Photopolymerization Analysis by Isomerization for Oxime Derivatives

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Negative photopolymerizing photoresists can be cured in a short time, as compared to thermosetting photoresists, and have advantages in reducing the energy, cost and volatile organic compound (VOC) generated therefore. They are utilized as a curing system for large-size liquid crystal panels, of which sizes are lengths more than 2 m. Therefore, novel photo polymerization initiators, which generate radicals more efficiently, have been investigated. However, compounds which substitute phenyl group in the oxime end have promptly occurred to E/Z-isomerization around C=N bonds. This isomerization remarkably decreases quantum yield of radical production in N-O bond cleavage. The authors investigate the influence to photolithography by the isomeric structure of O-acyloxime ester compounds and the selective synthetic process of isomeric structure. Consequently, a selective isomer synthesis method for E and Z isomers has been established by controlling the reaction temperature. Furthermore, evaluations of the pattern formation using these isomers are performed. The evaluations have revealed that patterns are formed by using the E isomer with lower energy than that required by using the Z isomer.

Keywords: photoresist, resin black matrix, oxime ester, geometrical isomer, EGA

1. Introduction

Negative photopolymerizing photoresists can be cured in a short time, as compared to thermosetting photoresists, and have advantages in reducing the energy, cost and volatile organic compound (VOC) generated therefore. They are utilized as a curing system for large-size liquid crystal panels, of which sizes have lengths more than 2 m.

In the negative photopolymerizing photoresists, it is important to increase the quantum efficiency of the initiator for the pattern imaging in low exposure dose.

It is well known that the O-acyloxime ester compounds can be photodegraded [1-4]. Some compounds with these features have been reported to make efficient polymerizations of acrylate monomers and unsaturated polyesters as components of photopolymer formulations.

Although, they show the issue of thermal unstability which occurs by comparatively weak bond energy of N-O bond.

Some styles have been suggested as initial processes of the photo reaction of O-acyloxime compounds.

Scheme 1 shows the photo cleavage mechanism of N-O bond of acyloximinoketone which has the alkyl group in the terminal of oxime function. This mechanism indicates certification of detecting the N-O radical by electron spin resonance (ESR) analysis [5] in the low temperature.

Scheme 1. Photo cleavage scheme of acyloximinoketone
An iminyl radical and a phenyl carboxyloxy radical, which are primary radical species, clearly show products of a benzoyl radical and a phenyl radical via thermal denitrile and decarboxylation by ESR analysis [6], radical trapping method [7] and the analysis of products by photo cleavage [8]. These acyloximinoketone compounds are very high quantum yield (cf. compound A: Φ = 0.91 [9]). In addition, the radical is generated by photo process which has high reactivity. The result shows good photo polymerization with compounds which have unsaturated bond.

2. Experiment
2.1. General analysis
Thermo gravimetric analysis (TGA) was recorded on a Seiko TG/DTA 6300 at a heating rate of 10 °C/min under an air. UV-visible spectra were recorded on a Shimadzu UV-3600. Evolved Gas Analysis (EGA) was measured on a Frontier Laboratories PY-2020iD. GC-MS analysis was recorded on a Perkin Elmer GC Auto System XL and MS Turbo Gold. 1H-NMR spectra were recorded on a Bruker Avance-600 (600 MHz) using tetramethyl-silane (TMS) as an internal standard.

2.2. Synthesis of compound
Procedures for the synthesis of O-acetyl-1-[6-(2-naphthyl)-9-ethyl-9H-cARBazole-3-yl]-3-(N-acetylamino-N-acetoxy) butanone oxime are shown in Scheme 2. A typical synthetic procedure was described below.

To a mixture of N-ethylcarbazole (5.00 g, 26 mmol), 1-naphthol chloride (5.37 g, 28 mmol) and dichloromethane (50 ml) were added a solution of anhydrous aluminum chloride, and the mixture was stirred at ice-cold condition for 2 hr. To the mixture, (E)-2-butenoyl chloride (2.94 g, 28 mmol) and anhydrous aluminum chloride (3.93 g, 29 mmol) were added, and the mixture was stirred at ice-cold condition for 1 hr. The reaction mixture was poured into ice-cold water (200 ml). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate / hexane) to give 8.55 g of 3-crotonoyl-6-(2-naphtyl) -9-ethyl-9H-cARBazole.

To mixture of Ⅱ (8.00 g, 19 mmol), acidified with 35 % hydrochloric acid (2.93 g, 42 mmol), triethylamine (4.15 g, 41 mmol) was added in a solution of ethanol (70 ml), and the mixture was heated under reflux with stirring for 3 hr. The reaction mixture was concentrated under reduced pressure, and added ethyl acetate and washed with brine (200 ml, 2 times). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give 8.92 g (100%, E-isomer / Z-isomer = 95% / 5%).

To a mixture of Ⅲ (8.00 g, 17 mmol), acetic anhydride (13.33 g, 130 mmol) was added in a solution of acetic acid (10 ml), and the mixture was stirred at 35 °C for 3 hr. The reaction mixture was cooled till room temperature, and was added in a solution of ethyl acetate and washed with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give 8.10 g (60%, E-isomer / Z-isomer = 95 % / 5 %) of 1-[6-(2-naphthyl)-9-ethyl-9H-cARBazole-3-yl]-3-(N-acetylamino-N-acetoxy) butanone oxime.

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1H-NMR (CDCl3, 600 MHz, δ in ppm) 8.64 (1H, d, J = 1.5 Hz), 8.43 (1H, d, J = 1.2 Hz), 8.15 (1H, dd, J = 1.7, 8.2 Hz), 8.06 (1H, dd, J =
1.2, 8.7 Hz), 8.03 (1H, dd, \( J = 1.2, 8.4 \) Hz), 7.96 (1H, dd, \( J = 1.7, 7.5, 8.7 \) Hz), 7.65 (1H, dd, \( J = 1.5, 7.5 \) Hz), 7.59 (1H, dd, \( J = 1.5, 8.4 \) Hz), 7.53 (1H, dd, \( J = 1.5, 7.7, 8.2 \) Hz), 7.52 (1H, dd, \( J = 8.4, 8.7 \) Hz), 7.49 (1H, d, \( J = 8.7 \) Hz), 7.46 (1H, d, \( J = 8.4 \) Hz), 4.89 (1H, br), 4.41 (2H, q, \( J = 7.2 \) Hz), 3.26 (2H, m), 2.31 (3H, s), 2.17 (3H, s), 1.81 (3H, s), 1.45 (3H, t, \( J = 7.2 \) Hz), 1.17 (3H, d, \( J = 6.3 \) Hz).

Scheme 2. Reaction scheme of O-acetyl-1-[6-(2-naphtyl)-9-ethyl-9H-carbazole-3-yl]-3-(N-acetylamino-N-acetoxy)butanone oxime

2.3. Photoresists

Five types of negative-tone photoresists were prepared, named as Sample A, Sample B, Sample C, Sample D and Sample E, respectively. Each photoresists were comprised of fluoren acrylate resin, acylate monomer, photo initiator, mill base contained carbon powder and casting solvent. Sample A, Sample B, Sample C, Sample D and Sample E were formulated with each photo initiator which is Compound B, Compound C, Compound D, Compound E and Compound F.

2.4. Photo imaging

The resist films were prepared on glass wafers at 1.0 μm-1.5 μm film thickness. The pre-bake condition was at 120 °C for 120 s. The photoresists films were exposed to 40 mJ / cm² by a Topcon TM E-150RTQ with i-line. A patterning mask made of a quartz glass was used, in which 40 μm 1 to 1.5 lines and spaces were designed, and in which a matrix pattern around 5 μm line was designed. The development condition was 0.11 M Pa Na₂CO₃ and NaHCO₃ aqueous solution at 25 °C and development time was varied. The post development rinse was carried with 0.35 M ap DI water at 25 °C for 40 s. The post-bake was at 220 °C for 20 minutes. The Critical Dimension (CD) was measured by optical microscope.

3. Results and Discussion

3.1. Photo imaging results of photo initiator

Generally, a negative polymerizing photoresists are composed of a polymer, a monomer and a photo initiator.

This reaction mechanism is that the molecular weight is increased by the polymerization of unsaturated polyester by the radical generated from a photo initiator.

Therefore, this polymerization system includes the mechanism of amplification which is higher sensitivity than other photoreaction mechanism.

The sensitivity fundamentally represents the conversion from a monomer to a polymer, and is generally shown by the following equation.

\[
\frac{dM}{dt} = \frac{kp}{kt^{1/2}} [M] (2.303 \cdot I_0 \cdot \Phi \cdot \mu \cdot [In])^{1/2}
\]

Where \( M \), kp, kt, \( I_0 \), \( \Phi \), \( \mu \) and \([In]\) describe the concentration of monomer, the propagation rate constant, the termination rate constant, the intensity of irradiation light, the quantum efficiency of photo initiator, the initiation efficiency, the molar extinction coefficient of photo initiator in the wavelength > \( \lambda \) and the concentration of photo initiator, respectively.

Table 1 shows molecular extinction coefficient of compound B which is generally photo initiator, compound C and D. They generate a methyl radical via N-O bond cleavage by photo process, compound E and F which are geometrical isomer and the result of photo imaging.

Table 1. Comparison of the molar extinction coefficient and dose of each photo initiators.

<table>
<thead>
<tr>
<th></th>
<th>( \mu (254 \text{ nm}) )</th>
<th>( \mu (365 \text{ nm}) )</th>
<th>Dose (mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound B</td>
<td>1900</td>
<td>1200</td>
<td>200</td>
</tr>
<tr>
<td>Compound C</td>
<td>31900</td>
<td>4000</td>
<td>100</td>
</tr>
<tr>
<td>Compound D</td>
<td>23200</td>
<td>9000</td>
<td>70</td>
</tr>
<tr>
<td>Compound E</td>
<td>30400</td>
<td>6700</td>
<td>70</td>
</tr>
<tr>
<td>Compound F</td>
<td>31700</td>
<td>4900</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig. 2 shows the structure of compound B-F. Dose (mJ) represents the energy which forms the width of the pattern of 20 µm by the width of the mask slit of 20 µm. The amount of dose indicates a different result though compound E and compound F which are geometrical isomers having the same molecular coefficient.

![Compound B](image1) ![Compound C](image2)

![Compound D](image3) ![Compound E](image4)

![Compound F](image5)

Fig. 2. Structures of photo initiator

3.2. Analysis of E/Z isomer structure

Fig. 3 shows a structural analysis by $^1$H-NMR made with respect to the E-Z isomer structure of compound E and F having O-acyloxime structure, which has confirmed high magnetic-field shift of the hydrogen atom (No.1) of carbazole at 4-position due to the unshared electron pair of oxygen atom of the oxime.

![Compound E](image6) ![Compound F](image7)

Fig. 3. $^1$H-NMR data of compound E and F

Fig. 4 TG/TGA and EGA-MS data of compound E and F. (a) TG/DTA data of compound E and F (b) EGA data of compound E and F (c) Mass spectra of peak A and peak B

![Compound E](image8) ![Compound F](image9)

Fig. 4. TG/TGA and EGA-MS data of compound E and F. (a) TG/DTA data of compound E and F (b) EGA data of compound E and F (c) Mass spectra of peak A and peak B
3.3. Thermal Analysis of E/Z isomer

As for compound E, which is E-isomer, radical generation efficiency by photo process is high, the weight loss has been observed at about 170 °C, as shown in Fig. 4 (a).

In addition, Fig. 4 (b) indicates that E-isomer has been evolved a gas about 150 °C by EGA TIC spectrum.

The evolved gas peak A of E-isomer indicates a structure of acetyl group substituted by methyl group, as shown in Fig. 4 (c).

On the other hand, peak B does not indicate leaving of acetyl group which has generated the radical but the structure of leaving of acetyl group from di-acetylamino group, following which substituted methyl group.

This result shows Z-isomer is stable to heat and low efficiency of radical generation by photo process.

Table 2. Results of the synthesis yield of O-acetyl-1-[6-(2-naphtyl)-9-ethyl-9H-carbazole-3-yl]-3-(N-acetylamino-N-acetoxy)butanone oxime

<table>
<thead>
<tr>
<th>Diketone</th>
<th>Oxime</th>
<th>Oxime-ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yields (%)</td>
<td>E-isomer</td>
<td>-</td>
</tr>
<tr>
<td>(%)</td>
<td>Low</td>
<td>-</td>
</tr>
<tr>
<td>(%)</td>
<td>Z-isomer</td>
<td>-</td>
</tr>
<tr>
<td>Yields (%)</td>
<td>E-isomer</td>
<td>-</td>
</tr>
<tr>
<td>(%)</td>
<td>Reflux</td>
<td>-</td>
</tr>
<tr>
<td>(%)</td>
<td>Z-isomer</td>
<td>-</td>
</tr>
</tbody>
</table>

3.4. A selective synthesis of O-acetyl-1-[6-(2-naphtyl)-9-ethyl-9H-carbazole-3-yl]-3-(N-acetylamino-N-acetoxy)butanone oxime

In consideration of section 3.3. result, we examine the selective synthesis method of E-isomer which has highly reactive for photo process.

We investigate the influence of temperature conditions in conversion of diketone derivatives into oxime derivatives. Table 2 shows the yield of two geometrical isomers. E-isomer was selectively obtained at low temperature (30 - 35 °C) conditions when conversion into oxime derivatives.

4. Conclusion

The authors report a structural analysis by 1H-NMR made with respect to the E-Z isomer structure of O-acetyl-1-[6-(2-naphtyl)-9-ethyl-9H-carbazole-3-yl]-3-(N-acetylamino-N-acetoxy) butanone oxime having an O-acyloxime structure, which has confirmed high magnetic-field shift of the hydrogen atom of carbazole at 4-position due to the unshared electron pair of oxygen atom of the oxime.

In addition, a selective isomer synthesis method for E and Z isomers has been established by controlling the reaction temperature for oximization of diketone derivatives during the synthesis. Furthermore, evaluations of the pattern formation using these isomers are performed, and reveal that patterns can be formed by using the E isomer with lower energy than that required by using the Z isomer.

References