 15 and 700 mJ/cm$^2$, while c at 254 nm was 1,600 and 27,500, respectively. Other PBGs also showed a similar tendency. These results indicate the low photo-reactivity of naphthalimide carbamates than oxime carbamates. Allonas et al. [21] explained the difference of the triplet sensitized dissociation of some oxime derivatives by the flexibility of the molecules which explores more different geometries than the rigid molecules, giving the possibility to reach more easily the transition state for the dissociation. Although PBGs were directly excited in this study, it is deduced that the low photo-reactivity of naphthalimide carbamates is due to the rigid naphthalimide moiety.
Fig. 5. Photolysis of (△)1a, (▽)1b, (○)2, (◇)3a, (□)3b, and (×)4 in ethanol under N₂ confirmed by normal phase HPLC analysis.

The rate of photolysis of PBGs in PMAN gave similar tendency compared to in ethanol.

Figure 6 shows the changes of generation of amines from naphthalimide carbamates on irradiation in ethanol. All of naphthalimide carbamates generated amines on irradiation. Plausible photoreactions are shown in Scheme 3, where generated iminyl radical 5 abstracts hydrogen from the surroundings to form secondary amine 6.

Oxime carbamates showed a different result. Although 4 generated butylamine as shown in Fig. 7a, the amount of generated amines from 1a and 1b was small. However, 2-acetonaphthone was detected from all of 1a, 1b and 4 (Fig. 7b). These results strongly suggest the formation of basic compounds other than amines from 1a and 1b. Possible basic compounds are 7, 11, and 13 that are shown in Scheme 4. Figure 8 is HPLC chromatograms of irradiated 1b solutions using another reversed phase HPLC system without derivatization process of amines. On irradiation

![Scheme 3](Image)

Scheme 3. Plausible photoreactions of naphthalimide carbamates.

Fig. 6. Photolysis of naphthalimide carbamates and photo-generation of amines in ethanol under N₂. (◇, ●)3a, (□, ■)3b, (○, ●)2. Open symbol: remaining carbamates, solid symbol: generated amine.

![Image](Image)

Fig. 7. a) Photolysis of oxime carbamates and photo-generation of amines, and b) photo-generation of 2-acetonaphthone in ethanol. Remaining (△)1a, (▽)1b, (×)4, generated amines from (△)1a, (▽)1b, (+)4, and generated 2-acetonaphthone from (●)1a, (■)1b, (●)4.)
at 60 mJ/cm², a new peak appeared at 65.0 min of retention time that disappeared on further irradiation. Although this peak was not due to 2-acetonaphthone and not identified at present, it might be due to intermediates 9 or 10.

3.4 Crosslinking of PGMA Films

The applicability of bases generated from PBGs was evaluated by the solubility changes of PGMA films containing the PBGs on irradiation followed by PEB. Figure 9 shows insoluble fraction of PGMA films containing PBGs on irradiation followed by PEB at 140 and 180 °C.

Fig. 8. Reversed phase HPLC chromatograms of ethanol solution of 1b (a) before and after irradiation at (b) 60 and (c) 300 mJ/cm². Numbers in the figure show retention time of the peaks.

Fig. 9. Insolubilization of PGMA films containing (△)1a, (▽)1b, (⊙)2, (◇)3a, (口)3b, (×)4 on irradiation followed by PEB for 10 min at a) 140 °C and b) 180 °C. [GMA unit] : [PBG] = 100 : 5 (mol/mol).
photolysis monitored by HPLC. For example, the insoluble fraction for 2, 3a and 3b reached plateau on irradiation at 2000 mJ/cm² where most of the PBGs photo-decomposed in PMAN.

Concerning to oxime carbamates, 4 showed the highest efficiency of the crosslinking, which is consistent with the high photo-reactivity and corresponding high rate of generation of amine as confirmed by HPLC study. However, 1a and 1b were not probably due to indirect formation of basic compounds on irradiation as discussed in 3.3.

On PEB at 180 °C (Fig. 9b), 1b and 3b were much effective for the insolubilization than others. These results indicate that amines bearing butyl groups were more effective than those bearing ethyl groups. 4 was not effective because of thermal decomposition at this baking temperature.

4. Conclusion

Novel photobase generators were prepared and investigated as a catalyst of crosslinking of polymer bearing epoxy groups. N,N-Dialkyl-substituted oxime carbamates showed higher Tg than N-monooalkyl-substituted carbamates, and naphthalimide carbamates showed higher thermal stability than oxime carbamates. Naphthalimide carbamates generated amines on irradiation in ethanol. Oxime carbamates showed higher photo-reactivity than naphthalimide carbamates. Although corresponding amines were not detected from oxime carbamates, the generation of 2-acetophenone was detected, suggesting the formation of other type of basic compounds. All carbamates in PGMA films showed insolubilization on irradiation followed by PEB. These results indicate that these carbamates were thermally stable PBGs.

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5. References