Terminal Group Analyses of Photopolymerized Products Using a MALDI-TOFMS for the Study on the Oxime Ester type Photoinitiators

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Terminal group analyses of photochemically initiated polymers were conducted using a matrix-assisted laser desorption / ionization time of flight mass spectrometry (MALDI-TOFMS) in combination with a preparative SEC, a real time FTIR and a gray scale photospeed method. The analysis enabled the assignment of the terminal groups of resulting oligomers from an acrylate monomer and oximate type photoinitiator. Identified built-in terminal groups revealed solvent chain-transfer and difference in photoinitiation due to the chemical structure of oximate.

Keywords: Photopolymerization, Oxime ester, MALDI-TOFMS

1. Introduction

Oxime ester type photoinitiator is known as the effective photoinitiator in the photoimaging systems [1-2]. The iminyl radical and acyloyl radical can be generated from O-acetyloxime. These are known as unimolecular photoinitiators, Norrish I type fragmentation [2]. New oximate photoinitiator, 1,2-octanediene-1-[4-(phenylthio)-2-(o-benzoyloxime)] (OXE-01), ethanone-1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazole-3-yl]-1-(o-acetyloxime) (OXE-02) were carefully designed and developed for electronic application [3]. These advantages of oximates are near UV sensitivity and stability. Especially the latter oximate (OXE-02) was depicted as designed for pigmented formulation. According to the study, this oximate generates a methyl radical via decarboxylation after N-O dissociation of oximate upon irradiation.

The MALDI-TOFMS technique, which ionizes molecules in a mild condition, is expected to be an effective tool for analyzing the structures of big molecules, especially polymer [4, 5]. We have reported a terminal group analysis of photo-chemically initiated polymer product in order to know initiating, terminating process of photo-polymer [6-7].

We focused on oximates, OXE-01 and OXE-02 and used MALDI-TOFMS to elucidate the mechanism of photoinitiation and termination.

2. Experimental Materials.

The matrix materials, 2, 5-dihydroxybenzoic acid (DHB), 1,8,9- anthracenetriol (dithranol) were purchased from Bruker Daltonik GmbH (Germany) and 2-(4- hydroxyphenylazo)benzoic acid (HABA) was purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). We purchased other matrix materials, trans-indole-acrylic acid (IAA), 1,4-diphenyl- 1,3-butadiene (DPB), 1,1,1,4,4- tetraphenyl-1,3-butadiene (TPB) from WAKO Pure Chemical Industries. The cationization reagent, sodium trifluoroacetic acid (NaTFA) and the
solvents (tetrahydrofuran (THF), methanol, acetone and toluene) were purchased from Wako Pure Chemical Industries.

Source and abbreviation of studied photoinitiators are as follows: 1,2-Octanediene-1-[4-(phenylthio)-2-(o-benzoyloxyime)] (BASF Japan, OXE-01), Ethanone-1-[9-ethyl-6-(2-methyl benzoyl)-9H-carbazole-3-yl]-1-(o-Acetyloxyime) (BASF Japan, OXE-02), 2-phenoxyethyl acrylate (Shin-Nakamura Kagaku, PEA), and EO-modified bisphenol-A dimethacrylate (Shin-Nakamura Kagaku).

All reagents were used as received without further purification.

Sample Preparation(Solution).

Mono-functional acrylic monomer, photoinitiator and solvent were weighed in a 25 mL recovery flask, and then acetone, toluene and methanol were added. 2-Phenoxyethyl acrylate (PEA) was used as a monofunctional monomer. The recovery flask was stirred as no solid remained in the solution. The recovery flask was capped with a rubber and exposed to UV light.

The compositions of studied samples are summarized in Table 1.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Solvent</th>
<th>Monomer</th>
<th>Photoinitiator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone</td>
<td>Toluene</td>
<td>methanol</td>
</tr>
<tr>
<td>No.1</td>
<td>75</td>
<td>150</td>
<td>75</td>
</tr>
<tr>
<td>No.2</td>
<td>75</td>
<td>150</td>
<td>75</td>
</tr>
<tr>
<td>No.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>No.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*No1, 2 are solution. No.3, 4 are film.

Size Exclusion Chromatography (SEC) Sample preparation.

All samples were prepared at a concentration from 50 mg/mL to 200 mg/mL in HPLC grade unstabilized THF.

MALDI Sample Preparation.

Polymer samples for MALDI analysis were prepared at a concentration of 10 mg/mL in THF. SEC conditions were previously described [4].

MALDI-TOFMS Instrumentation.

MALDI-TOFMS experiments were carried out using an Auto FLEX laser TOF mass spectrometer (Bruker Daltonik GmbH, Germany), equipped with dual microchannel plate detectors for both linear and reflection modes and nitrogen laser operating at 337 nm. Positive ion mode was utilized for all analyses, with an accelerating voltage of 19 kV.

Photospeed study.

Film preparation and evaluation method were same as in previously described [4].

Kinetics of photopolymerization (the real time FTIR).

DIGILAB FTS-3000MX equipped with an USHIO SP-7 deep UV lamp unit was used. All kinetics measurements were performed with a 365 nm bandpass filter. IR absorbance changes in >C=O< stretching band at 1637 cm⁻¹ were converted to the polymerization rate (Rp) for the initial 10s [4].

3. Results and Discussion

3.1 Terminal group analysis for OXE-01

A monoacrylate, 2-phenoxyethyl acrylate (PEA) was chosen as a monomer for MALDI-TOFMS study because of the simplicity and purity. Film and solution photopolymerized products were subjected to MALDI-TOFMS study. No polymer peak was observed from the direct measurement of the photopolymerized product mixture. MS spectra were only obtained from the fractioned samples using a preparative SEC. Its SEC chart is shown in Figure 1. Fraction 3, 4, and 5 were subjected to MALDI-TOFMS analyses. Figure 2 shows MS spectra for the fractioned samples obtained from photopolymerized OXE-01/PEA solution. The mass spectra from solution experiment, periodic molecular ion peaks were clearly observed. We classified the peaks in the spectra into several groups in which the peaks have the regular interval which is exactly equal to the molecular weight of the used PEA (Mw=192). After expressing the mass peaks to a progression formula; M=R+192x-Na.
The remainder (R) in the formula was allotted to chemical species involved in the photo-polymerization. We could assign from A to F of peak groups. These fractions which we used for analyses were mass number of roughly 1000-4000, more specifically, mass number of 1350-1900 for f3 in (a), 950-1650 for f4 in (b), and 850-1250 for f5 (C), which correspond to the oligomers having from three to ten repeating units. Table 2 summarizes general formulae of the molecular weight and the speculated structures of oligomers.

3.2 Terminal group analysis for OXE-02

Then oxime ester (OXE-02) was also studied. The mass experiment for solution samples with the combination of SEC fractioning was conducted. More complex mass spectra than the one from OXE-01 were obtained as shown in Figure 3. Each spectrum is showing mass number of 1700-2200 for f3 in (a), 1200-1600 for f5 in (b), 1200-1600 for f7 in (c), respectively. Table 3 summarizes the results of terminal structure analysis obtained from the solution experiment. Oligomer A and G seem to be products which were initiated by methyl radical and terminated by recombination and chain-transfer. Unfortunately we have not specified other oligomers (B to F).

3.3 kinetics

We have conducted photospeed study for film samples using gray scale method and FTIR method. Results were summarized in Table 4. OXE-02 was better in all parameters, conversion, polymerization rate and photospeed, than OXE-01.

According to previous work on photoinitiator [1-2], photochemically excited oxime ester
decomposes at –N-O– bond. It is believed that decomposed radicals undergo secondary decomposition, decarboxylation. Though the identification of terminal group in this study was not successful because many oligomers were remained unspecified in OXE-02 initiated system, methyl radical, instead of acetox radical, originated oligomers were specified. On the other hand, in OXE-01 analysis, no decarboxy originated oligomer was found. This is probably due to less activity of phenyl radical. It may be explained that the difference in photopolymerization rate and photo-sensitivity of OXE-02 initiated system was reflected the difference in methyl radical and phenyl radical activity.

![Scheme 1](image1)

![Scheme 2](image2)

Fig.3 MS spectrum obtained from OXE-02

Table 3 Results of terminal group analysis for OXE-02

<table>
<thead>
<tr>
<th>Peak group</th>
<th>General formula</th>
<th>Specified</th>
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<tbody>
<tr>
<td>A</td>
<td>62+192n</td>
<td>CH₃-(PEA)n-H₂C</td>
</tr>
<tr>
<td>B</td>
<td>85+192n</td>
<td>Not specified</td>
</tr>
<tr>
<td>C</td>
<td>154+192n</td>
<td>Not specified</td>
</tr>
<tr>
<td>D</td>
<td>168+192n</td>
<td>Not specified</td>
</tr>
<tr>
<td>E</td>
<td>176+192n</td>
<td>Not specified</td>
</tr>
<tr>
<td>F</td>
<td>190+192n</td>
<td>Not specified</td>
</tr>
<tr>
<td>G</td>
<td>32+192n</td>
<td>CH₃-(PEA)n-H</td>
</tr>
</tbody>
</table>

Table 4 Summary of photospeed and kinetics study

<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Conversion (%)</th>
<th>Rp (mol · kg⁻¹ · s⁻¹)</th>
<th>Photospeed (mJ · cm⁻²)</th>
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<tbody>
<tr>
<td>OXE-01</td>
<td>62</td>
<td>3.2 × 10⁻²</td>
<td>30</td>
</tr>
<tr>
<td>OXE-02</td>
<td>76</td>
<td>5.3 × 10⁻²</td>
<td>5</td>
</tr>
</tbody>
</table>

4. Conclusion

Photopolymerized product which initiated by new type of oxime esters were studied using MALDI-TOFMS technique. It was found that 1) solvent chain-transfer oligomers are involved for OXE-01 and 02, 2) secondary decomposed product was not essential initiating species in OXE-01, and 3) secondary decomposed product was essential initiating species in OXE-02.

We acknowledge to BASF Japan Research Center for providing oxime ester samples and discussion on mechanism.

References
3. H.Kura, Shikizai Kyoukaishi, 82,(2009), No.4 p151