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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*-acyloxime 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*-Acyloxime, 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.

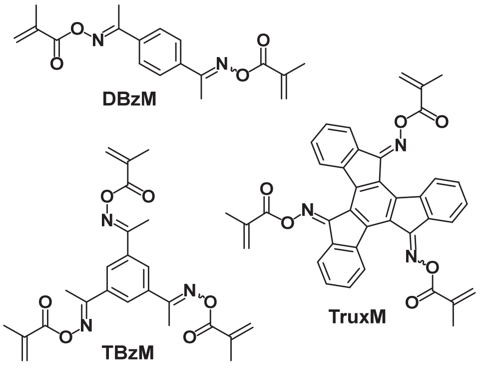

Fig. 1. Multifunctional methacryloyloximes.

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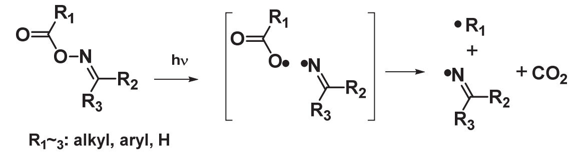


Scheme 1. Photoreactions of *O*-acyloximes.

In these molecules, *O*-acyloxime units were incorporated as photoreactive moieties. The *O*-acyloxime units show higher photoreactivity and moderate thermal and chemical stabilities. From the viewpoint of multi-functionality, the methacryloyloximes are easily derived from conventional multi-functional aromatic ketones and are advantageous compared to conventional *o*-nitrobenzyl moieties [10].

Detailed investigations of *O*-acyloxime photochemistry have been reported, and homolytic N–O cleavage in Scheme 1 was proposed as a main event for many types of *O*-acyloximes [11-13]. Resulting free-radicals and following chemical reactions have been utilized for photo-induced polymerizations [11,14-21], redox reactions [22,23], and cleavage of DNA [24,25].

When we use near UV region of light, deep penetration is possible even in the presence of aromatic compounds, pigments, and fillers, and many types of light sources including LEDs are available [26]. Thus, sensitized (DBzM and TBzM) and direct photoreactions of TruxM were attempted using near UV light. Truxene units absorb in this region of light, and truxene-based photoinitiators have been proposed recently [27-29].

2. Experimental

2.1. Materials

Methyl acrylate (MA), butyl acrylate (BA), and ethoxyethyl 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. Truxenone trioxime was obtained as described previously [30].

2.2. TruxM

In a flask, 2.15 g (4.99 mmol) of truxenone 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. $NaHCO_3$. The organic layer was dried with Na_2SO_4, 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 %. ^{1}H NMR ($CDCl_3$): 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, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.386, 158.254, 141.770, 140.225, 135.011, 132.716, 130.518, 129.583, 129.435, 128.594, 127.419, 19.028. IR (KBr): 1753 cm^{-1} (C=O). UV ($CHCl_3$): λ_{max} 251.6 (molar extinction coefficient ε: 6.52 x 10^4 L·mol^{-1}·cm^{-1}), 302.2 (4.75 x 10^4), 344.5 (2.76 x 10^4), and 373.9 nm (1.42 x 10^4).

2.3. Solubility measurement of copolymer films

Formulations composed of TPO, MA, and DBzM or TBzM were put on a quartz disc (20 mm$^{\phi}$) with a dispenser, covered with a PET film (20 mm$^{\phi}$), and irradiated with a Hayashi Watch-Works LA410 Xe-Hg lamp (250 mW/cm^2 at 365 nm) for 60 s. After removing the covering PET films, resulting films were baked on a hot plate at 80 °C for 2 min, further irradiated with an Ushio ULO-6DQ low pressure lamp (1.8 mW/cm^2 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$^{\phi}$ 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 N_2 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/cm^2, 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 ε at 365, 405 and 436 nm were 1.47×10^4, 7.24×10^3 and 1.28×10^3 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.

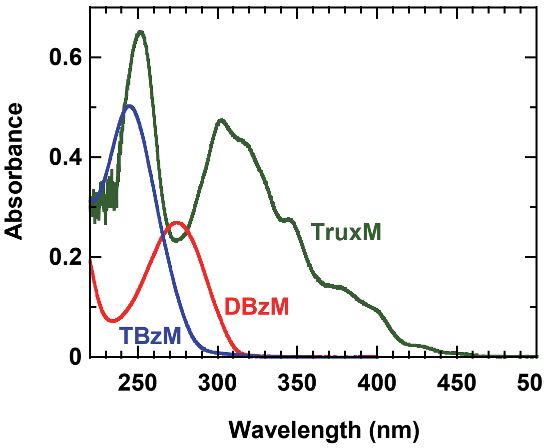


Fig. 2. UV spectra of 1.0×10^{-5} M solutions of DBzM (CH_3CN), TBzM (CH_3CN), and TruxM. ($CHCl_3$).

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.

Polymer[a]	*Mn*[b]	180° Peel strength[c] (N/20mm)
PBA	99,500	1.72
DBzM(0.025)-BA	119,500	6.76
TBzM(0.016)-BA	716,600	4.25

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-Acyloximes 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

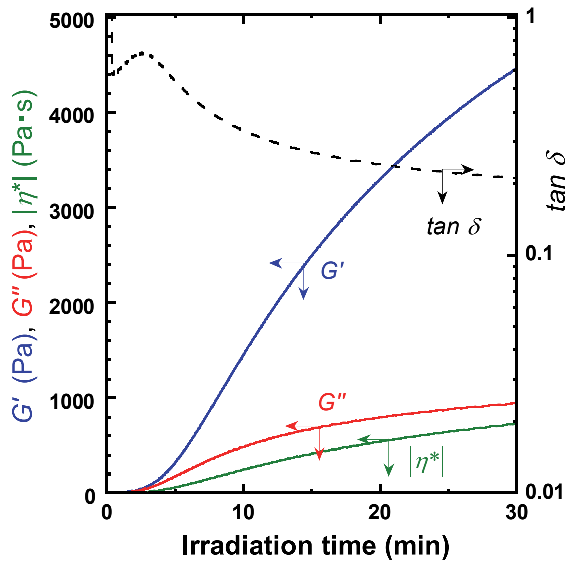


Fig. 3. Changes of viscoelastic parameters of TruxM / EGEA =0.05 /100 (mol/mol) on irradiation with 365 nm LED light (41 mW/cm^2). Plate gap: 500 μm.

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 (|*η**|), and *tan δ* (= *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.

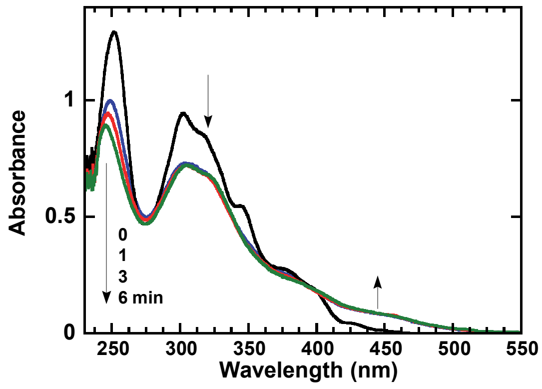


Fig. 4. UV spectral changes of 2.0 × 10^{-5} M chloroform solution of TruxM on irradiation with Hg-Xe lamp. Numbers in the figure show irradiation time (250 mW/cm^2 at 365 nm).

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

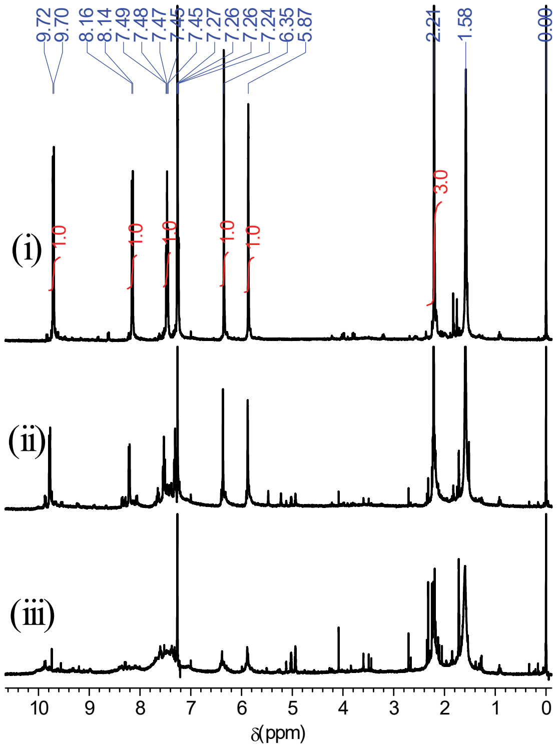


Fig. 5. ^{1}H NMR (CDCl$_3$) spectra of TruxM (i) before, and after irradiation for (ii) 5 min and (iii) 20 min with Hg-Xe lamp (250 mW/cm^2 at 365 nm).

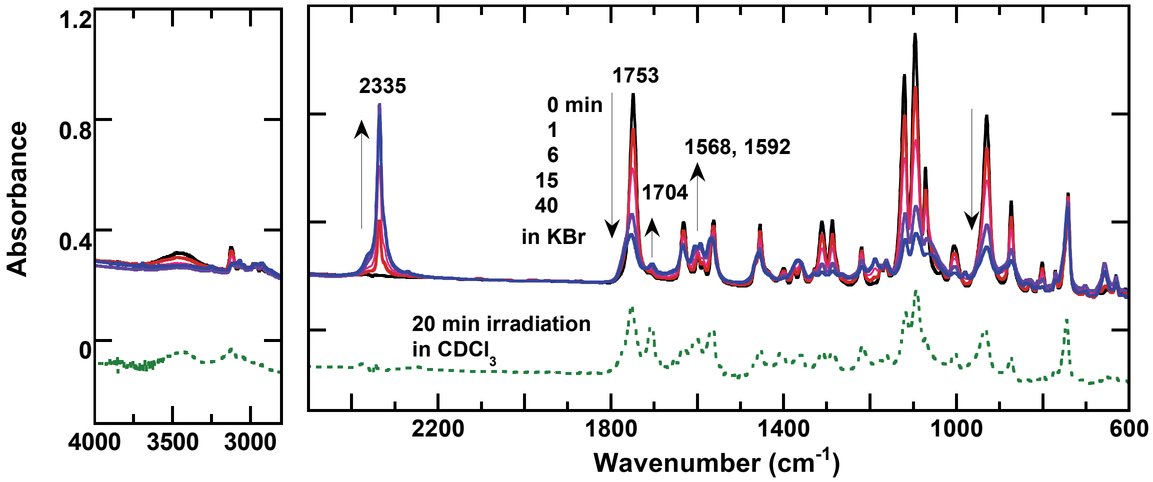
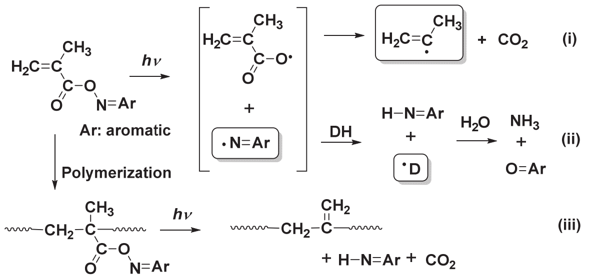


Fig. 6. IR spectral changes of TruxM in KBr pellet on irradiation with a Hg-Xe lamp (250 mW/cm^2 at 365 nm). Numbers in the figure show irradiation time and wavenumbers of peak top. The dashed line shows IR (KBr) spectrum of TruxM irradiation in $CDCl_3$ for 20 min followed by rotavapped with KBr powders.



Scheme 2. Proposed photoreactions of TruxM.

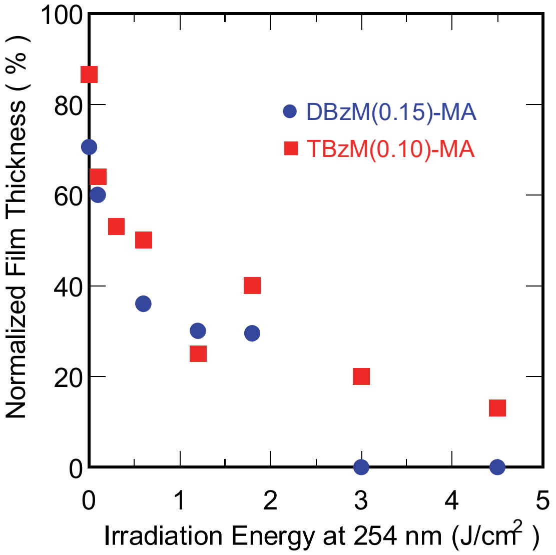


Fig. 7. Film thickness changes of photopolymerized copolymers of MA and methacryloyloximes on irradiation with a low pressure Hg lamp followed by soaking in THF for 3 min. Numbers in parenthesis show mol% of methacryloyloximes in feed. Film thickness before the soaking: 5 μm.

much faster and would be predominant in the early stage of photoreaction.

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 hexamethylenediisocyanate 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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