Photo-Induced Basicity Control of A DBU-Diarylethene Complex

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Photo-irradiation responsible resins have attracted intense interest in research area of photolithographic technology because of their application for semiconductors and organic EL displays. Although photosensitive resins including photoacid generators, which emit acidic moieties by photo-irradiation, have been developed, their utilization are limited because of corrosion of metals and resins due to residual acid. On the other hand, for the fabrication of materials available in long-term, resins containing photobase generators are focused because of prevention of the corrosions. However, there is no example of photobase generator in which strong bases are prepared. For the development of photobase generators, we purposed the investigation of basicity control based on the complexation of photo-isomerization of a diarylethene derivative (BDAE) having boronate ring and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU). Although decomposed products were obtained after UV-irradiation to an open-formed isomer of BDAE probably because of oxidative reaction, it was found that the basicity of a solution of a mixture of BDAE and DBU decreased due to complexation of DBU and phenylboronic acid produced by the decomposition of BDAE.

Keywords: Photobase generator, Diarylethene, Phenylboronate, DBU

1. Introduction

Photosensitive resins are one of the most attractive targets of research in materials science and technology because of their utilities such as organic electronics and semiconductor devices [1]. Among them, materials containing a catalytic amount of photoacid generators, in which photo-induced acidic substances act as catalyst for suitable chemical reactions, have been used for photolithographic technology. In general, sulfonium [2] and iodonium [3] salts are often used as photoacid generators. For example, Ito and co-workers have developed chemically amplified resist where the polarity of the resin was modified by deprotection of a polymer component having a protecting group due to an acid catalyst induced by photo-irradiation [4]. Although photoacid generators are indispensable to development of photolithography, it is difficult to produce materials which are used over the long-term such as thin films and adhesives because of the metal and resin corrosion by residual photo-induced acid. As an alternative substance, photobase generators has an attracted attention. In 1987, its first example was reported [5]. In addition, non-ionic (e.g. primary or secondary amines and imidazole derivatives) [6] and ionic (e.g. tertiary amines) [7] photobase generators have been developed. The advantage of photobase generators are not only to prevent the corrosion of materials but also to inhibit oxidation of materials due to oxygen. However, for the conventional photobase generators, the efficiency of the base generation is low, and it is not achieved to induce a strong base.

On the other hand, photochromic molecules, in which structural changes are induced by photo-irradiation, have been attracted intense interest. As a typical photochromic molecule, diarylethene derivative, which forms two isomers by reversible ring-opening and ring-closing reactions of adjacent
two thiophenyl groups via photo-irradiation with visible and UV lights, respectively, is widely used. In addition, both of isomers exhibit thermal stability in the atmosphere. Previously, using a diarylethene derivative (BDAE) having a central 5-membered boronate ring, it was reported that the Lewis acidity of a boron atom was controlled by the photo-irradiation [8]. In this system, a ring-open form (BDAE-o) shows aromatic stability due to $6\pi$ electron system of the boronate ring, while its aromaticity disappears by the UV light irradiation to form a ring-closed isomer (BDAE-c), and BDAE-c makes complex with pyridine due to the Lewis acidity of the boron atom. Based on the photo-conversion system, we expected that BDAE would be used as the photobase generator to produce a strong base. That is, the neutral BDAE-o are converted by the UV irradiation to BDAE-c, subsequently it forms complex with a strong base. By the visible light irradiation to the complex, the ring-opening reaction occurs, coincidently the strong base is released, which indicates the photobase generator system (Fig. 1). In this research, we used 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) as the strong base, and triethylamine and triethanolamine as normal bases for comparison.

![Fig. 1. Mechanism of the photo-induced basicity control using BDAE.](image)

2. Experimental
2.1. Apparatus
For the UV and visible light irradiations, a high pressure mercury lamp (HLR100T-2) and a xenon lamp (USHIO Optical ModuleX) were used. During the visible light irradiation, a 470 nm cutoff filter was used due to elimination of higher energy light. UV-vis absorption spectroscopy measurements were performed using a V-500 (JASCO Corporation). $^1$H-NMR (400 MHz) spectra were measured on a Bruker UltraShield Plus 400 spectrometer. The spectra were referenced to proton signal of tetramethylsilane (0 ppm) in CDCl$_3$ and benzene-$d_6$.

2.2. Reagents
All commercially available reagents were received from TCI and Wako Pure Chemical Industries, Ltd., and used without further purification. All solvents were distilled and dried over molecular sieves 4A before use.

3. Results and discussion
3.1. Synthesis of BDAE-o
Synthesis of BDAE-o was conducted through the previously reported methods [8,9].

3.2. Ring-closing reaction of BDAE-o
We performed the ring-closing reaction of BDAE-o by the UV light irradiation to form BDAE-c. A THF solution of BDAE-o ($9.6\times10^{-5}$ M) was irradiated with 312 nm light for 10, 20, 30, 60, and 120 sec. Figure 2 shows UV-vis spectra using the solution before and after the UV-irradiation. BDAE-o has no absorption at a visible part, whereas the absorbance at 360 and 535 nm, which are corresponded to the absorption of BDAE-c, increased with the irradiating time. It was considered that BDAE-o was converted to BDAE-c.

![Fig. 2. UV-vis spectra of the THF solution of BDAE-o ($9.6\times10^{-5}$ M) before and after photoirradiation with 312 nm light for 10, 20, 30, 60, and 120 sec.](image)
decreased, coincidently absorption at 450 nm appeared. Because \textbf{BDAE-o} has no absorption in the visible region, it is considered that the absorption observed after the visible light irradiation is attributed to a byproduct decomposed from \textbf{BDAE}.

In order to obtain further information, we performed $^{1}$H-NMR measurements in benzene-$d_{6}$. Enlarged $^{1}$H-NMR spectra of the solution of \textbf{BDAE-o} (6.8×10$^{-3}$ M) before and after the UV light irradiation for 120 sec and 2 h are shown in Figs. 4a, 4b, and 4c, respectively. The signal at 8.22 ppm corresponded to proton (H$_{a}$) at a position of a phenyl group attached to the boron atom was observed before the photo-irradiation, while, after the UV irradiation, signals at 8.28 and 8.13 ppm, which are corresponded to those of phenylboronic acid and \textbf{BDAE-c}, respectively, were observed besides the signal at 8.22 ppm. These are indicated that \textbf{BDAE} was decomposed to phenylboronic acid probably due to oxidative reaction induced by dissolved oxygen, unexpectedly, even in after the UV-irradiation for short time though decomposed product was not detected clearly in UV spectra (Fig. 2). Based on the integration ratios of signals in Figs. 4b and 4c, it was found that the molar ratios of phenylboronic acid and \textbf{BDAE-c} were calculated to be 7% and 6% (for short irradiation time), and 74% and 9% (for long irradiation time), respectively. Unfortunately, another decomposed product which is including the thiophenyl groups was not identified through these experiments.

3.3. Ring-closing reaction of \textbf{BDAE-o} after frozen deaeration treatment

In order to remove the dissolved oxygen, we performed the ring-closing reaction of \textbf{BDAE-o} after frozen deaeration of the solution. The solute concentration of \textbf{BDAE-o} was set to 3.1×10$^{-5}$ M. After the solution was frozen by liquid nitrogen, the system was evacuated with an oil pump. After three times of the frozen deaeration treatment, the UV light with 312 nm was irradiated to the solution for 10, 20, 30, 120, and 600 sec. As shown in Fig. 5, the absorption at ca. 450 nm was observed after the UV-irradiation although the presence of \textbf{BDAE-c} was
found due to the absorption at 360 and 535 nm. Regardless of oxygen, it was revealed that decomposed product was produced by the photo-irradiation.

3.4. Complexation of BDAE and DBU

Although unexpected reaction proceeded by the photo-irradiation to the THF solution of BDAE, we demonstrated the complexation experiments of BDAE with DBU in THF to investigate the possibility of modification of the basicity of the solution. We used a THF solution of a mixture of BDAE-<i>o</i> (1.3×10⁻⁵ M) and DBU (1.3×10⁻⁵ M) with a small amount of phenolphthalein as an indicator for the measurement of absorption spectra (Fig. 6). Before the irradiation, a peak at 565 nm, which is assigned to the absorption of phenolphthalein in basic solution, with a shoulder around 520 nm attributed to BDAE-<i>o</i> was observed (a solid line in Fig. 6). When irradiating the UV light with 312 nm for 4 min, the absorbance at 565 nm decreased (a long broken line in Fig. 6), which is indicated that basicity decreased with the ring-closing reaction. Subsequently, we demonstrated the light irradiation with more than 470 nm for 8, 16, and 24 min. Unexpectedly, further lowering of the absorption at 565 nm was detected. This is indicated that, by the visible light irradiation, no reproduction of basicity of the solution was observed. We considered that it was probably because of the complexation of DBU with phenylboronic acid produced by decomposition of BDAE.

In addition, we investigated the complexation by addition of the DBU solution to the UV-irradiated solution of BDAE-<i>o</i>. We prepared a THF solution of BDAE-<i>o</i> (3.1×10⁻³ M), subsequently the UV light with 312 nm for 2 h was irradiated. Then, a THF solution of DBU (2.7×10⁻³ M) was added. In this case, BTB was used as an indicator because its absorption is different wavelength range from that of BDAE. Before the visible light irradiation, the absorption of BDAE-<i>c</i> was observed around 550 nm although that of decomposed compound was also detected below at 500 nm (a solid line in Fig. 7). Moreover, a weak peak corresponded to BTB was observed at 635 nm, indicating that the solution is basic. When the visible light was irradiated to the solution, both of the absorptions at 550 and 635 nm disappeared as shown in Fig. 7 probably due to the complexation of phenylboronic acid produced by decomposition of BDAE with DBU.

3.5. Complexation of BDAE and DBU after frozen deaeration treatment

Although it was found that BDAE-<i>o</i> was decomposed after the photo-irradiation under the condition without oxygen, we investigated the complexation of BDAE and DBU with the frozen deaeration treatment. We prepared a mixture of BDAE-<i>o</i> (3.1×10⁻⁴ M) and DBU (2.8×10⁻⁴ M) with a small amount of BTB in THF. The frozen deaeration treatment of solution was demonstrated as the same method described in Section 3.3. Figure 8 shows UV spectra of the solution before and after the photo-irradiation. Before the UV-irradiation, a peak at 635 nm, which is assigned to the absorption of BTB in basic solution, was observed, whereas it decreased after the UV light irradiation with 312 nm for 60 sec. However, further lowering of the absorption at 635 nm was detected by the visible light irradiation, which is due to the complex of phenylboronic acid and DBU. It was concluded that, even in the complexation experiment, no effect of
oxygen for releasing the base was observed.

3.6. Investigation of complexation of BDAE and DBU based on $^1$H-NMR experiments

We also performed $^1$H-NMR measurements using a mixed solution of a benzene-$d_6$ solution of BDAE-$o$ (1.3×$10^{-2}$ M) irradiated with 312 nm for 2 h and a non-irradiated benzene-$d_6$ solution of DBU (7.2×$10^{-2}$ M) as shown in Fig. 9a. In Fig. 9b, $^1$H-NMR spectrum of a mixture of phenylboronic acid (4.7×$10^{-2}$ M) and DBU (5.1×$10^{-2}$ M) in benzene-$d_6$ without the photo-irradiation. In these spectra, a signal at 8.42 ppm, which was not observed in Fig. 4, was detected. Moreover, Fig. 9c shows a spectrum of a mixture of BDAE-$o$ and DBU in benzene-$d_6$ without the photo-irradiation. The signal corresponded to BDAE-$o$ at 8.22 ppm was not found, which is indicated that a complex of BDAE-$o$ with DBA was formed in spite of aromatic stabilization of the 5-membered boronate ring in BDAE-$o$. These results suggested that the basicity of the solution decreased probably due to the complexation of DBU with both of BDAE and phenylboronic acid produced by decomposition of BDAE because of the strong basicity of DBU.

3.7. Complexation of BDAE with weak basic amines

Considering the strong basicity of DBU, we investigated the complexation of BDAE with weak basic amines, triethylamine and triethanolamine. We measured $^1$H-NMR spectra using a mixture of a benzene-$d_6$ solution of BDAE-$o$ (1.3×$10^{-2}$ M) irradiated with 312 nm for 2 h and a benzene-$d_6$ solution of triethylamine (8.3×$10^{-2}$ M) or triethanolamine (5.4×$10^{-2}$ M). Figure 10a shows a spectrum using the mixture of BDAE and triethylamine. As is the case with DBU, a broad
peak was observed at 8.42 ppm. This result indicates that triethylamine is also formed a complex with phenylboronic acid. However, because the peak at 8.22 ppm was observed intensity, it was found that a large amount of $\text{BDAE-o}$ was remained. On the other hand, in Fig. 10b for the mixture of $\text{BDAE}$ and triethanolamine, these is no signal at 8.42 ppm, which is indicated that triethanolamine was not complexed with neither $\text{BDAE}$ or phenylboronic acid.

4. Conclusion

In order to develop a photobase generator, we investigated the complexation ability of a diarylethene derivative ($\text{BDAE}$) having a central 5-membered boronate ring, which has two photo-isomers, i.e. ring-open and ring-closed forms, converted reversibly by photo-irradiation, with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) as a strong base. Based on measurements of UV spectra, it was revealed that the basicity of the mixing solution of $\text{BDAE}$ and DBU decreased after both of the UV and visible light irradiation. The measurements of $^1\text{H}$-NMR spectra suggested that the presence of phenylboronic acid which is proceeded by decomposition of $\text{BDAE}$ after the photo-irradiation. That is, we concluded that the reduction of basicity of the solution is primarily due to complexation of phenylboronic acid and DBU, while weak bases, trimethylamine and triethanolamine, did not form complexes positively with $\text{BDAE}$. Although the information on the basicity control of $\text{BDAE}$ solution was obtained from these results, more proper molecular design is necessary for the construction of the photobase generation system.

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