Application of Novel Base Amplifiers with 3-Nitropentan-2-yl Group to UV-Curing Materials

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We reported that the addition of base amplifiers to photobase-sensitive materials such as photoresists and UV-curing materials resulted in the marked improvement of photosensitivity.[1–4] The base amplifiers reported so far have aromatic rings such as fluorenylmethyl groups[1–3] and phenylsulfonyl groups[4]. Higher loadings of these base amplifiers are restricted owing to their strong absorption of UV light which is a trigger of photolysis of PBG. This leads to reducing efficiencies of photodecomposition of PBG. Consequently, our primary concern in this communication is with providing novel base amplifiers which have no aromatic rings, giving to relatively low absorption coefficient in the region of UV. We report here novel base amplifiers with 3-nitropentan-2-yl groups and their application to UV-curing utilizing base-catalyzed reactions.

We designed 3-nitropentan-2-yl cyclohexylcarbamate (**1**) and 1,3-bis[(((3-nitropentan-2-yl)oxy)carbonyl)aminopropyl]tetramethyldisiloxane (**2**) as base amplifiers (Schemes 1 and 2). Both of them were anticipated to be decomposed autocatalytically to generate newborn base molecules by the action of a base catalyst, leading to the base proliferation reaction. They

were obtained by a conventional method.[5] The carbamate **2** exhibits $\epsilon_{\text{max}}=170 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 280 nm in ethanol. This ϵ_{max} is reduced to *ca.* 1/200 when compared with the carbamate with fluorenylmethyl groups. It was confirmed that **1** is subjected to the base-catalyzed decomposition to generate cyclohexylamine autocatalytically in the presence of a catalytic amount of the amine at 100 °C in a 1,4-dioxane-*d*₈ solution according to Scheme 1. Furthermore, thermal decomposition behavior of **2** was also examined in a polymer film by IR absorption spectral measurements. A solution was prepared by dissolving 0.10 g of polystyrene (PSt), 1,3-bis[(((2-nitro-4,5-dimethoxybenzyl)oxy)carbonyl)aminopropyl]tetramethyldisiloxane (**3**) as PBG (10 wt% relative to PSt), and **2** (20 wt% relative to PSt) in 1 g of chloroform. The solution was cast on silicon wafers and dried in vacuo for 60 min to give thin films of *ca.* 18 μm in thickness. The films were exposed to 365 nm light, followed by heating at 100 °C to be subjected to IR absorption measurements. The intensity of C=O band of **2** in a PSt film with initial UV-irradiation decreased immediately upon heat treatment as given in Fig. 1, supporting the photobase-catalyzed transformation of **2**. On the other hand, **2** in a PSt film without UV-irradiation decomposed abruptly after prolonged heating for 45 min at 100 °C, illustrating an S-shaped conversion curve. These results show clearly that photoinduced base proliferation reaction of **2** proceeds in a PSt film during post-exposure baking (PEB) to generate 1,3-bis(3-aminopropyl)tetramethyldisiloxane (**4**).

To examine the effect of the involvement of

Scheme 1 Base proliferation reaction of **1**.

Fig. 1 Decomposition behavior of 20 wt% of **2** in a PSt film sensitized with 10 wt% of **3** heated at 100 °C without (◆) and with initial 365 nm light irradiation of an exposure dose of 300 mJ/cm² (□).

the base proliferation reaction, **2** was added to UV-curable organic-inorganic hybrids composed of **3** as PBG and a silicone resin tethering 3-glycidoxypopyl groups (**5**) (Scheme 2). We anticipated that the silicone resin **5** sensitized with **3** is cured by UV irradiation and PEB, owing to the crosslinking reaction of epoxy groups with photogenerated amines and base-catalyzed hydrolytic condensation of residual methoxysilyl groups and the base amplifier **2** can accelerate the UV-curing.

A UV-curable resin solution was prepared by dissolving 0.20 g of **5**, **2** (10 wt% relative to **5**) and **3** (5 wt% relative to **5**) in 0.5 g of chloroform. The solution was coated on glass plates and heated at 100 °C for 60 sec to give *ca.* 3 μm-thick films. UV-curing was achieved by exposing the films to 365 nm light of an exposure dose of 300 mJ/cm², followed by PEB at 100 °C. The pencil-hardness 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). The film doped with **2** as a base amplifier was efficiently

Scheme 2 Chemical structures of compounds used in the UV-curing system.

cured, showing a level of F after heating at 100 °C for 120 min as given in Fig. 2. On the other hand, the film was too soft to evaluate the pencil-hardness in the absence of **2**. These results support that the enhancement of UV-curing efficiency arises from the base proliferation reaction of **2** to form diamine **4** which acts as an effective crosslinker for epoxy groups and a catalyst for base-catalyzed hydrolytic condensation of **5**.

Fig. 2 Pencil-hardness of coating films of **5** containing 5 wt% of **3** as PBG heated at 100 °C after 365 nm light irradiation of an exposure dose of 300 mJ/cm² in the absence (□) and in the presence of 10 wt% of **2** (◆).

In conclusion, we developed novel base amplifiers with 3-nitropentan-2-yl group. Base-catalyzed decomposition of the base amplifiers proceeds nonlinearly in a solution and a polymer film. The addition of the base amplifier to UV-curing materials relying on base-catalyzed reactions resulted in the enhancement of curing efficiency.

References

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