Reduction of Oxygen Inhibition in Photopolymerization of Cyclic Allylic Sulfide Monomer

Satoru Yamada¹ and Yasutomo Goto²

¹Synthetic Organic Chemistry Laboratories, FUJIFILM Corporation, 4000 Kawashiri, Yoshida-cho, Haibara-gun, Shizuoka, 421-0396, Japan.
²Analysis Technology Center, FUJIFILM Corporation, 200 oonakazato, fujinomiya-shi, Shizuoka, 418-8666, Japan.

Free-radical photopolymerization of Cyclic Allylic Sulfide monomer (CAS monomer) was investigated. Polymerization reaction was monitored by NMR and Photo-DSC in the presence or in the absence of oxygen. The reaction of CAS monomer was much less affected by oxygen than that of usual methacrylate monomer. Chain propagation species of the CAS monomer react with oxygen to produce peroxy radical which terminates polymerization reaction. Then the peroxy radical was lead to two kinds of radical spices which originate from SH and CH₂ group at β position of the sulfur atom in the terminated ring-opening CAS polymer. The reduction of oxygen inhibition occurs by a series of chain transfer and oxygen scavenging reaction.

Keyword: Cyclic allylic sulfide, Oxygen Inhibition, ring-opening, radical polymerization

1. Introduction

For the past several decades, the influence of oxygen on free radical photopolymerization has been a subject of much interest [1-4] since free radical polymerizations are severely inhibited by oxygen, and most free radical photocuring processes proceed in air. Oxygen inhibition causes numerous undesirable effects on free radically cured products including slow polymerization rate, long induction periods, low reaction conversion and tacky surface properties. Hoyle et al [5], has reported a number of possible chemical species and additives with potential for reducing oxygen inhibition such as amines [6, 7], thiols [8-11], and N-vinyl amides [12]. One interesting aspect that has yet to be explored in quite detail is the effect of monomer structure on oxygen inhibition of free radical polymerization. It has been reported in which (meth)acrylate monomers containing ether groups, and thioether groups reduce oxygen inhibition during free radical polymerization in air [13-18]. Ether and thioether groups present in (meth)acrylate monomers consume oxygen by the repetition of hydrogen abstraction and radical scavenging reaction.

Previous research has revealed that thiol-ene polymers reduce oxygen inhibition [8, 19-22]. Successful reduction of the sensitivity to oxygen in the photocuring system would provide a significant advantage in industrial products.

On the other hand, free radical ring-opening polymerizations have received considerable attention as an effective means of constructing low volume shrinkage curing system [23-33]. A series of studies dealing with free radical polymerization of several Cyclic Allylic Sulfide monomers (CAS monomers) have been reported by the Australian CSIRO group and by Harrisson et al. According to the literatures [34-42], the properties of photopolymerization in the absence of oxygen has revealed, but the
one in the presence has not been studied yet. In this paper, the degree of oxygen inhibition of CAS monomer will be reported.

2. Experimental

2.1. Materials

2,2'-azobis(2,4-dimethylvaleronitrile (V-65) and 2-Ethylhexylmethacrylate were purchased from Wako Pure Chemical Industries Ltd. (2,4,6-trimethylbenzoyl)ethoxy phenylphosphine oxide (lucirin TPO-L) was purchased from BASF. Other reagents and solvents were commercially available.

2.2. Preparation of Monomer

Monomer 1 was prepared according to a literature procedure [37].

2.3. Measurement of polymerization conversion

$^1$H-NMR spectra were recorded at a Bruker 400 MHz spectrometer. The conversion of the polymerization was measured by NMR analysis of the allylic double bond at 5.2 ppm (CH$_2$=C). The rate of conversion was calculated from the decrease of the integral calculus values of NMR signal of the sample that the film after exposure was dissolved in CDCl$_3$ solution. A high pressure mercury lamp (EXECURE 3000, HOYA) was used as the exposure light. Films for the measurement of photopolymerization were prepared in the following procedure. The CAS monomer 1 and a photoinitiator (lucirin TPO-L) were dissolved a polymeric binder (Mitsui Chemicals, Inc., MN1500, Mw=1500). The weight ratio of 1/polymeric binder was 1/1 and the molar ratio of photoinitiator/1 was 0.02/1. The mixture was casted on a silicon wafer by spin coating process. The thickness of thus obtained film was about 1μm. A commercially available 2-ethylhexylmethacrylate monomer was used as a reference monomer.

2.4. Photo-DSC analysis

The heat of the photopolymerization reactions was measured by Q-1000, a differential scanning calorimeter (DSC) by TA Instruments, modified with a Photo-DSC set up. A UV lamp with a 200 W mercury Bulb (OmniCure, S2000, Canada) was connected to the DSC cell through an optical fiber. The cell was sealed with a quartz window that let the UV light pass onto the open aluminum sample pans. The sample space was flushed with nitrogen or air. The measurements were carried out at 2 mW/cm$^2$ and at 25°C. All the results were analyzed for the corrected base line. The sample was 10mg of the monomer containing 2 mol% lucirin TPO-L as photoinitiator.

2.5. Measurement of molecular weight

Molecular weight and molecular weight distribution were obtained by gel permeation chromatography (GPC) using a Tosho-800 series GPC system equipped with TSK-gel columns G5000HHR, GMultiporeHXL-M, GMHHR-L connected in this order, employing tetrahydrofuran (THF) as an eluent at 40°C. Poly(St) standards (Mn=500-1 000 000) were used for calibration. GPC measurements were carried out by injecting the sample that dissolved in THF. The sample was extracted from reaction mixtures of the photopolymerization which was carried by using CAS monomer and 1 mol% of lucirin TPO-L casted on a glass plate in the presence and absence of oxygen. A high pressure mercury lamp (EXECURE 3000, HOYA) was used as the exposure light.

3. Results and Discussion

3.1. Free-radical photopolymerization

The mechanism of the ring-opening polymerization is shown in Scheme 1. These monomers propagate the polymerization reaction via an addition-fragment type mechanism. After radical addition occurs to the monomer, the allylic carbon-sulfur bond fragments to give a new vinylidene group. A simultaneous product sulfur-centered radical adds to another monomer. The final polymer resembles the structure of the monomer as it contains both the allylic sulfide units and exo carbon-carbon double bonds.

![Scheme 1. Mechanism of CAS monomer ring-opening polymerization.](image-url)
The measurement of the oxygen inhibition of photopolymerization is generally investigated by real-time FT-IR [18, 21]. In the case of the monomer I, we had difficulty with the analysis by IR because allylic double bond used in the analysis is regenerated by polymerization process. Therefore, by comparison of the integral calculus values of the NMR [37, 39], we estimated the oxygen inhibition of photopolymerization.

Figure 1 shows that photopolymerization conversion of monomer I (A) and 2-ethylhexyl methacrylate monomer (B) in the presence or in the absence of oxygen.

![Figure 1](image1.png)

**Figure 1.** Conversion of photopolymerization versus exposure time plot of (A) monomer I(nitrogen (a) and air (b)) and (B) 2-Ethylhexyl metacrylate (nitrogen (a) and air (b)) in the presence and absence of oxygen measured by NMR analysis with 2.0 mol% lucirin TOP-L.

The photopolymerization reaction of CAS monomer I proceeded much faster than that of 2-Ethylhexylmethacrylate and reached near full conversion even in the presence of oxygen. There is little difference in the reaction conversion of CAS monomer I in air and in nitrogen, on the contrary 2-Ethylhexylmethacrylate showed approximately 80% decrease in reaction conversion during the 30 minutes’ light exposure. As a result, the photopolymerization reaction of CAS monomer I was much less affected by oxygen than that of 2-Ethylhexylmethacrylate using 2.0 mol% lucirin TOP-L as photoinitiator.

3.2. Photo-DSC analysis experiments

Figure 2 shows that the ratio of exotherm values for Monomer I and 2-Ethylhexylmetacrylate monomer in photopolymerization reaction with photo-DSC analysis. As for the methacrylate monomer, the ratio of exotherm values decreases to 70% by oxygen inhibition. On the other hands, monomer I was not influence by oxygen. This result was supported by NMR analysis.

![Figure 2](image2.png)

**Figure 2.** The ratio of exotherm values for monomer I and 2-ethylhexylmethacrylate containing 2 mol% lucirin TPO-L. Samples were polymerized in nitrogen and air at a light intensity of 2mW for 10 min using high pressure mercury lamp.

3.2. Molecular weight

Table 1 shows Molecular weight (M w) and molecular weight distribution (M w/M n) of photopolymerization of CAS monomer. Interestingly, M w and M w/M n of CAS monomer increased in presence of oxygen. In the case of CAS monomer, oxygen may work
as an inhibitor of the termination reaction in polymerization.

Table 1. Molecular weight and molecular weight distribution of Polymerization of monomer I using 1 mol% lucirin TPO-L.

<table>
<thead>
<tr>
<th>entry</th>
<th>conditions</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>in N$_2$</td>
<td>136000</td>
<td>37000</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>in air</td>
<td>233000</td>
<td>36000</td>
<td>6.32</td>
</tr>
</tbody>
</table>

From these results, a plausible mechanism of CAS monomer’s photopolymerization was proposed (Scheme 2). In the presence of oxygen, propagating radicals react with oxygen to produce peroxy radical. The peroxy radical then abstracts a hydrogen atom from SH or CH$_2$ group at α position of the S atom in the ring opening CAS polymer that terminates polymer chain.

The hydrogen atom at the α position of the heteroatom is generally easy to form a radical. In addition, it is known that the radical can act to scavenge oxygen in the related reaction [13-18]. In the presence of oxygen, readily abstracted hydrogen atoms mainly lead to rapid oxygen consumption followed by oxidation of the carbon radical generated by a hydrogen abstraction chain transfer reaction.

On the other hand, a sulfur-centered radical (thiyl radical) that generates form terminated CAS polymer reacts with oxygen to give a peroxy radical. Thus thiyl radical reduces oxygen inhibition. In addition, The thiyl radical restarts polymerization with CAS monomer.

Generally, hydrogen abstraction chain transfer induces the formation of more highly crosslinked networks as the chain transfer reaction which is followed by reinitiation of radical [18]. In the case of CAS monomer, it was not reinitiation of α position of the S atom. If reinitiation causes, it would produce the branched and crosslinked polymer chain. Since no insoluble material for THF or CH$_3$Cl was detected at photopolymerization in presence of oxygen. It was suggest that the propagation reaction was exclusively induced at thiyl radical.

![Scheme 2. The proposal mechanism for reduced oxygen inhibition of CAS monomer](image)

4. Conclusion

The Photopolymerization of CAS monomer was investigated using NMR and Photo-DSC analysis in the presence or in the absence of oxygen. Compared to Methacrylate monomer, CAS monomer was found to be insensitive to oxygen inhibition. Molecular weight of thus obtained polymer was increased in presence of oxygen. Highly reactive CAS monomer of the photopolymerization under an air atmosphere would open up an exciting field of future growth in the photocuring technology.

Acknowledgements

The author would like to thank Mr. Kazunori Nigorikawa at Analysis Technology
Center in FUJIFILM Corporation for Photo-DSC measurements and Dr. Hiroyuki Suzuki and Mr. Hiroo Takizawa at Synthetic Organic Chemistry Laboratories in FUJIFILM for their many helpful suggestions.

References and Notes
40. S. Harrison, T. P. Davis, R. A. Evans, E.
41. S. Harrison, T. P. Davis, R. A. Evans, E.
42. S. Harrison, T. P. Davis, R. A. Evans, E.