Synthesis and Properties of Highly Sensitive Ether Ring Fused O-Acylloxime Esters as Photoradical Initiator

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High sensitivity of O-acyloxime ester, which is widely used as a photo radical polymerization initiator for color resist, was investigated. Introduction of an ether ring structure to the periphery of oxime was aimed at increasing rigidity of dye scaffold. As a result, the absorption spectrum at i-line (365 nm) became sharp, the absorption efficiency was greatly improved, and the sensitivity was increased by about five times as much as conventional linear type oximes by improving the radical generation quantum yield.

Keywords: Photoradical initiator, O-Acylloxime ester, Carbazole dye, Ether ring-fused structure, i-Line, Radical curing reaction, High sensitivity

1. Introduction

Among nonionic initiators, O-acyloxime based photo-radical polymerization initiators have an absorption spectrum on the long wavelength side and achieve high sensitivity with corresponding UV light [1-4]. In recent years, O-acyloxime ester has been used in fields requiring a fine pattern using a single wavelength, particularly an i-line (365 nm) light source, such as a color resist, making use of its high sensitivity [5,6]. For example, the following 1a and 1b having an alkyl chain at the oxime moiety are generally known and commercially available (Fig. 1). These are typical oxime type initiators having a carbazole or diphenylsulfide as the dye scaffold [7,8].

The photolysis process of O-acyloxime has been described in following Scheme 1 [9-12]. First, one electron transits to a singlet excited state by light absorption, followed by intersystem crossing to the triplet excited state. In the decomposition process from the triplet excited state, biradical formation due to homolytic cleavage of N-O bonds, and decarboxylation of the carboxy radicals generated thereby generate polymerization initiation active carbon radicals.

Scheme 1. Mechanism of O-acyloxime photolytic degradation and radical generation.

In order to increase the photosensitivity of the oxime initiator, it is necessary to make each process more efficient. Specifically, there are the
following three key points, (I) improving light absorption efficiency, (II) improving intersystem crossing efficiency, and (III) improving decomposition quantum efficiency. In this paper, we will describe the improvement of each efficiency of (I) and (III).

In order to improve the light absorption efficiency (I), it is necessary to improve the molar extinction coefficient at i-line (365 nm). Moreover, in order to improve the decomposition quantum efficiency (III), it is important to suppress the process of thermal inactivation, which returns from the excited state to the ground state.

Photoradical initiators 1a and 1b are presumed to have high molecular mobility by the presence of the O-acyloxime ester moiety on the linear alkyl chain. Therefore, in addition to the electron transition from the ground state to the excited state, it was considered that the transition process became complicated by the addition of oscillatory and rotational transition, the absorption spectrum was easy to broaden, and the molar extinction coefficient was not high [13]. Also, the energy in molecules with high molecular mobility is released as heat, and it is easy to achieve heat inactivation.

In order to verify the hypothesis, a rigid ring-fused cyclic structure was introduced around the oxime moiety to design oxime initiators 2a-6a with suppressed molecular mobility (Fig. 2).

2. Experimental

2.1. Synthesis materials and methods

Starting materials, 4-hydroxycarbazole (4-HCB), was purchased from Wako Pure Chemical Ltd. and was used without further purification. A commercially available reagent was used as the organic solvent for the synthesis.

2.2. Synthetic strategy of cyclic oxime 3a

The synthesis scheme of 3a is shown in Scheme 2. 4-Hydroxycarbazole (4-HCB) was alkylated with a hydroxyl group at 4-position and an amino group, and cyclization by intramolecular dehydration condensation of carboxylic acid with strong acid was performed. After the Friedel-Crafts reaction, oxime formation from the ketone was carried out according to a conventional method [14].

2.2.1. Synthesis of 3a-C

4-Hydroxycarbazole (100 g, 0.546 mol) was dissolved in 1 L of acetone. To this solution, potassium carbonate (150.6 g, 1.09 mol) and bromoethyl acetate (100.2 g, 0.600 mol) were simultaneously added, and the resultant mixture was gently refluxed for 5 h. This mixture was crystallized in 2 L of 1N hydrochloric acid and filtered, thereby obtaining 3a-E (134.5 g, 91% yield).

The obtained 3a-E (30 g, 0.114 mol) was dissolved in 200 mL of N-methylpyrrolidone (NMP). To this solution, 85% potassium hydroxide (30.1 g, 0.456 mol) and sodium iodide (20.5 g, 0.137 mol) were added. To this reaction liquid, ethyl bromide (14.9 g, 0.137 mol) was added dropwise, and the mixture was stirred at 50°C for 3 h. The reaction liquid was added by dropping to 1N hydrochloric acid, and a solid was filtered and dried at 40 °C for 5 h, thereby obtaining 3a-D (54% yield).

When 27.0 g of 3a-D thus obtained was dissolved in 270 mL of methanesulfonic acid, the solution changed from a light brown color to a dark brown color. This solution was stirred at 95 °C for 3 h. A solid was crystallized in 1.5 L of distilled water and filtered. The solid is dissolved in 300 mL of NMP and further recrystallized in 1.5 L of distilled water, thereby obtaining 3a-C (yellow powder, 94% yield. \(^1\)H-NMR (300 MHz, DMSO): \(\delta\) 1.34 (t, 3H), 4.54 (q, 2H), 4.99 (s, 2H), 7.33 (t, 1H), 7.38 (d, 1H), 7.52 (t, 1H), 7.57 (d, 1H), 7.77 (d, 1H), 8.11 (d, 1H).
2.2.2. Synthesis of 3a-B

The obtained 3a-C (10.0 g) was added to 200 mL of chlorobenzene, and dissolved at 50°C, thereby forming a clear liquid with an orange color. After aluminum chloride (10.5 g) was added to this solution, and the mixture was stirred for 10 min, o-toluic acid chloride (6.1 g) was added by dropping to the resultant mixture over 10 min. After this solution was heated and stirred at 50°C for 3 h, the solution was added dropwise to 1 L of cool 1 N hydrochloric acid. Then, the water phase was decanted off, 200 mL of hexane was added to the remnants, and the mixture was stirred, thereby precipitating into a brown solid. This solid was leached by filtration, washed with water and methanol, and dried at 50 °C for 5 h, thereby obtaining 3a-B (60% yield). 1H-NMR (300 MHz, DMSO): δ 1.37 (t, 3H), 2.25 (s, 3H), 4.60 (q, 2H), 4.97 (s, 2H), 7.38-7.54 (m, 5H), 7.71 (d, 1H), 7.92 (d, 1H), 7.98 (d, 1H), 8.37 (s, 1H).

2.2.3. Synthesis of 3a-A

In a flask, hydroxylamine hydrochloride (3.9 g, 56 mmol) and sodium acetate (4.6 g, 56 mmol) were placed and dissolved with 25 mL of pure water. To this, a solution of 3a-B (17.3 g, 47 mmol) in 100 mL of NMP was added, and the mixture was heated and stirred at 90 °C for 3 h under a nitrogen atmosphere. After completion of the reaction was confirmed by TLC (Chloroform / MeOH = 20/1), the reaction solution was added dropwise to 1 L of cool 1 N hydrochloric acid. Then, the reaction solution was added dropwise to 1 L of 1 N HCl aqueous solution cooled to 5°C in an ice bath to precipitate a crude product. The crude product was collected by filtration, washed with 200 mL of water, and it was confirmed that the filtrate was neutral. Moreover, it was washed with 100 mL of hexane, and obtained 3a-A ((cis / trans = 80 / 20 mixture), cream yellow solid, 14.8 g, 39 mmol, 82% yield).

2.2.4. Synthesis of 3a

3a-A (3.0 g, 7.8 mmol) was dissolved in 50 ml of pyridine, followed by the addition of triethylamine (1.18 g, 11.7 mmol). After cooling to 0°C, acetyl chloride (0.79 g, 10.1 mmol) was added by dropping over 20 min, followed by increasing the temperature to room temperature and stirring for 2 h. The reaction solution was added by dropping to 150 ml of distilled water having been cooled to 0°C, followed by extraction of the organic layer using ethyl acetate. Then, magnesium sulfate was added to dry the extraction, followed by evaporation of the solvent under reduced pressure. The resultant crystals were washed with 2-propanol and then recrystallized using 2-propanol, thereby obtaining 3a (pale yellow solid, 2.2 g, 66% yield). 1H-NMR (400 MHz, CDCl 3): δ 1.49 (t, 3H, J= 6.8 Hz), 2.26 (s, 3H), 2.36 (s, 3H), 4.43 (q, 2H, J=6.8 Hz), 5.41 (s, 2H), 7.15 (d, 1H, J=7.8 Hz), 7.20-7.50 (m, 5H), 7.92 (d, 1H, J=7.8 Hz), 8.00 (d, 1H, J=7.8 Hz), 8.65 (s, 1H).

2.3. General methods

2.3.1. 1H-NMR spectroscopy

1H-NMR spectra were recorded on a Varian Gemini 2000 (1H at 300.77 MHz). Chemical shifts are expressed in δ ppm referenced against TMS.

2.3.2. UV-Vis spectroscopy

The molar extinction coefficient of a specific oxime compound refers to a value measured at a concentration of 2.41 × 10⁻⁵ mol/L using an ethyl
acetate solvent in a UV-visible spectrophotometer (Cary-5 Varian).

2.4. Molecular orbital calculation

Molecular orbital calculation was carried out by the density functional method (B3LYP/6-31G *) with Gaussian 03 [15]. The excitation energy was calculated by the TD-DFT method (B3LYP/6-31+G**).

2.5. Amount of radical generation

The amount of radicals generated per photon was regarded as the same amount as the decomposition amount of the initiator. The number of photons absorbed by the initiator was estimated from the change amount of the absorption spectrum before and after exposure and the decomposition amount of the initiator was estimated by quantifying the residual amount of initiator by HPLC before and after exposure.

2.6. Method of measuring C=C consumption

Sample preparation: 50 mg (82 μmol) of oxime initiator, 120 mg (520 μmol) of hexanediol diacrylate (HDDA), 1.3 g of 20% propylene glycol monomethyl ether acetate (PGMEA) solution of poly(methylmethacrylate) (PMMA) and 3.6 g of PGMEA was prepared, applied to an SUS plate, and air-dried at 100 °C for 1 min. The thickness of the photosensitive layer at the time of drying was 1 μm.

Exposure and Measurement: Exposure and IR measurement were performed using RealTime-IR (light source Xe lamp (Execure 3000 by HOYA), light amount 18 mW/cm 2 with 365 nm band pass filter, 360 mJ/cm 2 (20 s exposure)) under nitrogen atmosphere. A change in peak area of 1260 cm -1 to 1280 cm-1 identified in C=C in FT-IR(Nicolet 6700 by Thermo Electron) was tracked in real time.

2.7. Exposure sensitivity evaluation using red dye resist

Sample Preparation: 55% of a red dye (Dye-A / Dye-B), 31.4% of multifunctional acrylate monomer and polymer binder, 13.6% of oxime initiator were dissolved in cyclohexanone as a coating solvent to adjust the solid content to 20%. It was coated on a silane coupling treated glass substrate by spin coating and dried at 100 °C for 2 min. The film thickness at the time of drying was about 1 μm.

Exposure and measurement: Under an air atmosphere, the light source selectively transmitted i-line through a 365 nm bandpass filter using a Xenon lamp (Asahi Spectra MAX-301, 300 W) and radiated 100 mJ/cm 2. A scale mask with different light transmittance was used. Alkali development treatment was performed with an aqueous tetramethylammonium hydroxide (TMAH) solution, and the exposure amount of the cured film was read (Fig. 3).

Fig.3. Pattern formed by grayscale mask used.

3. Results and discussion

3.1. Strategy

As a result of estimating the absorption spectrum of 2a by molecular orbital calculation, the three main absorptions bands (A, B, C) attributed to each transition energy, and further absorption on the shorter wavelength side were observed (Fig. 4). In particular, the λmax values of A were very close to the measured absorption spectra of 1a, suggesting the validity of molecular orbital calculation in the oxime initiator having a carbazole dye.

![Fig. 4. Calculated absorption wavelength of 2a.](image)

The absorption on the longest wavelength side attributed to the HOMO-LUMO transition (A) was shown to be mainly an electron transition from the orbital spreading over the carbazole ring of HOMO to the C=N and N-O semi-bonding orbital of LUMO (Fig. 5).
(a) HOMO ground state and (b) LUMO excited state orbital of 2a.

On the other hand, absorption (B) was due to electronic transition from HOMO to LUMO+1 and absorption (C) was due to electronic transition from HOMO-1 to LUMO. From this, it is important to increase the absorption efficiency of absorption (A) on the longest wavelength side, that is, to increase the oscillator strength factor “f value” to enhance the anti-coupling properties of C=N and N-O bonds and efficiently lead to the decomposition process effective for radical generation.

3.2. Prediction of absorption spectrum of cyclic oxime initiators 2a-6a

For each of 1a and cyclic oxime initiators 2a-6a, the wavelength of the absorption (A) on the longest wavelength side attributable to the HOMO-LUMO electron transition and its oscillator strength factor were calculated (Fig. 6). The wavelength of 2a was shorter than that of 1a, but 3a-6a with o-tolyl group introduced thereto were shown to be longer wavelengths. Furthermore, it was inferred that the cyclic structure having an ether bond at the 4-position as shown in 2a, 3a, 4a has high oscillator strength. On the other hand, oscillator strength was decreased in 5a having an ether linkage in the 2-position and 6a having a cyclic structure containing carbazole nitrogen atom.

3.3. Measured absorption spectrum

Cyclic oxime initiators 2a, 3a and 6a [16] were synthesized and absorption spectra were measured. In reference photoinitiator 1a, HOMO-LUMO absorption on the long wavelength side broadened, whereas 2a and 3a condensed with ether ring showed remarkably high absorption and unexpected sharpness were confirmed (Fig. 7).
other hand, in 6a, absorption was low as predicted by molecular orbital calculation, but the expected of sharpest of spectrum was not observed.

The maximum wavelength of 3a was longer by 5 nm than that of 2a. This is probably due to the increase in the conjugation length by the o-tolyl group. The oxime ester 3a is optimum for which (I) improving light absorption efficiency, because the maximum absorption wavelength is 365 nm which coincides with the i-line which is the exposure wavelength and has a very high absorption intensity (Table 1).

Table 1. Values of maximum wavelength \( \lambda_{\text{max}} \) (nm) and molar extinction coefficient \( \varepsilon \) (L mol\(^{-1}\)cm\(^{-1}\)).

|     | \( \lambda_{\text{max}} \) (nm) | \( \varepsilon \) at \( \lambda_{\text{max}} \) (L mol\(^{-1}\)cm\(^{-1}\)) | \( \varepsilon \) at 365 nm (L mol\(^{-1}\)cm\(^{-1}\)) |
|-----|-------------------------------|-----------------------------|------------------------|
| 1a  | 335                           | 19900                       | 1560                   |
| 2a  | 360                           | 30700                       | 7410                   |
| 3a  | 365                           | 29900                       | 29900                  |
| 6a  | 375                           | 9130                        | 7390                   |

As for the absorption characteristics of 3a, high light absorption also occurs in monochromatic light exposure such as a 365 nm LED light source, which has recently been used for its excellent environmental characteristics, hence, likely to obtain high sensitivity.

The \( f \) value obtained by calculation and the measured \( \varepsilon \) at \( \lambda_{\text{max}} \) showed a good correlation (Fig. 8).

![Fig. 8. Relationship between calculated \( f \) value and measured value.](image)

3.4. Efficiency of radical generation

Next, we will describe (III) improving decomposition quantum efficiency as a viewpoint of high sensitivity. As described above, cyclic oxime initiator is considered to have improved molecular rigidity by cyclizing the skeleton around oxime.

Typically, deactivation from the singlet and triplet excited states can be considered as energy relaxation by fluorescence or phosphorescence, and release of excitation energy by thermal vibration of molecules. When the radical generation quantum yield (\( \Phi_r \)) per one photon absorption was measured, no significant difference was observed in the presence or absence of a ring structure in the solution. On the other hand, when the initiator was dispersed in the PMMA film, the radical generation quantum yield of 3a was improved by about 1.4 times (Table 2).

Table 2. Radical generation quantum yield in solution and in polymer film.

|     | \( \Phi_r \) (in AcOEt) | \( \Phi_r \) (in PMMA) |
|-----|-------------------------|-----------------------|
| 1a  | 0.15                    | 0.36                  |
| 3a  | 0.17                    | 0.50                  |

In the solution, in addition to the vibration of the initiator molecules themselves, a shift of the center of gravity with a larger energy occurred easily, so it has been found that there was hardly any difference. The effect of deactivation by molecular thermal oscillation was clarified by comparing in the polymer film constraining the movement of molecules, and it is considered that high radical generation quantum yield was observed in 3a having a cyclic structure.

3.5. C=C bond consumption in model film

In order to evaluate the sensitivity of the synthesized oxime initiators 2a, 3a and 6a, C=C consumption of hexanediol diacrylate (HDDA) in the PMMA film was measured using RT-IR (Fig. 9).

Compared to reference photoinitiator 1a, the C=C consumption rate at the initiation of polymerization using 2a and 6a, was almost equal or lower, and the C=C consumption was small. On the other hand, 3a had a very high polymerization rate of C=C in the initial stage of polymerization, and C=C consumption was even higher. 3a rapidly converted the radicals by the multiplication of the absorption based on the HOMO-LUMO transition to the i-line (365 nm), which took place the absorption efficiency and the radical generating quantum yield were high. This is because it is considered that polymerization reaction could take place efficiently.
3.6. Improvement of solvent solubility

Although the ether cyclic oxime 3a was found to be highly sensitive, there was a problem that its solubility in a coating solvent was too low in order to be incorporated into a practical evaluation system of a color resist. Therefore, we investigated a method of imparting solvent solubility by introducing a ballast group, while keeping a rigid dye moiety intact. The ballast group was introduced into the substituent on carbazole nitrogen atom which does not have the electron orbit of LUMO and does not affect the absorption spectrum, and 3b-3g was synthesized.

Ethyl group such as 3a had high melting point and poor solubility in cyclohexanone, but it was confirmed that the melting point was reduced and solubility was improved by introducing a large branched structure of ballast group (Table 3). Introduction of a hydrophilic functional group such as ether, 3d and 3f, was not sufficient for improving the solubility and introduction of a functional group having a larger steric hindrance was more effective in improving the solubility. In particular, it was found that 3g having 2-ethylhexyl group introduced therein had a low melting point and was completely soluble in cyclohexanone by 15 wt%. Even when the ethyl groups were changed to other alkyl groups, as expected, the absorption spectrum of 3b-3g was almost the same as that of 3a.

3.7. Photosensitivity evaluation using red dye color resist

Evaluation of practical sensitometric sensitivity of dye resist for color filters was carried out using 3a-3g with different substituents on carbazole nitrogen atom. The color resist was matched on the added weight based on the high concentration (13.6% in solid content) of the initiator, and insoluble initiators was removed because the insoluble matter was filtered.

In the ether cyclic oxime initiators 3a-3g synthesized in this experiment, variations in sensitivity were observed. In the case of 3a-3c with low solvent solubility due to the evaluation with a high addition amount of initiators, sufficient sensitivity could not be obtained due to the rest of initiators. On the other hand, for 3f and 3g, which secured solubility at a high concentration, a sensitivity of about 5 times or higher than that of 1a was confirmed (Fig. 10). 3e was insufficient to alkali development treatment in the unexposed area in photosensitivity and did not lead to sensitivity measurement. It is speculated that the initiator 3e has high hydrophobicity due to the alicyclic group.

Likewise, novel oxime 3g was highly soluble in various resist solvents (PGMEA or propylene glycol monomethyl ether (PGME)), and high curability was able to be obtained with a small exposure amount even in other resist applications [18].

Table 3. Solubility of substituent groups at R imparted to cyclohexanone in 15 wt%.

| R              | melting point (°C) | Solubility in Cyclohexanone |
|----------------|--------------------|-----------------------------|
| 3a Ethyl       | 210                | Slightly                    |
| 3b Methyl      | 167                | Insoluble                   |
| 3c Isobutyl    | 197                | Insoluble                   |
| 3d Methoxyethyl| 186                | Slightly                    |
| 3e Cyclohexylmethyl | 213      | Partially                   |
| 3f Tetrahydrofuryl | 154            | Partially                   |
| 3g 2-Ethylhexyl| 84                 | Completely                  |

Fig. 9. C=C consumption ratio of HDDA in 1a, 2a, 3a and 6a by using RT-IR.
4. Conclusion

Improvement of photosensitivity of the O-acyloxime radical initiators was achieved from two viewpoints of (I) improving absorption efficiency (increasing $\varepsilon$ to high) and (III) improving radical generation efficiency. By condensing an ether cyclic structure at the periphery of the oxime moiety, the absorption efficiency of $3a$ at the exposure wavelength of 365 nm reached 20 times and the radical generation efficiency reached 1.4 times the conventional linear type oxime $1a$. The reason for this is due to the molecular vibration of ether ring-fused oxime is suppressed by rigidifying the initiator dye part, sharpness of the absorption spectrum, and the deactivation process by thermal vibration from the excited state are suppressed. 2-Ethylhexyl group is effective as a ballast group connected to the dye, which has lower in solubility reduction due to dye rigidification. Moreover, a novel photoinitiator $3g$ with improved solubility has been found, which has a practical sensitivity 5 times as that for the color resist relative to conventional linear type oxime $1a$.

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