Novel Photobase Generators and Their Application to Photopolymers

Koji Arimitsu*, Ayumu Kushima and Ryosuke Endo

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
arimitsu@rs.noda.tus.ac.jp

Keywords: photobase generator, photodecarboxylation, ketoprofen, amine

1. 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, leading to low photosensitivity of photoreactive materials sensitized with photobase generators. 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) undergoes photodecarboxylation reaction with high quantum yield upon UV-irradiation (Scheme 1).[6] If a salt comprising ketoprofen 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, 2a–2c, which can be simply prepared by mixing ketoprofen (1) with a corresponding base molecule.[7] Our primary concern in this paper is to demonstrate photobase generation from the salt and to show that a novel photopolymer system is realized by the combination of the salt with a base-sensitive resin 3 (Scheme 2).

2. Experimental

2.1. Physical measurement

$^1$H-NMR spectra were measured on a JEOL JNM-ECP500. IR spectra were recorded on a JASCO FT/IR-410. UV absorption spectra were taken on a Shimadzu MultiSpec-1500 spectrophotometer. Photolrradiation was carried out by a San-iei Supercure-203S Hg-Xe lamp.

2.2. Preparation of 2a, 2b, and 2c

A solution of ketoprofen (1) and corresponding amine in appropriate organic solvent were stirred till a precipitate was formed. The
resulting precipitate was separated from the solution by filtration and recrystallized to afford the salt 2a (72% yield), 2b (55% yield), or 2c (74% yield) as yellowish crystals.

2a: M.p.(DSC): 162.5 °C. 1H-NMR (CDCl3): δ (ppm) 0.95-1.14 (m, 5H, CH2), 1.44 (d, J=7.5 Hz, 3H, CH3), 1.52-1.72 (m, 5H, CH2), 2.62 (s, 1H, CH), 3.60 (q, J=7.5 Hz, 2H, N-CH2), 7.32-7.79 (m, 9H, Ar-H).  IR (KBr, cm⁻¹): 3418, 2946, 2862, 1650, 1533, 1390.  UV (CH3OH): ε255 = 16000.  Anal. Found: C, 74.91; H, 7.38; N, 4.86.  Calcd for C33H37N2O3: C, 73.78; H, 7.40; N, 4.86.

2b: M.p.(DSC): 55.3 °C. 1H-NMR (CDCl3): δ (ppm) 1.43 (s, 4H, CH2), 1.49 (d, J=7.5 Hz, 3H, CH3), 1.56 (quint, J=5.5 Hz, 2H, CH2), 2.76 (t, J=8.5 Hz, 4H, NCH2), 3.66 (q, J=7.5 Hz, 1H, Ar-CH), 5.65-7.15 (br, 2H, N'-CH2), 7.34-7.81 (m, 9H, Ar-H).  IR (KBr, cm⁻¹): 3422, 2946, 2862, 1650, 1533, 1390.  UV (CH3OH): ε255 = 17000.  Anal. Found: C, 74.16; H, 7.65; N, 4.06.  Calcd for C32H35N2O3: C, 74.31; H, 7.42; N, 4.13.

2c: M.p.(DSC): 121.5 °C. 1H-NMR (CDCl3): δ (ppm) 1.06 (s, 4H, CH2), 1.25 (s, 4H, CH2), 1.44 (d, J=7.5 Hz, 6H, CH3), 2.57 (s, 4H, NCH2), 3.62 (d, J=7.5 Hz, 2H, CH), 4.21-5.00 (br, 6H, N'-H), 7.23-7.78 (m, 18H, Ar-H).  IR (KBr, cm⁻¹): 3431, 2943, 2946, 2862, 1650, 1533, 1391.  UV (CH3OH): ε355 = 33000.  Anal. Found: C, 72.68; H, 7.32; N, 4.86.  Calcd for C38H40N2O6: C, 73.05; H, 7.10; N, 4.48.

2.3. Photoreaction in solution
Salt 2 (3.1 x 10⁻⁵ mol/L) dissolved in methanol was irradiated with 313 nm light from a Hg-Xe lamp. The solution was subjected to UV spectrum measurement at intervals.

2.4. Photoreaction in a polymer film
A solution of 1.0 g of polystyrene in chloroform containing 2b (3.0 x 10⁻⁵ mol) was spin-coated on a silicon wafer and dried in vacuo at room temperature for 60 min to give ca. 0.85 µm-thick film. The film was irradiated 313 nm light to be subjected to IR absorption spectral measurement.

2.5. Photosensitivity characteristics
A UV-curable resin solution was prepared by dissolving epoxy resin 3 (Mw=3900, Mw/Mn=2.1) and 2 (2.6-15 mol% relative to 3) in ethanol. The solution was coated on glass plates and dried in vacuo at room temperature for 60 min to give ca. 0.6 µm-thick films. UV-curing was achieved by exposing the films to 313 nm light, followed by post-exposure baking (PEB) at 100 °C for 30 min. 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).

3. Results and discussion
3.1. Photoreaction of 2a and 2b in solution
Photodecomposition of 2a and 2b was investigated in methanol. Fig. 1 shows UV spectral changes of 2a in methanol upon irradiation with 313 nm light. As shown in Fig. 1, the absorption band at longer wavelength side of λmax at 255 nm decreased slightly, and new band appeared at 230 nm. An isosbectic point exists at ca. 260 nm, indicating that the photoreaction of 2a proceeds through the A-to-B type conversion. This suggests that photodecarboxylation reaction of 2a proceeded in methanol. Photoinduced decomposition behavior of 2b was similar to 2a. Gas chromatography revealed that 2b in methanol irradiated with 313 nm light contained free piperidine. These results show that 2a or 2b underwent photodecarboxylation reactions in methanol upon UV-irradiation, leading to the formation of free amine molecules.

3.2. Photoreaction of 2b in a polymer film
A thin film of polystyrene containing 2b was spin-coated on a silicon wafer and irradiated with 313 nm light. The absorption band due to carboxylate of 2b at 1390 cm⁻¹ in the FT-IR
spectrum decreased after UV-irradiation. This means that photodecarboxylation reaction of \(2b\) proceeded in a polystyrene film. Furthermore, decrease of the absorption band due to carbonyl groups of benzophenone structure was observed. This is probably because of that hydrogen abstraction reaction was caused by UV-irradiation.

3.3. Photosensitivity characteristics

Base-sensitive resin 3 is expected to be cured in the presence of 2 upon UV-irradiation and subsequent heating, owing to the crosslinking reaction of epoxy groups of 3 with the photogenerated amine and the crosslinking reaction based on the base-catalyzed condensation reactions of residual alkoxysilyl units of 3.

Fig. 2 shows UV-curing behavior of coating films of 3 sensitized with \(2a\). A cured film doped with \(2a\) showed a level of F after 313 nm-light irradiation with an exposure dose of 20 J/cm\(^2\) without PEB. This suggests that UV-irradiation to the coating film of 3 doped with \(2a\) led to the formation of cyclohexylamine which induced the crosslinking reactions of resin 3. Furthermore, a cured film doped with \(2a\) revealed a level of 4H after 313 nm-light irradiation with an exposure dose of 8 J/cm\(^2\) when an exposed film was heated at 100 °C for 30 min. This is due to the enhancement of photobase-induced crosslinking reactions by heat treatment. These results are landmark events because curing efficiency of anion UV-curing systems are generally thought to be very low.

UV-Curing of 3 was more efficient when we used \(2c\) to lead to the generation of diamines which can act as effective crosslinkers toward epoxy groups of 3. Fig. 3 exhibits UV-curing behavior of coating films of 3 sensitized with \(2c\). A cured film doped with 15 mol% of \(2c\) showed a level of 2H after 313 nm-light irradiation with an exposure dose of 16 J/cm\(^2\) without PEB, although a coating film was not cured in the presence of 2.6 mol% of \(2c\).

4. Conclusion

We proposed novel photobase generators (\(2a\)–\(2c\)) based on photodecarboxylation reactions. These photobase generators can be easily prepared by mixing ketoprofen (1) with a corresponding amine. We also demonstrated that anion UV-curing was achieved by exposing coating films of resin 3 doped with 2 to 313 nm light without PEB.

References