Photochemical generation of superbases and its application to photoreactive materials

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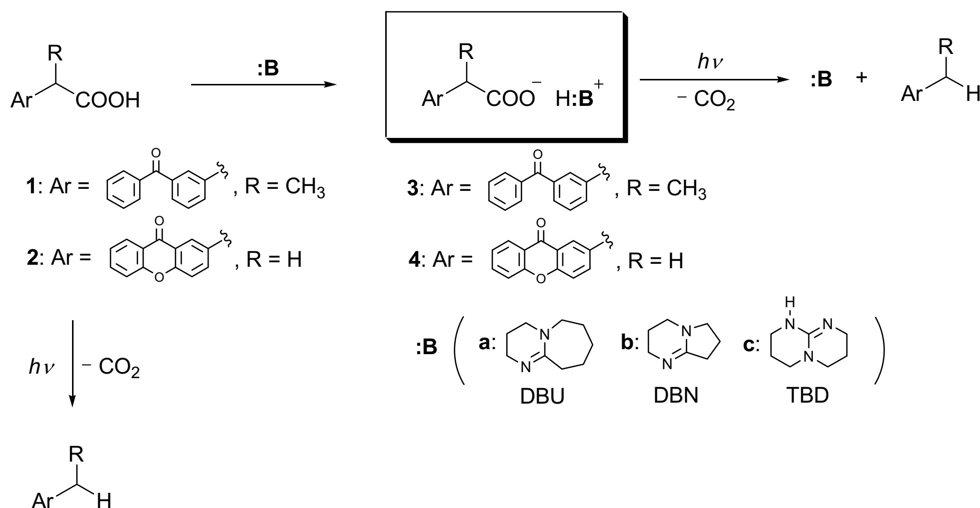
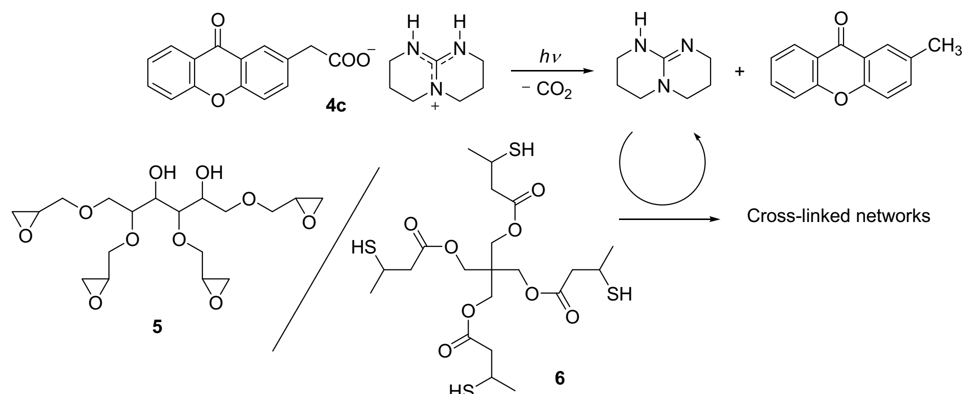
Introduction

Only a few articles have mentioned photoreactive materials relying on base-catalyzed transformations although a large number of investigations concerning analogous systems utilizing acid-catalyzed reactions such as chemically amplified photoresists[1] and cationic UV-curing materials[2] have been reported. This is probably due to relatively low quantum yields for photobase generation and weaker basicity of photogenerated bases, leading to low photosensitivity of photoreactive materials sensitized with photobase generators. Furthermore, many of the photobase generators reported are generally prepared via several synthetic steps.[3-5] On the other hand, it is well known that ketoprofen (**1**) and xanthone acetic acid (**2**) undergo photodecarboxylation reactions with high quantum yields (Φ=0.75 for **1**, Φ=0.64 for **2**) upon UV-irradiation (Scheme 1).[6, 7] If a salt comprising ketoprofen (**1**) (or xanthone acetic acid (**2**)) and a base molecule could undergo photodecarboxylation reaction, a free base should be produced with high efficiency. This idea led us to carry out the molecular design of novel photobase generators, **3** and **4**, which can be simply prepared by mixing ketoprofen (**1**) or



Scheme 1 Photodecarboxylation reactions of **1** and **2** and preparation of photobase generators **3** and **4**.

xanthone acetic acid (**2**) with a corresponding base molecule.[8, 9] If we use a superbase as a base molecule, the photobase generator should release a corresponding superbase. Our primary concern in this paper is to demonstrate photobase generation from salts (**3** and **4**) and to show that a novel anionic UV-curing system without heat treatment is realized by the combination of **4c** with epoxy monomer **5** and thiol monomer **6** (Scheme 2).



Scheme 2 Application of **4c** to anionic UV-curing systems without heat treatment.

Experimental

Photoreaction in solution

Salts **3a** and **4c** (3.0×10^{-5} mol/L) dissolved in methanol were irradiated with 254 nm and 365 nm light from a Hg-Xe lamp, respectively. The solution was subjected to UV spectrum measurement at intervals.

Detection of photogeneration of TBD from 4c by phenol red

A methanol solution containing **4c** (1 mL, 9.0×10^{-3} mol/L) was put into a quartz cell. After the solution in the quartz cell was irradiated with 365 nm light, a methanol solution of phenol red (1 mL, 5.0×10^{-5} mol/L) was added. UV spectra of the methanol solution were measured.

Photoreaction in a polymer film

A solution of 0.1 g of polystyrene in chloroform containing **4c** (20 wt% relative to polystyrene) was spin-coated on a CaF_2 plate and prebaked at 80°C on a hot stage for 1 min to give a film. The film was irradiated with 365 nm light to be subjected to IR absorption spectral measurement.

Application to anionic UV-curing

A UV-curable monomer solution was prepared by dissolving 0.50 g (1.2×10^{-3} mol) of **5**, 0.67 g (1.2×10^{-3} mol) of **6**, and **4c** (10 mol% relative to **5**) in methanol. The solution was coated on glass

plates and prebaked at 60°C on a hot stage for 30 sec to give a film. UV-Curing was achieved by exposing the films to 365 nm light. The pencil-hardness of the film was evaluated by scratching UV-cured coatings with pencils according to JIS K5400. The hardness is arranged in the following order; 6B (softest), 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, and 9H (hardest).

Results and discussion

Photoreaction of 3a and 4c in solution

Photodecomposition of **3a** and **4c** was investigated in methanol. Fig. 1 shows UV spectral changes of **3a** in methanol upon irradiation with 254 nm light. As shown in Fig. 1, the absorption band at longer wavelength side of λ_{max} at 255 nm decreased slightly, and new band appeared at 230 nm. **3b** and **3c** behaved quite similarly. On the other hand, the absorption band of λ_{max} at 240 nm decreased slightly in the case of **4c** as shown in Fig. 2. **4a** and **4b** decomposed in a same way. These suggest

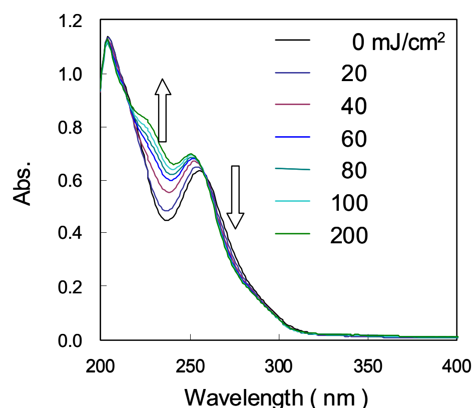


Fig. 1 UV spectral changes of **3a** in methanol during 254 nm light irradiation.

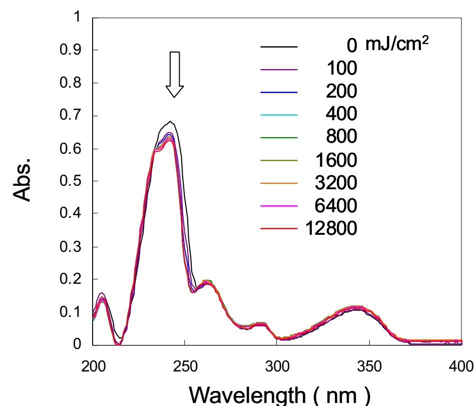


Fig. 2 UV spectral changes of **4c** in methanol during 365 nm light irradiation.

that photodecarboxylation reaction of **3** and **4** proceeded in methanol.

Upon addition of irradiated methanol solution of **4c** to the methanol solution of phenol red, a new band at 560 nm appeared, assigned to the deprotonated phenol red after reaction with released base, and its intensity increased with an increase of irradiation energy (Fig. 3).

These results show that **3** and **4** underwent photodecarboxylation reactions in methanol upon UV-irradiation, leading to the formation of free bases.

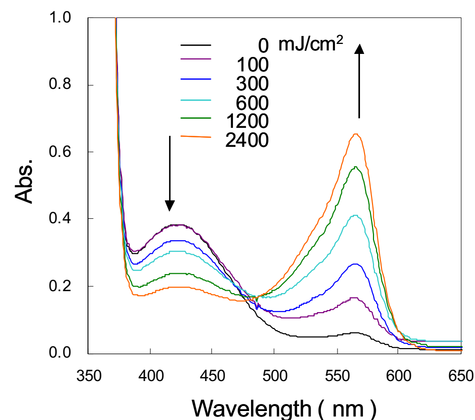


Fig. 3 Changes of UV-Vis spectra of phenol red solution upon addition of a solution of **4c** being irradiated over time.

Photoreaction of 4c in a polymer film

A thin film of polystyrene containing **4c** was spin-coated on a CaF_2 plate and irradiated with 365 nm light. The absorption band due to carboxylate of **4c** at 1372 cm^{-1} in the FT-IR spectrum decreased after UV-irradiation as shown in Fig. 4. This means that photodecarboxylation reaction of **4c** proceeded in a polystyrene film.

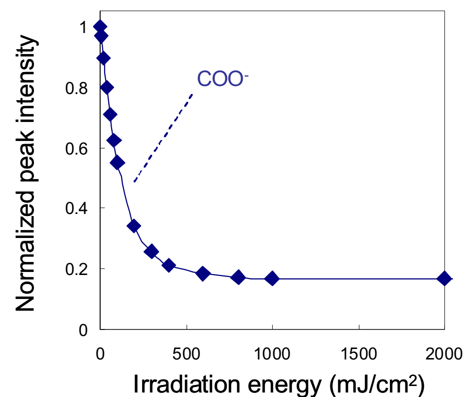


Fig. 4 Time courses of the consumption of **4c** in a film.

Application of 4c to anionic UV-curing

A mixture of **5** and **6** is expected to be cured in the presence of **4c** upon UV-irradiation, owing to the crosslinking reaction of epoxy groups of **5** with thiolate anions which are generated by photobase-induced deprotonation reactions of **6**. Fig. 5 shows UV-curing behavior of coating films consisting of monomers (**5** and **6**) sensitized with **4c**. Surprisingly, the coating film showed a level of 3H after 365 nm light irradiation with an exposure dose of 1000 mJ/cm^2 without post-exposure baking. By contrast, the coating film showed a level lower than 6B when we use **4d** which generates cyclohexylamine. This is because of that basicity of cyclohexylamine is too weak to induce deprotonation reaction of thiol monomer **6**.

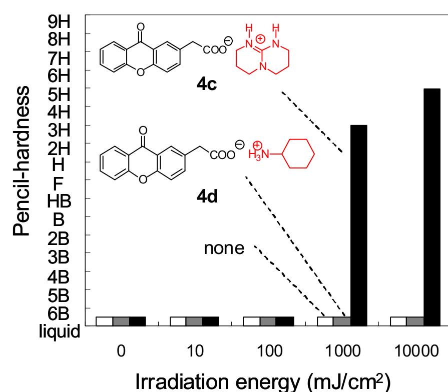


Fig. 5 Pencil-hardness of coating films of monomers (**5** and **6**) sensitized with 10 mol% of **4c** or **4d** as a function of irradiation energy of 365 nm light without post-exposure baking.

Conclusion

We proposed novel photobase generators (**3** and **4**) based on photodecarboxylation reactions. These photobase generators can be easily prepared by mixing ketoprofen (**1**) or xanthone acetic acid (**2**) with a corresponding superbase. We also developed a novel anion UV-curing system without post-exposure baking, which consists of an epoxy monomer, a thiol monomer, and photo-superbase generator **4**.

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