Multifunctional Methacryloyloximes: Molecules Playing the Role of Monomer, Photoinitiator, and Photolabile Units

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Photo-induced polymerization and degradation processes provide drastic physical changes of monomeric and polymeric systems. Herein we demonstrate three multifunctional methacryloyloximes composed of core aromatic rings and photolabile O-acryloxime units, including newly prepared truxenone tris(O-methacryloyl)trioxime. These molecules afforded covalently crosslinked copolymers by free-radical polymerization. The methacryloyloximes also worked as photoinitiators that release free-radicals on irradiation with near UV light. Furthermore, resulting polymers degraded on irradiation due to the cleavage of covalent bonds. These results indicate that the methacryloyloximes played multiple roles in the formation and degradation of networked polymeric materials.

**Keywords:** O-Acryloxime, Photopolymerization, Photoinitiator, Photodegradation, Near UV sensitive, Photolabile crosslinker

1. Introduction

The presence of crosslinking points enables higher mechanical and thermal properties of polymeric materials as well as stability against chemical reagents [1]. Especially, crosslinking points made of covalent bonds are stable compared to those of ionic and hydrogen-bonded interactions. Therefore, controlled formation and degradation of the covalently crosslinked points are attractive techniques in adhesives, packaging, coatings, composites, photolithography, and biomedical applications [2,3].

Photoreaction is a useful tool for the control of covalent crosslinking points in polymeric materials in terms of easy spatiotemporal control, and small damage on many kinds of substrates [4]. Remote activation allows the decrosslinking of networked structures where reagents are difficult to reach.

In this paper, we report the behavior of multifunctional methacryloyloximes in Fig. 1, as molecules that playing role of monomer, photoinitiator, and photodegradable units. Two methacryloyloximes, 1,4-diacetylbenzene 1,4-bis(O-methacryloyl)dioxime (DBzM) and 1,3,5-triacetylbenzene 1,3,5-tris(O-methacryloyl)trioxime (TBzM) were already published molecules based on benzene cores [5-9], and truxenone tris(O-methacryloyl)trioxime (TruxM) is a novel one based on truxene. These have multiple arms composed of polymerizing units, and the uniform incorporation of the crosslinking points is easier.

![Fig. 1. Multifunctional methacryloyloximes.](image-url)
After cooling the flask in an ice bath, methacryloyl methacryloyl chloride were equipped to the flask. A dropping funnel containing 2.24 mL (22.5 mmol) of triethylamine. Then a thermometer and a cresol and 3.60 mL (2.61 g, 25.83 mmol) of dichloromethane with 24 mg of 2,6-di-trioxime was dissolved in 100 mL of 2.2. TruxM was obtained as described previously [30].

Truxene trioxime isopropylthioxanthene-9-one (ITX) were recrystallized from hexane. Truxene units before use. Diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) and 2-arylthioxanthene were subjected to activated alumina column to remove inhibitors before use. Diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) and 2-isopropylthioxanthene-9-one (ITX) were recrystallized from hexane. Truxene trioxime was obtained as described previously [30].

## 2. Experimental

### 2.1. Materials

Methyl acrylate (MA), butyl acrylate (BA), and ethoxymethyl acrylate (EGEA) were subjected to activated alumina column to remove inhibitors before use. Diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) and 2-isopropylthioxanthene-9-one (ITX) were recrystallized from hexane. Truxene trioxime was obtained as described previously [30].

### 2.2. TruxM

In a flask, 2.15 g (4.99 mmol) of truxene trioxime was dissolved in 100 mL of dichloromethane with 24 mg of 2,6-di-tert-butyl-p-cresol and 3.60 mL (2.61 g, 25.83 mmol) of triethylamine. Then a thermometer and a dropping funnel containing 2.24 mL (22.5 mmol) of methacryloyl chloride were equipped to the flask. After cooling the flask in an ice bath, methacryloyl chloride was added dropwise over 18 min, keeping the internal temperature at 0 ~ 3 °C. Then, the ice bath was removed, and stirring was kept for 22 h at room temperature. The mixture was quenched by 30 mL of 1.2 N HCl with cooling, washed with sat. NaHCO3. The organic layer was dried with Na2SO4, and rotavapped to afford 3.11 g of light tan solid. A part of the solid was chromatographed repeatedly to afford 150 mg (0.236 mmol) of yellow powder. Yield: 4.7 %. 1H NMR (CDCl3): δ 9.71 (3H, d, J = 8.0 Hz, aromatic), 8.15 (3H, d, J = 7.2 Hz, aromatic), 7.45 (3H, m, aromatic), 7.26 (3H, s, aromatic), 6.35 (3H, s, =CH), 5.87 (3H, s, =CH), 2.21 (9H, s, CH3). 13C NMR (CDCl3): δ 164.386, 158.254, 141.770, 140.225, 135.011, 132.716, 130.518, 129.583, 129.435, 128.594, 127.419, 118.028. IR (KBr): 1753 cm⁻¹ (C=O). UV (CHCl3): λmax 251.6 (molar extinction coefficient ε: 6.52 x 10⁴ L·mol⁻¹·cm⁻¹), 302.2 (4.75 x 10⁴), 344.5 (2.76 x 10⁴), and 373.9 nm (1.42 x 10⁴).

### 2.3. Solubility measurement of copolymer films

Formulations composed of TPO, MA, and DBzM or TBzM were put on a quartz disc (20 mmϕ) with a dispenser, covered with a PET film (20 mmϕ), and irradiated with a Hayashi Watch-Works LA410 Xe-Hg lamp (250 mW/cm² at 365 nm) for 60 s. After removing the covering PET films, resulting films were baked on a hot plate at 80 ºC for 2 min, further irradiated with an Ushio ULO-6DQ low pressure lamp (1.8 mW/cm² at 254 nm), and soaked in THF for 3 min at room temperature. Film thickness was measured with a Mitsutoyo SJ210 contact profilometer (Kawasaki, Japan) using a 5 µm ϕ tip stylus with 4 mN measuring force.

### 2.4. Peel strength measurement

Thermal polymerization of BA and DBzM or TBzM was carried out in ethyl acetate in the presence of 2,2’-azobisisobutyronitrile at 60 ºC with bubbling N₂ gas until the bubbles raised slowly. Obtained polymers were reprecipitated from methanol. The purified polymers were dissolved in acetone (30 wt%), coated on 50 µm PET films with an applicator, and dried overnight in reduced pressure at room temperature. The thickness of the films was estimated to be 30 μm from the amount of loaded solution. Then the films were cut into 20 mm × 80 mm and irradiated with an Ushio UM102 medium pressure Hg lamp (254 and 365 nm were 1.6 and 2.1 mW/cm², respectively) from polymer layer side.

Then the films were fixed on SUS plates, overlapped with another PET film, and pressed by a
roller with 2 kgf. After leaving for 20 min, 180° peel strength was evaluated using an Instron 5582 Materials Testing System.

2.5. Rheological measurement
Rheological experiments were performed with a Thermo Scientific HAAKE MARS III rotational rheometer. Formulations were placed between parallel plates and applied an oscillation with a constant frequency at 1 Hz under a constant strain amplitude ($\gamma = 0.01$) in the rheometer. During the measurement, the formulations were illuminated at 25 °C with 365 nm LED light which was introduced through a quartz bottom plate [7-9,30].

3. Results and discussion
3.1. Characteristics of methacryloyloximes
Methacryloyloximes were prepared by oximation of corresponding aromatic ketones followed by coupling with methacryloyl chloride. By this easy processes, DBzM were obtained in good yield, although isolated yields of TBzM and TruxM were low. The solubility of the methacryloyloximes was fairly low in organic solvents, probably due to highly symmetric and planar structures.

$^1$H NMR spectra of the methacryloyloximes were simple even in aromatic regions, reflecting their symmetrical structures. Isomers on C=N units have been discussed [14,15,18], especially for α-oxoacyloximes. Although two isomers $E,E/E,Z$ (DBzM) and $E,E,E/E,E,Z$ (TBzM and TruxM) are possible, we did not identified the isomer distribution from the spectra.

Figure 2 shows UV-vis spectra of the methacryloyloximes. DBzM and TBzM have π-π* absorption bands around 275 and 250 nm, respectively, and are transparent above 325 nm. TruxM has an absorption band in the region of 470-290 nm along with a strong band around 250 nm. The absorption edge is extended to 472 nm, and $\varepsilon$ at 365, 405 and 436 nm were $1.47 \times 10^4$, $7.24 \times 10^3$ and $1.28 \times 10^3$ L·mol$^{-1}$·cm$^{-1}$, respectively.

3.2. Methacryloyloximes as monomers
Methacryloyloximes can be polymerized in free-radical mode. DBzM and TBzM were photopolymerized with MA in the presence of TPO as a photoinitiator. Here, only TPO would absorb light from Hg-Xe lamp, and liquid formulations containing small amount of DBzM and TBzM turned into hard and smooth-surfaced films with 5 μm thickness on irradiation. These films were insoluble into THF, suggesting the formation of networked structures. In the absence of methacryloyloximes, resulting MA homopolymer was not hard film but viscous tar which was soluble in THF.

BA was also polymerized thermally to form tacky, low glass transition temperature materials which can be applied to pressure-sensitive adhesives (PSAs). As shown in Table 1, 180° peel strength of the PSA layers were much improved by the presence of small amount of the methacryloyloxime.

Table 1. Peel strength of PSAs obtained by thermal polymerization of methacryloyloximes and BA.

<table>
<thead>
<tr>
<th>Polymer$^a$</th>
<th>$M_n$$^b$</th>
<th>180° Peel strength$^c$ (N/20mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>99,500</td>
<td>1.72</td>
</tr>
<tr>
<td>DBzM(0.025)-BA</td>
<td>119,500</td>
<td>6.76</td>
</tr>
<tr>
<td>TBzM(0.016)-BA</td>
<td>716,600</td>
<td>4.25</td>
</tr>
</tbody>
</table>

a) Numbers in parenthesis show mol% of methacryloyloximes in feed.
b) Measured by size exclusion chromatography with polystyrene standards and THF eluent.
c) 100 N load cell at 300 mm/min. Sample layer: 30 μm thickness and 20 mm wide on PET substrates.

3.3. Methacryloyloximes as photoinitiators
$O$-Aclyoximes and their derivatives have been known as good photoinitiators, and some are commercially available [16,17]. Therefore, methacryloyloximes are also anticipated as photoinitiators.

In order to confirm the ability of initiation, viscoelastic parameters changes during irradiation at 365 nm light using a photorheometer for BA/TBzM/ITX and BA/DBzM/ITX systems were monitored [7-9]. On irradiation, storage ($G'$) and
loss ($G''$) moduli for both systems increased even in the absence of TPO. In the same condition, the photopolymerization for BA alone, BA/DBzM, and BA/TBzM systems did not proceed, and the photopolymerization of BA/ITX system was very slow. These results suggest that photoreaction of $O$-acyloxime units sensitized by ITX initiated the polymerization.

Similar photopolymerization was attempted for TruxM/EGEA system without an additive. Figure 3 shows the profiles of $G'$, $G''$, absolute value of complex viscosity ($|\eta^*|$), and $\tan \delta (= G''/G')$ on irradiation at 365 nm, where the parameters increased with increasing irradiation time. These results indicate that direct photolysis of $O$-acyloxime units proceeded in the absence of sensitizer.

Spectral changes of TruxM on irradiation were measured to analyze its photoreaction. As shown in Fig. 4, UV spectral changes of TruxM solution on irradiation with a Hg-Xe light indicate that peaks at 251 and 302 nm and some shoulders decreased on irradiation for 1 min, and only the former peak decreased on further irradiation. In $^1$H NMR spectral changes, all peaks due to TruxM decreased on irradiation, resulting only broad aromatic band at 7–8 ppm as shown in Fig. 5. These results were not informative, although IR spectral changes in KBr pellet in Fig. 6 show peak appearance at 2335, 1704, and 1568–1592 cm$^{-1}$ along with a decrease in most of characteristic peaks including 1753 cm$^{-1}$ due to C=O stretching band, showing that the photolysis C=O moiety in $O$-acyloxime unit and the formation of CO$_2$ aromatic ketone units.

The above initiation reactions are explained by the generated free radicals in paths i and ii in Scheme 2. Although the photolysis of $O$-acyloxime units leads to the degradation of polymerized methacryloyloximes (path iii), polymerization caused by generated free-radicals is

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**Fig. 3.** Changes of viscoelastic parameters of TruxM / EGEA =0.05 /100 (mol/mol) on irradiation with 365 nm LED light (41 mW/cm$^2$). Plate gap: 500 μm.

**Fig. 4.** UV spectral changes of 2.0 $\times$ 10$^{-3}$ M chloroform solution of TruxM on irradiation with Hg-Xe lamp. Numbers in the figure show irradiation time (250 mW/cm$^2$ at 365 nm).

**Fig. 5.** $^1$H NMR (CDCl$_3$) spectra of TruxM (i) before, and after irradiation for (ii) 5 min and (iii) 20 min with Hg-Xe lamp (250 mW/cm$^2$ at 365 nm).
3.4. Photolabile properties
The photolabile property was accomplished for DBzM-MA and TBzM-MA crosslinked films. Although the films were almost insoluble in THF, film thickness after irradiation followed by soaking in THF decreased on irradiation at 254 nm as shown in Fig. 7. These results clearly indicate the proceeding of decrosslinking to form linear polymer chains [5,6]. Soluble fractions in THF were collected, filtered, and their molecular weights were measured by SEC. Although the SEC profiles of MA homopolymer, DBzM-MA, and TBzM-MA were almost identical, the molecular weights of TBzM-MA was slightly smaller than that of DBzM-MA.

For DBzM-BA or TBzM-BA systems, the degradation was confirmed by the decrease in peel strength after irradiating with medium-pressure Hg lamp [9]. Unfortunately, we have not detected the degradation behavior for systems containing TruxM. However, polyurethane films composed of truxenone trioxime, polyethylene glycol, and hexamethylenedisocyanate showed the decrease in $G'$, $G''$, and $|\eta^*|$ on irradiation at 365 nm, suggesting that slow photoreaction of O-acyloxime units proceeded [30].

4. Conclusion
Three methacryloyloximes were successfully incorporated in networked polymers, and sensitized (DBzM and TBzM) and direct (TruxM) photolysis reactions initiated the polymerization of acrylates.
Furthermore, DBzM and TBzM clearly showed the physical property changes due to the degradation of networked structure, although that of TruxM was not observed clearly. These results show the possibility of the methacryloyloximes as potential functional molecules.

Multifunctional monomers have been applied to many types of polymer architectures such as star, hyper-branched, comb, and cyclized / knotted structures [31]. Methacryloyloximes might be useful to constitute crosslinking points of these architectures.

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References