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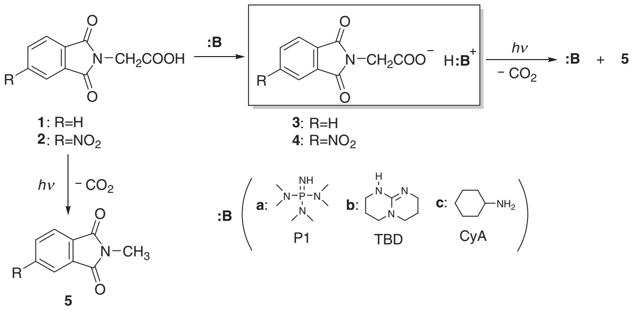
Photochemical Generation of Superbases from Carboxylates Consisting of Phthalimidoacetic Acid Derivatives and Superbases

Koji Arimitsu,*[1] Ken Fukuda,[1] and Nobuhiko Sakai[2]
[1]*Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510*
[2]*Specialty Chemicals Division, Wako Pure Chemical Industries, Ltd., 1633 Matoba, Kawagoe, Saitama 350-1101*

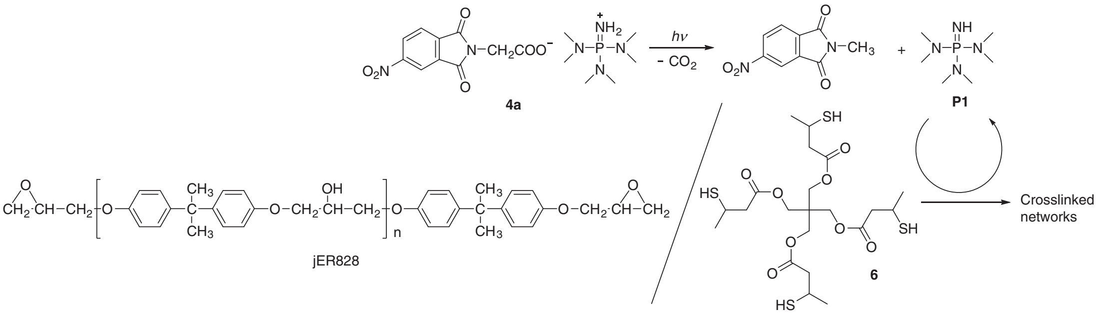
(E-mail: arimitsu@rs.noda.tus.ac.jp)

We have developed simple and powerful photobase generators capable of highly efficient production of superbases. These photobase generators were prepared by simply mixing phthalimidoacetic acid derivatives with the corresponding superbases. The use of photobase generators enabled anionic UV curing at lower temperatures, in contrast to previous anionic UV curing materials that required heat treatment above 150 °C after UV irradiation. The cured films showed no volume shrinkage.

A large number of investigations concerning photoreactive materials utilizing acid-catalyzed reactions, such as chemically amplified photoresists[1] and cationic UV curing materials,[2] have been reported. On the other hand, only a few articles have described analogous systems. This is probably due to the relatively low quantum yields for photobase generation and the weaker basicity of photogenerated bases, leading to low photosensitivity of photoreactive materials doped with photobase generators. Moreover, many of the photobase generators reported are generally prepared via several synthetic steps.[3–12] Recently, Sun et al. reported bicyclic guanidinium tetraphenylborate as a novel photobase generator to generate a strong base, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).[13] The quantum yield of the tetraphenylborate ($\Phi_{254} = 0.18$) is not very high, although the tetraphenylborate is an attractive photobase generator. Lately, we have proposed novel photobase generators based on photodecarboxylation reactions as more powerful and simple photobase generators for the first time.[14] Concretely, carboxylates comprising a superbase and ketoprofen or xanthoneacetic acid, which undergoes photodecarboxylation reactions with high quantum yields, $\Phi_{313} = 0.75$[15] or $\Phi_{350} = 0.64$,[16] respectively, upon UV irradiation. Furthermore, we have applied the photobase generators to anionic UV curing materials, leading to highly sensitive UV curing systems without postexposure baking.[14c] On the other hand, it is well-known that *N*-phthaloyl-α-amino acids such as phthalimidoacetic acid (**1**) also undergo photodecarboxylation reactions to form *N*-methylphthalimide (**5**) with high efficiency.[17,18] Therefore, we designed novel photobase generators **3** that can be prepared by simply mixing **1** with the corresponding base molecule, imino-tris(dimethylamino)phosphorane (P1), TBD, or cyclohexylamine (CyA) (Scheme 1). According to this concept, we can prepare a variety of photobase generators **3a**, **3b**, and **3c** that photochemically generate superbases, as well as aliphatic amines. Although **1** offers many advantages, it has one limitation, which stems from the poor absorption above 300 nm. We have designed substituted phthalimidoacetic acid **2** by nitration, which shows much better absorption above 300 nm. Therefore, we designed novel photobase generators **4** as well as **3**. Our primary concern in this paper is to demonstrate the photochemical generation of superbases from carboxylates **3** and **4** and to show that a novel anionic UV-curing system is realized by the combination of **4a** with an epoxy–thiol formulation[19,20] comprising epoxy resin jER828 and thiol monomer **6** (Scheme 2).



Scheme 1. Photochemical generation of organic bases from photobase generators **3** and **4**.



Scheme 2. Application of **4a** to anionic UV-curing systems.

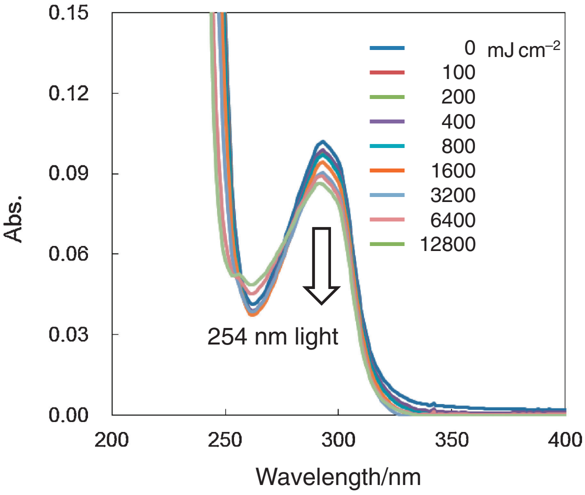


Figure 1. UV spectral changes of **3a** (4.0×10^{-5} mol L^{-1}) in methanol following 254-nm-light irradiation.

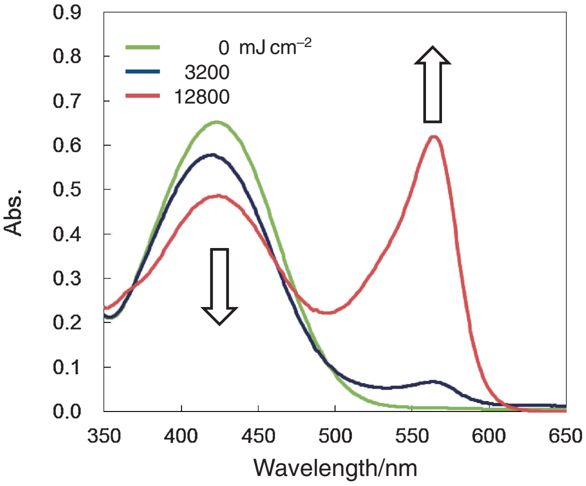


Figure 2. UV–vis spectral changes of phenol red solution upon addition of a solution of **3a** being irradiated as a function of irradiation dose.

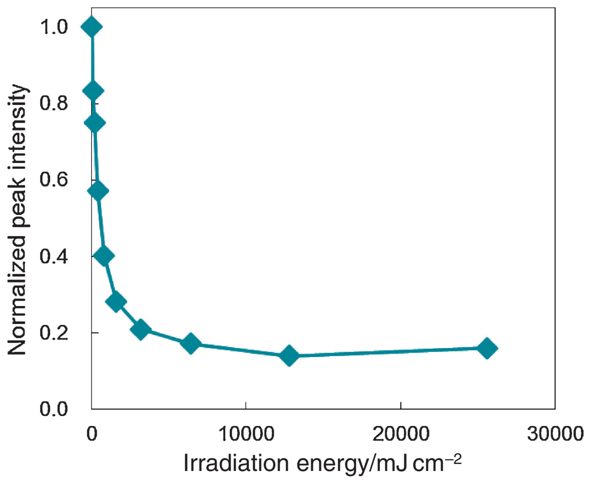


Figure 3. Power dependence for the consumption of the carboxylate of **4a** in a polystyrene film during 365-nm-light irradiation.

Salts **3** (or **4**) were prepared by mixing **1** (or **2**) and a strong base (P1 and TBD) in organic solvents at room temperature. The photodecomposition of **3** in methanol and **4a** in $CHCl_3$ was investigated by UV–vis absorption spectral measurements when **3** and **4a** were irradiated with 254- and 365-nm light from a Hg–Xe lamp, respectively. The absorption band at λ_{max} decreased slightly when **3a** in methanol was irradiated with 254-nm light (Figure 1). This result suggests that the photodecarboxylation of **3a** proceeded in methanol. The photobase-generating ability of **3a** was confirmed by using phenol red indicator.[13] Upon the addition of the irradiated methanol solution of **3a** to a methanol solution of phenol red, a new band at 562 nm appeared, which was assigned to the deprotonated phenol red after its reaction with a released base, and the intensity of the band increased with an increase in irradiation energy (Figure 2). These results show that the photoinduced decomposition of **3a** leads to the generation of free bases. A similar behavior was seen for **3b**, **4a**, and **4b**. These results indicate that the photodecarboxylation reactions of **3** and **4** proceeded in solution, leading to the generation of free bases.

A 2.0-µm-thick film of polystyrene containing **4a** was spin-coated on a silicon wafer and irradiated with 365-nm light. The absorption band arising from the carboxylate of **4a** at 1370 cm^{-1} in the FT-IR spectrum decreased after UV irradiation, as shown in Figure 3. This means that the photodecarboxylation of **4a** proceeded smoothly in a polystyrene film. Other carboxylates behaved in a similar manner. In addition, the quantum yield for the photobase generation of **3b** ($\Phi_{254} = 0.20$) in a poly(methyl methacrylate) film was determined.[21] The quantum yield was higher than that of conventional photobase generators generating organic strong bases. These results show that **3** and **4** underwent photodecarboxylation reactions in solution and a polymer matrix upon UV irradiation, leading to the formation of free superbases.

A mixture of jER828 and **6** is expected to be cured in the presence of **4a** upon UV irradiation, owing to the ring-opening addition of thiolate anions to epoxy groups.[19,20] Thiolate anions should be generated by photobase-induced deprotonation reactions of **6**. This anionic UV curing was achieved by exposing the coating films consisting of **4a**, jER828, and **6** to 365-nm light.[22] Figure 4 shows the UV-curing behavior of coating films consisting of jER828, **6**, and a catalytic amount of **4a**. The hardness of the coatings was monitored by the pencil-scratch method based on JIS K5400.[23] The pencil hardness was evaluated by scratching the UV-cured coatings with pencils, and the hardness showed the following trend: 6B (softest), 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, and 9H (hardest). The coating film showed a level of 3H after 365-nm-light irradiation with an exposure dose of 10000 mJ cm^{-2}, followed by heating at 80 °C for 5 min, which is sufficient for practical use. This means that the anionic UV curing material sensitized with **4a** is highly sensitive, taking into account the fact that conventional anionic UV curing materials were cured by heating at 150–200 °C for ca. 1 h after UV irradiation.[24] By contrast, the coating films showed a level lower than 6B when we used **4c**, which generates CyA. This is because the basicity of CyA is too weak to induce deprotonation reactions of thiol monomer **6**.

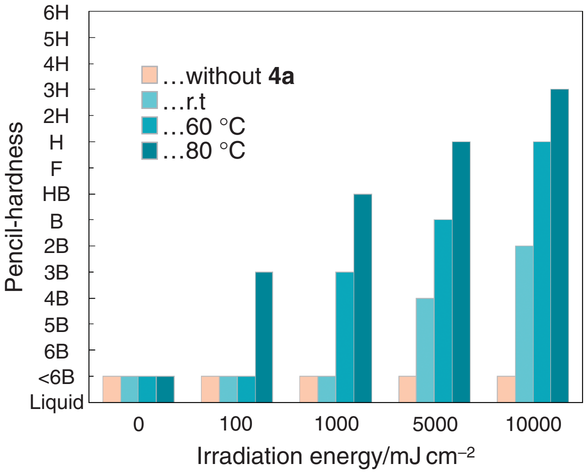


Figure 4. Pencil hardness of coating films comprising jER828 and **6** sensitized with 20 wt % of **4a** (relative to jER828) as a function of irradiation energy from 365-nm light without postexposure baking.

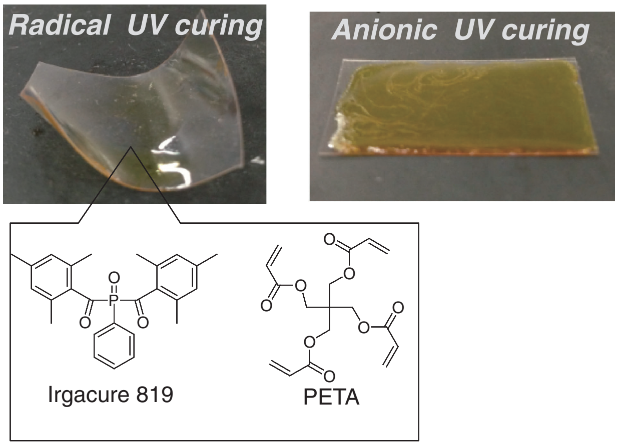


Figure 5. Comparison of volume shrinkage between anionic UV curing and radical UV curing systems.

Radical UV curing materials that are well established in the marketplace have drawbacks because of their high volume shrinkage and oxygen inhibition. Our anionically cured film showed no volume shrinkage, in contrast to a conventional radical UV curing system, which showed large volume shrinkage, as illustrated in Figure 5.[25]

In conclusion, we present novel photobase generators **3** and **4** based on photodecarboxylation reactions. These photobase generators can be easily prepared by mixing **1** or **2** with the corresponding superbases. We have also developed a novel anionic UV curing system, which consists of an epoxy resin, a thiol monomer, and the photosuperbase generator.[26]

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21 Φ was determined according to the literature.[3]
22 A UV-curable resin solution was prepared by dissolving 0.10 g of jER828 (Weight per epoxy equivalent is 184–194), 0.060 g of **6**, and 0.020 g of **4a** (20 wt % relative to jER828) in CHCl$_3$. The solution was coated on glass plates and prebaked at 80 °C on a hot stage for 30 s to give a liquid film. UV curing was achieved by exposing the films to 365 nm light. The pencil hardness of the films was evaluated by scratching UV-cured coatings with pencils according to JIS K5400. Thickness of the cured film was 1.8 µm.
23 JIS K5400 defined by Japanese Industrial Standards is a simple method to test the scratch hardness of coatings. In this test, pencils in a range of 6B to 9H hardness grade are used. The pencil is moved scratching over the surface of the coating at a 45° angle with a constant pressure.
24 On comparison, a coating film consisting of jER828, **6**, and **4c** which generates a weak base, which is a model of conventional anionic UV curing materials, showed a level of H after 365-nm-light irradiation with an exposure dose of 10000 mJ cm^{-2} followed by heating at 150 °C for 1 h.
25 An anionic UV-curable resin solution was prepared by dissolving 0.10 g of jER828, 0.060 g of **6**, and **4a** (20 wt % relative to jER828) in acetone. The solution was coated on an OHP sheet and prebaked at 80 °C on a hot stage for 30 s to give 7 µm-thick film. UV curing was achieved by exposing the film to 365-nm-light (1 J cm^{-2}). A radical UV-curable resin solution was prepared by dissolving 0.1 g of PETA and 5 wt % of Irgacure 819 in acetone. UV curing was achieved in a similar manner. Thickness of the cured film was 2.2 µm.
26 Experimental methods and preparation of photobase generators. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.