CL-150405 Received: April 28, 2015 | Accepted: May 25, 2015 | Web Released: June 4, 2015

Photobase Generators Liberating Two Bases by Absorbing One Photon and Their Application to Photosensitive Materials

Koji Arimitsu,* Yuya Maruyama, and Masahiro Furutani
Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 278-8510

(E-mail: arimitsu@rs.noda.tus.ac.jp)

We propose a photobase generator (PBG) that liberates two bases by absorbing one photon. Phototriggered decarboxylation proceeds first to generate one base, and subsequently the unstable reaction intermediate is thermally decarboxylated to generate another base. It was found that the photosensitivity of poly(glycidyl methacrylate) films containing the PBG is much higher than that of films containing a conventional PBG that generates one base by absorbing one photon.

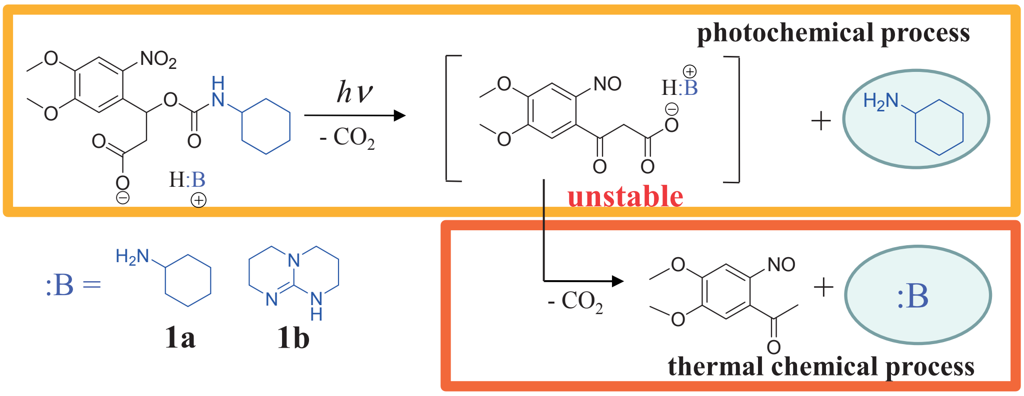
Photosensitive materials have been studied extensively because they are widely used in industrial processes. They are utilized in the fields of printing, resists, coatings, adhesion, and electronic materials.[1–3] In a UV curing system, radical or cationic initiators are often used, because such species have relatively high photosensitivity. However, they also have crucial problems such as oxygen inhibition and volume shrinkage in a radical process, or corrosion of metallic substrates in a cationic process. Now, an anionic UV curing system using photobase generators (PBGs) is in the limelight because it could circumvent these problems. However, in general, basic species from PBGs are weak bases, and their quantum yields are very low,[4–11] which leads to low photosensitivity of the system.

As PBGs generate strong bases, Sun et al. developed a tetraphenylborate that generates a superbase, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), although its quantum yield is not high ($\Phi_{254} = 0.18$).[12] Suyama et al. reported the use of a benzoformate-type PBG to generate 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).[13] Our group has focused on photodecarboxylation reactions of ketoprofen and xanthone acetic acid, which could be photodecomposed with high quantum yields ($\Phi_{313} = 0.75$ for ketoprofen and $\Phi_{350} = 0.64$ for xanthone acetic acid), and developed their carboxylate-type PBGs generating superbases such as TBD, DBU, and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).[14,15] However, these PBGs generate only one base molecule with one photon, where the maximum achievable quantum yield is $\Phi_{\mathrm{max,ach}} = 1$.

We have designed PBGs using a new concept, wherein one PBG could release two base molecules with one photon. In this case, $\Phi_{\mathrm{max,ach}} = 2$, which would be realized by combining a photochemical process with a thermochemical process in the photodecomposition reaction (Scheme 1). First, the *o*-nitrobenzyloxycarbonyl group of the PBG is photodecomposed to generate an amine and an unstable β-keto acid salt in a decarboxylation reaction. Subsequently, the β-keto acid salt is thermally decomposed by another decarboxylation reaction to liberate another base molecule at room temperature. Not only weak aliphatic amines but also strong organic bases could be chosen to liberate base in the thermochemical process. Whereas PBG **1a** generates two cyclohexylamines, PBG **1b** generates one cyclohexylamine and one TBD.

For the shared acidic part, 3-cyclohexylcarbamoyloxy-3-(4,5-dimethoxy-2-nitrophenyl)propionic acid was synthesized in a 24% total yield via three reaction steps from *tert*-butyl acetate and 6-nitroveratraldehyde as the starting compounds (see Supporting Information). Cyclohexylamine or TBD was simply mixed with the carboxylic acid in THF to precipitate each product, **1a** or **1b**, in 70% or 48% yield, respectively. The one-to-one salt formation was confirmed by ^{1}H NMR and high-resolution mass spectroscopy (HR-MS) measurements.

Carboxylate-type PBGs **1a** and **1b** were dissolved in methanol and in chloroform. The photodecomposition behaviors during 365 nm light irradiation were examined using their methanol solutions (Figure 1). The maximum absorption wavelength, $\lambda_{\max}$, for each PBG was 339 nm. Before UV irradiation, the molar extinction coefficients, ε_{339}, were 5.0 ×



Scheme 1. Mechanism of generation of two base molecules by absorbing one photon from PBGs **1a** and **1b**.

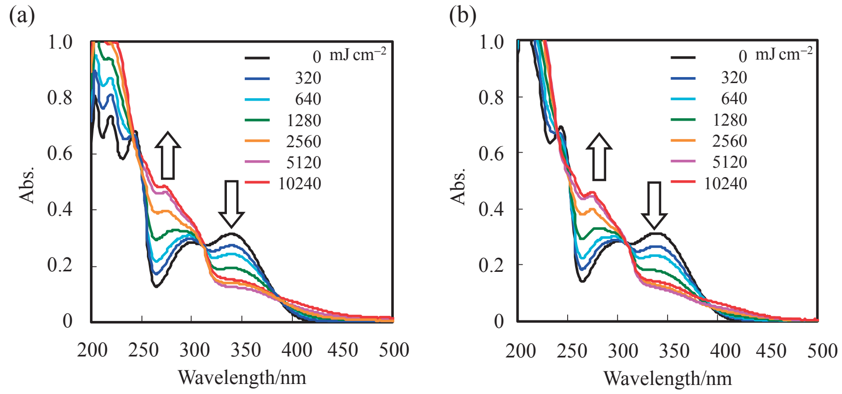


Figure 1. UV–vis spectral changes of **1a** (a) and **1b** (b) in methanol during 365 nm light irradiation. The concentration of PBG was 6.0×10^{-5} mol L^{-1}, in both cases.

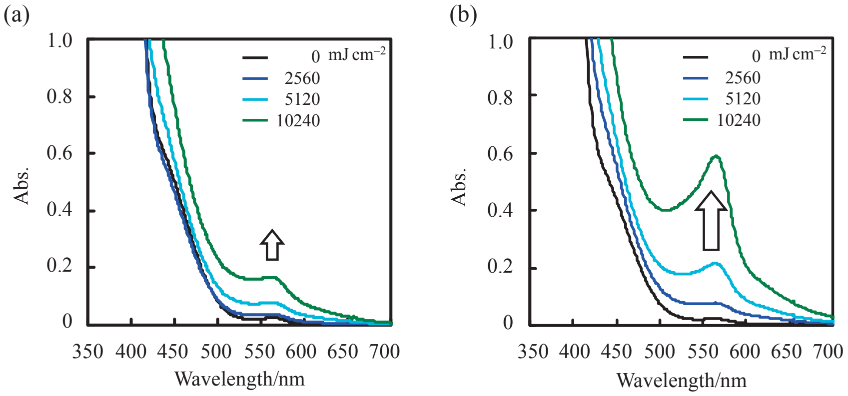


Figure 2. UV–vis spectral changes of **1a** (a) and **1b** (b) with phenol red in methanol during 365 nm light irradiation. The concentrations of PBG and phenol red were 4.4×10^{-3} and 2.4×10^{-5} mol L^{-1}, respectively.

10^3 L mol^{-1} cm^{-1} for **1a** and 5.7×10^3 L mol^{-1} cm^{-1} for **1b**. In each case, a spectral change was clearly observed during UV irradiation. The absorption peak at 339 nm decreased, indicating a smooth photodecomposition. The isosbestic points were observed at 310 and 390 nm. These spectral changes would result from the decomposition of the carboxylate part of the PBGs.

Generation of basic species from PBGs **1a** and **1b** was examined using their methanol solutions containing phenol red as an indicator.[13] In both cases, with 365 nm light irradiation, a new absorption peak appeared at 562 nm, indicating an increase in the basicity (Figure 2). The peak intensity with **1b** was much larger than with **1a**. This is probably because superbases (TBDs) are generated during the thermal decomposition of **1b**, while only weak bases (cyclohexylamines) are generated in the case of **1a**. It is noteworthy that, in both cases, no basicity was detected without UV irradiation.

The photodecomposition behavior of PBG **1a** in a polystyrene (PSt) film was also examined with FT-IR (Figure 3a). During 365 nm light irradiation, the intensities of the peaks at 1520 cm^{-1} (assigned to nitro groups), 1720 cm^{-1} (carbamates), and 1390 cm^{-1} (carboxylates) were decreased, indicating the photodecomposition of **1a**. Each of the peaks was decreased at about the same rate (Figures 3b and 3c). This is probably because the decarboxylation of β-keto acid salts in the thermochemical process follows the photochemical process. On the other hand, the peak appeared at 1480 cm^{-1} was assigned to the nitroso groups of the corresponding by-products.

PBG **1a** was applied to an anionic UV curing system of poly(glycidyl methacrylate) (PGMA, $M_w = 12000$, $M_w/M_n = 1.5$). The generated primary amines reacted with the epoxy groups of PGMA, resulting in the formation of crosslinking sites and causing insolubilization. The PGMA film containing 5 mol % of **1a** (toward epoxy groups of PGMA) was insolubilized with at least 400 mJ cm^{-2} of irradiation (Figure 4). On the other hand, in the case of a conventional PBG **2** (10 mol % toward the epoxy groups of PGMA), the PGMA films were not insolubilized, even after 10000 mJ cm^{-2} of irradiation. Indeed, the generation of two bases by absorbing one photon would contribute to a much higher photosensitivity of the PGMA films containing **1a** than of films containing **2** that photodecomposes into one base by absorbing one photon.

In conclusion, carboxylate-type PBGs **1a** and **1b** were designed and synthesized: they could liberate two base molecules with one photon by combining a photochemical process with a thermochemical process. Their smooth photodecomposi-

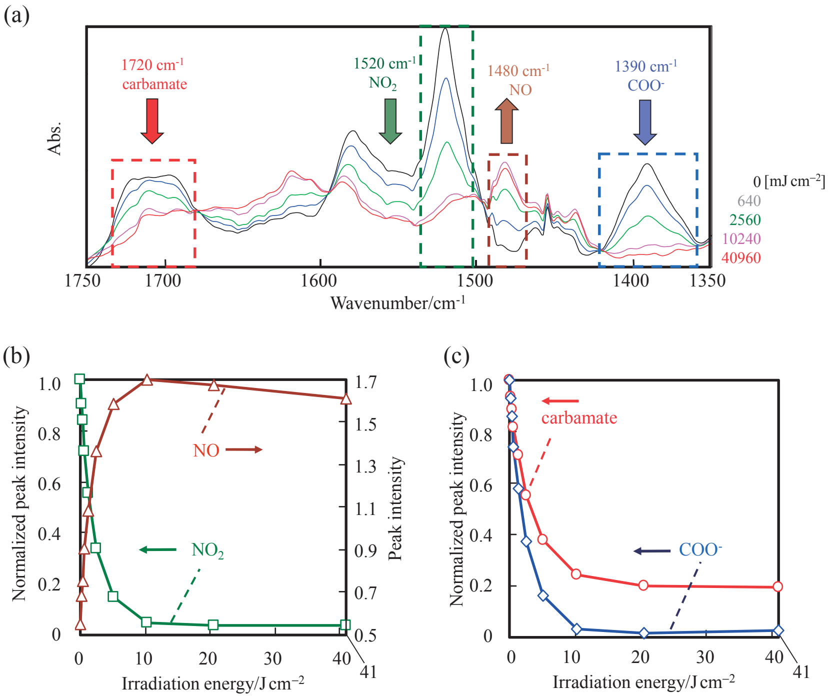


Figure 3. (a) FT-IR spectral changes of **1a** in PSt during 365 nm light irradiation. (b) Consumption of nitro groups (1520 cm^{-1}) and generation of nitroso groups (1480 cm^{-1}) during UV irradiation. (c) Consumption of carbamates (1720 cm^{-1}) and carboxylates (1390 cm^{-1}) during UV irradiation.

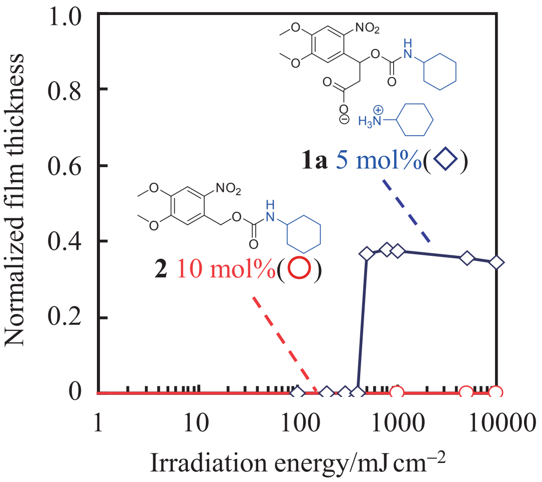


Figure 4. Photosensitivity curves of PGMA films containing 5 mol % of **1a** (◇) and 10 mol % of **2** (○) after heating at 80 °C for 15 min.

tion and generation of basic species were confirmed in a solution and a polymer matrix. The photosensitivity of PGMA films containing the PBG designed in this study was much better than that of films containing the corresponding amount of a conventional PBG. This result is encouraging and may improve the photosensitivity of other base-reactive polymers.

Supporting Information is available electronically on J-STAGE.

References

1 T. Scherzer, U. Decker, *Vib. Spectrosc.* **1999**, *19*, 385.
2 S. Sepeur, N. Kunze, B. Werner, H. Schmidt, *Thin Solid Films* **1999**, *351*, 216.
3 T. Scherzer, A. Tauber, R. Mehnert, *Vib. Spectrosc.* **2002**, *29*, 125.
4 S. K. Weit, C. Kutal, R. D. Allen, *Chem. Mater.* **1992**, *4*, 453.
5 K. Ito, Y. Shigeru, Y. Kawata, K. Ito, M. Tsunooka, *Can. J. Chem.* **1995**, *73*, 1924.
6 J. F. Cameron, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4303.
7 J. F. Cameron, J. M. J. Fréchet, *J. Photochem. Photobiol., A* **1991**, *59*, 105.
8 J. F. Cameron, C. G. Willson, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1996**, *118*, 12925.
9 K. Arimitsu, K. Fukuda, N. Sakai, *Chem. Lett.* **2014**, *43*, 831.
10 a) N. Ishikawa, K. Arimitsu, T. Gunji, Y. Abe, *Chem. Lett.* **2014**, *43*, 612. b) N. Ishikawa, K. Arimitsu, M. Furutani, T. Gunji, Y. Abe, *J. Photopolym. Sci. Technol.* **2014**, *27*, 223.
11 K. Arimitsu, A. Oguri, M. Furutani, *Mater. Lett.* **2015**, *140*, 92.
12 X. Sun, J. P. Gao, Z. Y. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 8130.
13 K. Suyama, H. Araki, M. Shirai, *J. Photopolym. Sci. Technol.* **2006**, *19*, 81.
14 a) K. Arimitsu, A. Kushima, R. Endo, *J. Photopolym. Sci. Technol.* **2009**, *22*, 663. b) K. Arimitsu, R. Endo, *J. Photopolym. Sci. Technol.* **2010**, *23*, 135.
15 K. Arimitsu, R. Endo, *Chem. Mater.* **2013**, *25*, 4461.