Base Generation by the Photolysis of an Amineimide with Triplet-sensitizers and Its Use for an Epoxide/Thiol Curing System

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Sensitized base generation from an amineimide is achieved by using triplet-sensitizers having a triplet energy of more than $289 \, kJ \cdot mol^{-1}$, which enables the lower temperature curing of an epoxide/thiol system with a low UV dose.

Epoxide curing systems combined with photobase generators (PBGs) which produce bases by UV irradiation have been reported in the last decade.[1] Since bases play a role as nucleophilic catalysts, this system has the potential to lower the curing temperature of epoxides with thiol, phenol, and carboxylic acids. Recently, we have found that amineimides generate a base via photolysis that promotes the thermal curing of epoxide with thiol.[2,3] Most of the PBGs including amineimides, however, absorb only the light less than 320 nm; hence, it is difficult to produce a base with commonly used light source such as a medium-pressure mercury lamp which has strong emission between 365 and 436 nm. As an example, Figure 1 shows the absorption spectra of 1,1-dimethyl-1-(2-hydroxy-3-phenoxypropyl)amine *p*-cyanobenzimide **1** and the thermal curing behavior of epoxide/thiol with 0.3 mol% of **1** after UV irradiation.[4]
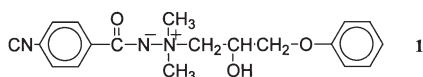
Since **1** has poor absorption in the region longer than 320 nm (Figure 1(a)), the photochemical efficiency of base generation from **1** was predicted to be quite low. In fact, a UV dose more than $3 \, J \cdot cm^{-2}$ is needed to cure epoxide with thiol at lower temperatures (Figure 1(b)). In order to obtain effective photobase generation from **1** with low UV dose less than $1 \, J \cdot cm^{-2}$, we focused on the photosensitized decomposition of **1** with the triplet-sensitizers **2a–h**. This communication reports the

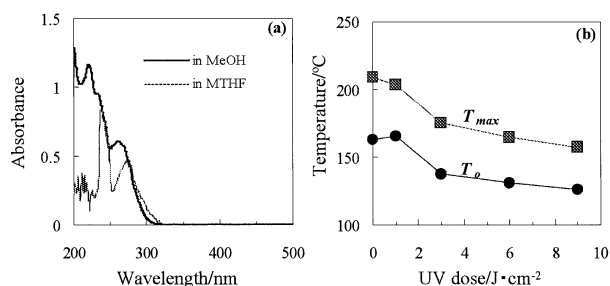base generation from **1** sensitized with **2a–h** and the thermal curing behavior of epoxide with thiol using the base.
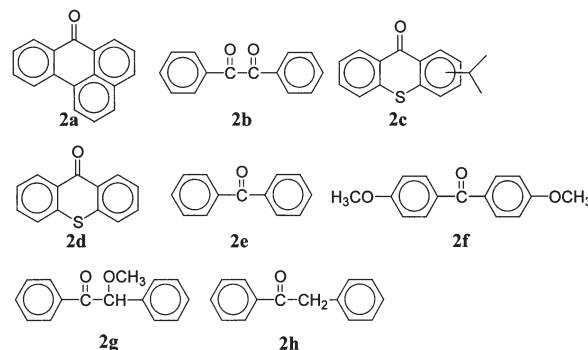

Figure 2 shows phosphorescence and excitation spectra of **1** in 2-methyltetrahydrofurane (MTHF) at 77 K. It exhibited strong phosphorescence between 360 and 600 nm with the phosphorescence lifetime of 0.97 s. Since the lifetime is relatively long, the triplet state of **1** is specified as $\pi\text{-}\pi^*$ state. The lowest triplet energy E_T^1 of **1**, also, was determined to be $289 \, kJ \cdot mol^{-1}$.
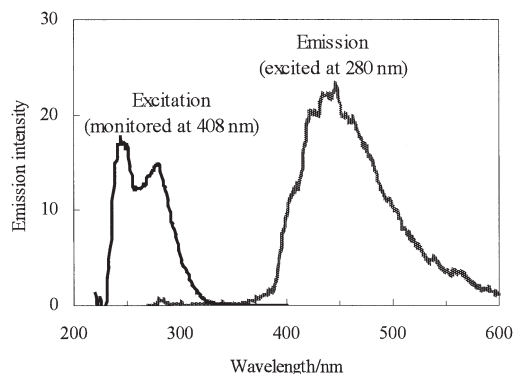

Figure 2. Phosphoresence and excitation spectra of **1** ($6.2 \times 10^{-5} \, mol \cdot L^{-1}$) in 2-methyltetrahydrofurane at 77 K.

In a previous paper, we reported that amineimides gave the corresponding benzamide and base via photolysis.[3] On the basis of the result, the conversion of photolysis of **1** with triplet-sensitizers in 2-propanol was determined by GC-MS (Table 1). It is clear that the photolysis of **1** is promoted by using **2e** and **2h** that have a lowest triplet energy E_T^S of more than $289 \, kJ \cdot mol^{-1}$. Taking account of E_T^1 ($289 \, kJ \cdot mol^{-1}$), we can conclude that the behavior well agrees with the classical theory of energy transfer.[6]

Since some triplet-sensitizers promoted the photolysis of **1**,

Figure 1. (a) Absorption spectra of **1** ($6.2 \times 10^{-5} \, mol \cdot L^{-1}$) in methanol and 2-methyltetrahydrofurane. (b) Curing temperatures of epoxide/thiol with **1** (0.3 mol%) after UV irradiation. ●: onset temperature T_o, ■: maximum exothermic temperature T_{max}.

Table 1. Conversion of photolysis Φ for **1** (3×10^{-4} M) in the presence of triplet-sensitizers (2×10^{-4} M) in 2-propanol after UV irradiation if $1 \, \text{J} \cdot \text{cm}^{-2}$

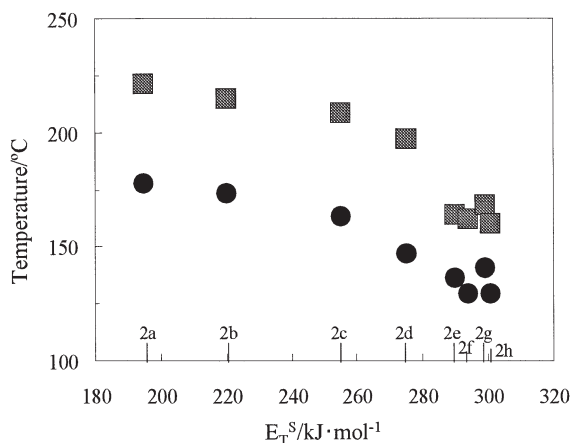| triplet-sensitizer	$E_T{}^S/\text{kJ} \cdot \text{mol}^{-1a}$	$\Phi/\%^b$
none	—	15
2b	220	6
2c	255	12
2e	289	27
2f	294	37

[a]Cited from Ref. 5. [b]Measured by GC-MS

Figure 3. Relationship between the triplet-energies $E_T{}^S$ of the triplet-sensitizers combined with **1** and the curing temperatures of epoxide/thiol system after UV irradiation of $1 \, \text{J} \cdot \text{cm}^{-2}$. ●: T_o, ■: T_{max}.

it was of interest to see whether the curing of epoxide with thiol could proceed at lower temperatures after UV irradiation. Figure 3 depicts a plot of the onset temperature T_o and the maximum exothermic temperature T_{max} versus $E_T{}^S$ of the triplet-

sensitizers added. It is clear that the systems with **2e**–**2h**, which have the $E_T{}^S$ larger than $E_T{}^1$, resulted in lower T_o and T_{max}. This result indicates that **1** generates a base via triplet-sensitization, and that the curing of epoxide with thiol is accelerated. In a further study, the sensitization mechanism will be studied with laser flash photolysis.

References and Notes
1   a) J. F. Cameron and J. M. J. Frechet, *J. Am. Chem. Soc.*, **113**, 4303 (1991). b) Y. Kaneko, A. M. Saker, and D. C. Neckers, *Chem. Mater.*, **11**, 170 (1999). c) H. Tachi, T. Yamamoto, M. Shirai, and M. Tsunooka, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 1329 (2001).
2   S. Katogi and M. Yusa, *J. Photopolym. Sci. Technol.*, **15**, 35 (2002).
3   S. Katogi and M. Yusa, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 4045 (2002).
4   The curing behaviors were measured by DSC as following: equimolar mixtures of polyglycol diepoxide (D.E.R 736®, Dow Chemical Co., Ltd.) and pentaerythritol tetra(mercaptoacetate) in terms of epoxy and thiol equivalent with 0.3 mol% of **1** and 0.2 mol% of triplet-sensitizers **2a**–**h** were prepared. Samples (2.5 to 3.0 mg) were placed in aluminium DSC pans. After the samples were irradiated at room temperature with a Fusion AEL 1B/M lamp (the light intensity at 365 nm was between 21.4 and 22.7 mW·cm^{-2}). The curing profiles were measured with DSC in air.
5   S. L. Murov, I. Carmichael, and G. L. Hug, in "Handbook of Photochemistry," 2nd ed., Marcel Dekker, Inc. (1993), Sect. 1, p 4.
6   N. J. Turro, in "Mordern Molecular Photochemistry," University Science Books (1991), Chap. 9, p 309.