Synthesis of a Novel Photo-Radical Initiator Based on Naphthalic-1 8-N-alkylimide Derivatives

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INTRODUCTION

UV-curable plastics with good productivity and low energy cure process have been widely used in electric industries, compared to traditional thermosetting plastics. Among them, UV-curable plastics using radical polymerizations (UV-CRP) in the presence of photo-radical initiators are the most important ones and have been used as print inks, over-coatings of prints, protection coatings of printed-circuit boards (solder resist layer), and color filter resists of liquid crystalline display, etc, because of low production costs and easy handlings.¹

The photo-radical initiators are classified into two types; a self-cleavage type and a hydrogen-transfer one. The former, such as benzoin-ether, produces radicals according to a Norrish I process. Although the photosensitivity of the self-cleavage type photoinitiators is high, the decomposed residues of them remain in the coatings and volatilize easily. The latter, such as benzophenone, abstracts a proton from a proton donor to generate a radical. This type of photo-radical initiators does not decompose by radical generation and shows low photosensitivity in the absence of a proton donor such as tertiary amines.
Tertiary amines cause degradation of coatings and have odor. Furthermore, these compounds partly bring toxic consequences.\(^2\)

Jonsson et al. reported that maleimides work as a photo-radical initiator of acrylates or vinyl compounds without self-cleavage or co-initiator like a tertially amine.\(^{3a-c}\) However, thermal resistance and photosensitivity of maleimides are low due to their lack of aromatic rings in their structures. Recently, an aromatic imide such as phthalimide was reported to act as an effective photo-radical initiator when it was used with a sensitizer and a proton-donor.\(^4\) Kubo et al. reported that naphthalimide reacts with \(p\)-xylene via the hydrogen-transfer process by UV-irradiation in \(\text{H}_2\text{O-CH}_3\text{CN}\), and produces \([3+3]\)-adducts and water-incorporated adducts.\(^5\) Naphthalimide derivatives have a \(\pi\)-conjugate plane structure, so they show high thermal stability and a wide absorption band in their UV spectra.\(^6\) These reports prompted us the development of a new thermally stable photoinitiator without decomposed substances in the process of UV curing.

This article reports the development of new thermally stable and highly efficient photo-radical initiators containing naphthalimide moieties for UV-CRP.

**RESULTS AND DISCUSSION**

**Synthesis of Photo-Radical Initiators (NI1~NI4)**

NI1~NI4 were prepared by the condensation reaction of 1,8-naphthalic anhydride and primary amines followed by imidization.\(^7\) The amic acids were easily converted into corresponding imides by thermal treatment. Conversion of amic acids to NI derivatives proceeded at 130°C (Scheme 1).

NI derivatives having a six-membered ring imide are more

\[\text{Scheme 1. Synthesis of NI1–NI4.}\]
stable than the five-membered ring such as phthalimide because of the low ring-strain. Accordingly, NI derivatives were obtained from their amic acids more easily compared to 5-membered ring imide derivatives.

**Thermal Properties of NI1~NI4**

The thermal properties of NI1~NI4 were examined with TG-DTA. The results are summarized in Table 1. Their decomposition temperatures are higher than the conventional hydrogen-transfer type photo-radical initiators such as BPA, cyclohexylmaleimide (CM) and a typical self-cleavage type photo-radical initiator 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone (MMMP). These results indicate NI1~NI4 are thermally stable enough for use of the coatings.

**UV Spectra of NI1~NI4**

A high absorption of a photo-radical initiator to an incident light is an essential factor to estimate the photosensitivity of the photo-radical initiator. Therefore, matching the absorption spectrum of the photo-radical initiator with the emission spectrum of a light source and designing molecules having high molar extinction coefficients (ε) are very important.

<table>
<thead>
<tr>
<th>Table 1. Thermal properties of NI 1~4 and photoinitiators</th>
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<tbody>
<tr>
<td>Naphthalimide and Photoinitiator</td>
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<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>NI1</td>
</tr>
<tr>
<td>NI2</td>
</tr>
<tr>
<td>NI3</td>
</tr>
<tr>
<td>NI4</td>
</tr>
<tr>
<td>BPA</td>
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<tr>
<td>CM</td>
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<tr>
<td>MMMP</td>
</tr>
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\(^a\) in nitrogen from TG-DTA at a heating rate of 10 \(^\circ\)C/min, \(^b\) liquid at 23 \(^\circ\)C

Figure 2 shows the UV absorption spectra of a series

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of NI derivatives substituted with a methoxyethyl group as the side-chain. The UV absorption spectra were measured at $1.0 \times 10^{-5}$ mol/L in acetonitrile. The UV spectrum of NI1 shows the absorption from 270 to 360 nm, and the $\varepsilon$ at 330 nm is $1.4 \times 10^4$, and the $\varepsilon$ at 365 nm, which is the highest emission intensity by the high-pressure mercury arc lamp, is $2.0 \times 10^2$ (Table 2).

On the other hand, the UV-absorptions of NI2 and NI3 having halogen-substituted aromatic moieties are red-shifted about 10 nm compared to that of NI1. The $\varepsilon$ of NI2, and NI3 are $1.2 \times 10^4$ and $1.1 \times 10^4$ at 340 nm, and $2.2 \times 10^3$ and $2.8 \times 10^3$ at 365 nm, respectively. The UV-absorption spectra of NI derivatives exhibit steep shape, and the absorptions remarkably increase their molar extinction coefficients at 365 nm. Furthermore, NI4 with a isoproxy group on an aromatic moiety shows a large red-shift, and its local absorption maximum exists at 365nm, and the $\varepsilon$ reaches to $1.2 \times 10^4$.

**Table 2** Molar absorbance coefficient ($\varepsilon$) of $1 \times 10^{-5}$ mol/L solutions of NI1~4 in acetonitrile.

<table>
<thead>
<tr>
<th>Naphthalimide</th>
<th>$\lambda_{\text{MAX}}$ (nm)</th>
<th>$\varepsilon_{\text{MAX}}$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
<th>$\varepsilon_{365}$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI1</td>
<td>330</td>
<td>$1.4 \times 10^4$</td>
<td>$2.0 \times 10^2$</td>
</tr>
<tr>
<td>NI2</td>
<td>340</td>
<td>$1.2 \times 10^4$</td>
<td>$2.2 \times 10^3$</td>
</tr>
<tr>
<td>NI3</td>
<td>340</td>
<td>$1.1 \times 10^4$</td>
<td>$2.8 \times 10^3$</td>
</tr>
<tr>
<td>NI4</td>
<td>365</td>
<td>$1.2 \times 10^4$</td>
<td>$1.2 \times 10^4$</td>
</tr>
</tbody>
</table>

**Photosensitivity of NI1~NI4**

The photosensitivity of NI1~NI4 for radical polymerizations was determined by UV-IR (Ultraviolet infrared spectroscopy)$^8$ The polymerization rate of PETA with NI1~NI4 was examined by the decrease of the vinyl group peak at 810 cm$^{-1}$ in the acryloyl group. The molar feed ratio of PETA and NI1~NI4 was 17 to 1 (The molar ratio of vinyl group of PETA and NI1~NI4 was 50 to 1.). The film was
spin-coated from the solution of PETA containing NI in CHCl₃ on a chrome-plated glass surface, and the
decrease rate of the vinyl group peak was measured by
the reflection infrared spectroscopy in nitrogen
atmosphere. The results are shown in Figure 3.

NI1 and NI2 have relatively high photosensitivity. NI4 with the largest absorption at 365 nm, however,
exhibits low sensitivity because of its strong fluorescence as shown in Figure 4. The absorbed energy
in NI4 is emitted as a light instead of radical generation.

The color of the films containing NI2~NI4 turned yellow after UV curing. Especially, the halogenated
NI2 and NI3 separated from PETA during film formation, and the films became opaque. NI1~NI4 worked as the photo-radical initiator in the absence of tertiary amines, whereas the hydrogen-transfer type
photo-radical initiator such as benzophenone and phthalimide shows very low photosensitivity in the
reaction without the tertiary amine and sensitizer.

Synthesis of Photo-Radical Initiators Containing Acrylate Groups (NI5~NI7)

To prevent the generation of the volatiles from coatings after UV exposure, mainly two methods have
been studied. One is the introducing a vinyl group to photo-radical initiator such as benzophenone acrylate,⁹ and the other one is to use photo-radical initiators with high molecular weights.¹⁰ As described
above, NI2 showed the highest photosensitivity among NIs, but the UV-cured film became yellowed.
Coloration of films is not suitable for wide application of UV-curable plastics. On the other hand, NI1 showed a good photosensitivity and compatibility to acryl monomers, producing the colorless film after UV cure. Thus, acrylate units were introduced in NI1 to form new low volatile photo-radical initiators. To investigate the influence of types of spacer between imide ring and acryloyl moiety for their radical generation, NI6 having an ether unit and NI7 having an isopropyl unit were prepared (Scheme 2). The methylene ether generally acts as a proton donor, so the side-chain containing this unit is favorable to form an intramolecular exiplex or a radical ion pair. The tertiary hydrogens of alkanes are also easily abstracted because the formed radicals are stabilized by hyperconjugation.

**Thermal Properties of NI5~NI7**

The thermal properties of NI5~NI7 are summarized in Table 3. These compounds also showed high thermal stability.

**Photosensitivity of NI5~NI7**

Figure 5 shows the decrease rate of the acryloyl group in coatings containing NI5~NI7 and PETA. NI6 shows high photosensitivity. On the other hand, the photosensitivity of NI5 and NI7 is low. From these result, it is considered that photosensitivity of NI5~NI7 concerns the proton-donating ability of side-chain. It was reported that phthalimide generates a radical by α-deprotonation via single electron

![Scheme 2. Synthesis of NI5–NI7.](image)

![Table 3. Thermal properties of NI5–7](image)

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transfer. The oxygen of carbonyl group of phthalimide would abstract a proton of its side-chain.\(^\text{11}\)

NI6 with a methylene ether linkage in the side-chain could generate radicals by intramolecular proton transfer. It is speculated that the acryloyl group of the end of side-chain would have an influence on the initiation of polymerization of PETA. The introduction of acryloyl group improved the compatibility between the NI component and PETA, so the efficiency of a radical generation derived from NI6 would be increased.

**Comparison of Photosensitivity between NI, MMMP, BPA, and CM**

The photosensitivity of NI6 that showed the highest sensitivity in NI1~7 was compared to those of reported photo-radical initiators. The results are shown in Figure 6. NI6 exhibits lower photosensitivity than MMMP, but higher photosensitivity than BPA and CM. The decrease rate of vinyl groups of PETA in the presence of MMMP is very rapid due to unimolecular radical formation. It is supposed that BPA and CM generate radicals mainly via bimolecular reaction, so acryloyl groups decrease slowly in beginning stage of UV-cure. NI6 is higher photosensitivity than BPA having a similar side chain structure because of wide UV-absorption and

![Figure 5. Decrease rates of vinyl group of the mixture containing PETA and NI5~NI7 (Lighting intensity of high-presser mercury-arc lamp : 55 mW/cm\(^2\)).](image1)

![Figure 6. Decrease rates of vinyl group of the mixture containing PETA and NI6, BPA, CM, and MMMP. (Lighting intensity of high-presser mercury-arc lamp : 55 mW/cm\(^2\)).](image2)
characteristic conformation. Furthermore, NI6 could form an exiplex or a radical ion pair between the carbonyl group of imide structure and the methylene ether unit, which act as the proton donor. Therefore NI6 would partly show unimolecular radical generation.

**Comparison of Transmittance of Films between NI6 and MMMP**

Clear coatings are very important for various applications. The film was obtained by spin coating the solution on the glass and cured with the exposed doses of 2 J/cm², where the molar ratio of PETA and NI 6 or MMMP was 17 to 1. The film thickness was 4.5 μm. Figure 8 shows the transmittances of the film containing NI6 and MMMP, which indicate the film containing NI6 is very transparent (97%) at 400 nm comparable to that having MMMP.

**Comparison of Thermal Stability of Films Containing NI6 and MMMP**

In a process of manufacturing the electronics devices, the materials are heated over 200 °C, thus, the coatings without the volatiles by heating are required.

Figure 9 shows the TG curve of the film containing NI6 used in the determination of transmittance. A 1 wt% loss temperature in nitrogen is observed at 320 °C. On the other hand, that of the film containing MMMP is 250 °C. The gas chromatograph mass
spectrometry of the film consisting NI6 after heating at 250 °C for 1 h, indicated the all detected components were derived from PETA. In the case of the film containing MMMP, the morpholine and benzaldehyde derivatives were observed. These results clearly indicate NI6 has better thermal stability than MMMP.

CONCLUSIONS
Various naphthalimides (NI1–NI7) were prepared from 1,8-naphthalic anhydride and primary amines followed by imidization, and investigated their thermal stability and photosensitivity using the mixture of PETA. Among them, NI6 was the best photo-radical initiator for clear coatings without a proton donor such as tertiary amines, and showed high photosensitivity and thermal stability. The coatings consisting of NI6 were transparent and didn’t yield volatiles from NI6 by heating up to 250 °C. Thus, NI6 has high potential to solve the current problem of UV-cured coatings.

REFERENCES AND NOTES