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Photodegradable ROMP Polymers

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Photodegradable ROMP Polymers

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Thesis

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ABSTRACT

The pollution of plastic has laid a big chemical burden on our environment and has aroused serious attention to sustainable development. The development of degradable polymers is an effective strategy to address the plastic pollution caused by the accumulation of synthetic polymers post-consumer-waste (PCW) plastics.

Compared with chemically stimulated degradation, photolabile polymers can degrade into small molecules under light stimuli without treated with organic solvents and other special chemical reagents which may cause additional environmental issues. *o*-Nitrobenzyl (*o*-NB) alcohol derivatives, as a kind of efficient photolabile compounds, can photocleave to form *o*-nitrosobenzaldehyde under UV irradiation (300 nm ~ 365 nm)[1]. Although a series of photolabile polymers containing *o*-NB units have been developed and investigated, most of them are prepared via step-growth by using *o*-NB containing diols as monomers. Ring-opening metathesis polymerization (ROMP) as a powerful chain-growth tool is widely used to prepare functional polymers for different applications[2].

Herein, we developed a new kind of *o*-NB containing cyclic olefin as ROMP-type monomer. The monomer can be homopolymerized or copolymerized with other commercially available cyclic olefins such as dicyclopentadiene or norbornene to form photodegradable ROMP polymers. These polymers are expected to exhibit similar mechanical and chemical stability as the original polynorbornene and polydicyclopentadiene, while they also have photodegradable

properties due to the introduction of the photolabile *o*-NB unit. This contribution affords a useful strategy to develop photodegradable polymers and address the environmental issue of plastic pollution.

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It's my great honor to take this opportunity to express my special thanks to a variety of people who have helped me a lot during the past two years. Without their support and encouragement, I can not finish this thesis.

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CHAPTER I

Introduction

1.1 Green chemistry and degradable polymers

Green chemistry is a type of chemistry through which the production of hazaradous substances is reduced or eliminated. This concept was first proposed at the early period of the 1990s, and it aims to achieve the global sustainability at the molecular level. Subsequently, Paul Anastas and John Warner futher developed the concept and outlined the twelve important principles of green chemistry (Table 1-1).[3]

1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time analysis for Pollution Prevention

12.	Inherently Safer Chemistry for Accident Prevention

Table **1-1**: Twelve principles of green chemistry.[3]

Currently, the methods in the generation and disposal of synthetic polymers are largely unsustainable. With the development of industry, the pollution of the chemical industry has laid a big chemical burden on our environment. For example, plastic has been widely used in many aspects of our daily life due to its low costs, durability, good mechanical strength and convenient. But less than 10% of plastic can be recycled leading to an increasing amount of plastic waste both on land and sea.[4] In general, there are two approaches to reduce the accumulation of this kind of synthetic polymers: recycling of existing polymers and development of new degradable polymers.[5]

Degradable polymers are a type of polymers that have cleavable functional groups on their backbone and can be broken down into monomers or low molecular weight oligermers. Based on the stimuli that are applied to trigger degradation, degradable polymers can be divided into photodegradable polymers[6,7], thermally degradable polymers[8], biodegradable polymers[9], and mechanochemical degradable polymers[10,11], etc. Among these degradable polymers, photodegradable polymers attract much attention because light can be a green, convenient and controllable stimulus.

1.2 UV-light induced depolymerizable polymers

The mechanism of photo-induced depolymerization is that when the labile bonds in the backbone of a degradable polymer absorb light energy, transition from the ground state to the excited state occurs and generates free radicals, thus leading to the breakdown of the polymer chain. Compared with polymers consist of C-C and C-H bonds, the polymers with heteroatoms like O, S, P, Cl and N, etc. in their backbones are more photolabile[12,13]. It is due to the higher light absorption coefficients and wider wavelengths of light absorption of the heteroatoms (especially ultraviolet light).[14,15]

In our project “Photodegradable ROMP Polymers”, we use *o*-nitrobenzyl group as a photolabile functional group to achieve the purpose of degradation.

1.3 *o*-Nitrobenzyl alcohol derivatives photolabile functional groups

o-Nitrobenzyl (*o*-NB) oxy moiety is one of the most commonly used photolabile functional groups, and it has received extensive attention in the field of synthetic chemistry and other fields. The use of *o*-NB alcohol derivatives as photodegradable functional group was first proposed by Schofield and co-workers[16], then this concept was widely recognized and became the most popular photodegradable groups after Woodward and co-workers utilized it[17]. This photo-cleavable unit can be used in many fields such as photodegradable hydrogels with *o*-NB-based cross-linkers, block copolymers contain *o*-NB side chain, thin film patterning with *o*-NB side chain, *o*-NB for self-assembled monolayers and photocleavable bioconjugates.[18]

The mechanism of *o*-NB alcohol derivatives photoisomerization shows in Figure1-1. Upon the irradiation of the UV light, the double bond at the nitro functional group breaks to forms two radicals. One free radical takes the proton from the benzylic carbon. Then this structure will form a two double bonds resonance structure. After that the negative charged oxygen atom attached the double bond carbon to give a five-member ring. Finally, the ether group will leave to form alcohol and *o*-nitrosobenzaldehyde. Through this photoisomerization the *o*-NB alcohol derivatives can be cleaved into an *o*-nitrosobenzaldehyde and alcohol under 300-365 nm UV light without any other stimulus.

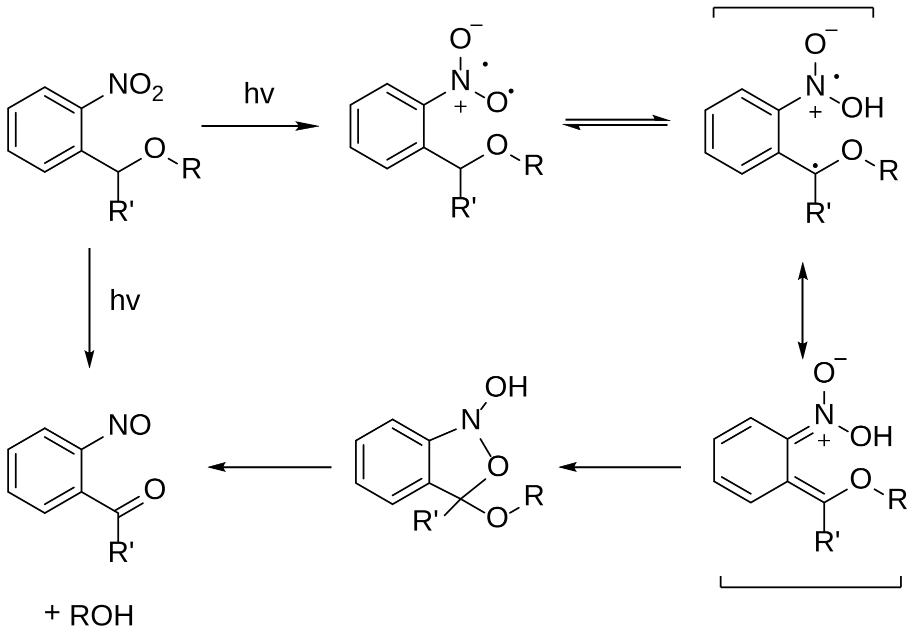

Figure **1-1:** Photoisomerization mechanism of *o*-NB alcohol derivatives.

Moreover, different substituents at the benzylic position of *o*-NB have different effects on their performance. Compared with the *o*-NB parent structure **1** which the leaving group (X) can be attached to the benzylic site directly, the carbonic acid derivatives **2** can be more frequently used as the better leaving groups and more convenient synthesis[19] (Figure1-2). In addition, most of polymers with *o*-NB photolabile functional group are synthesized by step-growth polymerization and few of them are through chain-growth polymerization. Therefore, we synthesized a type of *o*-NB functional group polymers via chain-growth polymerization and the polymers are easy to be controlled and synthesized.

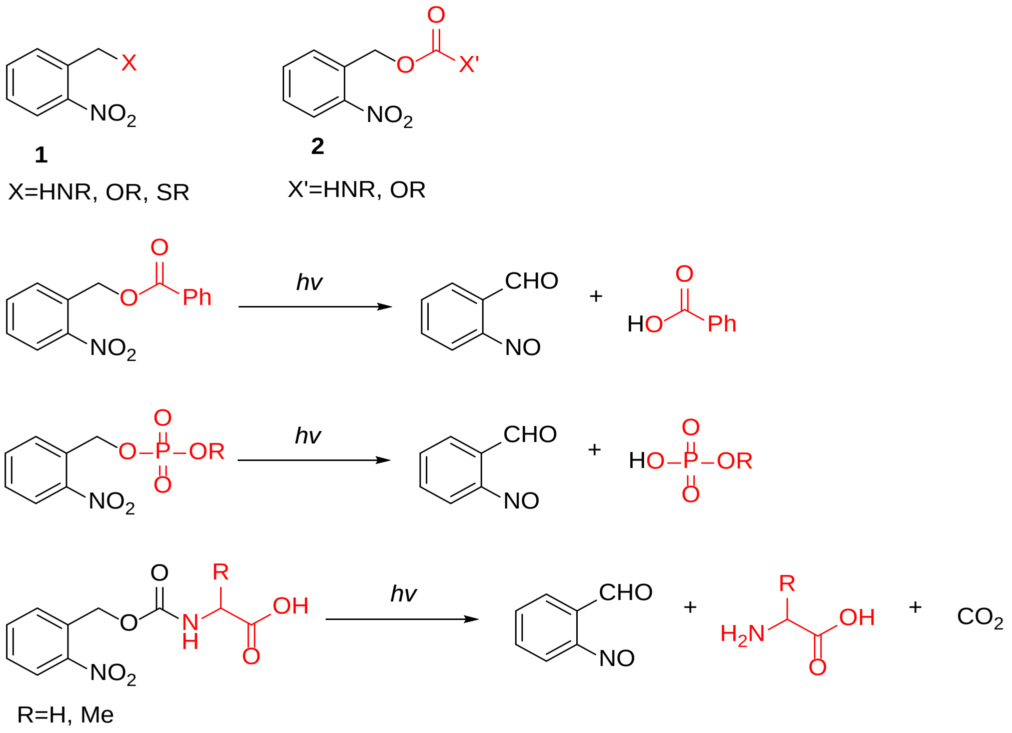

Figure **1-2:** Photolysis of different *o*-NB derivatives.

1.4 Ring-opening metathesis polymerization (ROMP)

Ring-opening metathesis polymerization (ROMP) is a powerful and widely applicable method for synthesizing polymer materials with unique structures and excellent functions. ROMP is a type of chain-growth polymerization that can convert cyclic olefins into linear polymers containing olefins in their main chain (Figure1-3).[20]

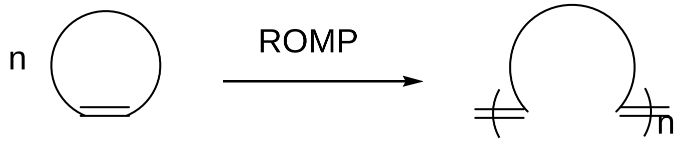

Figure **1-3:** Ring opening metathesis polymerization (ROMP).

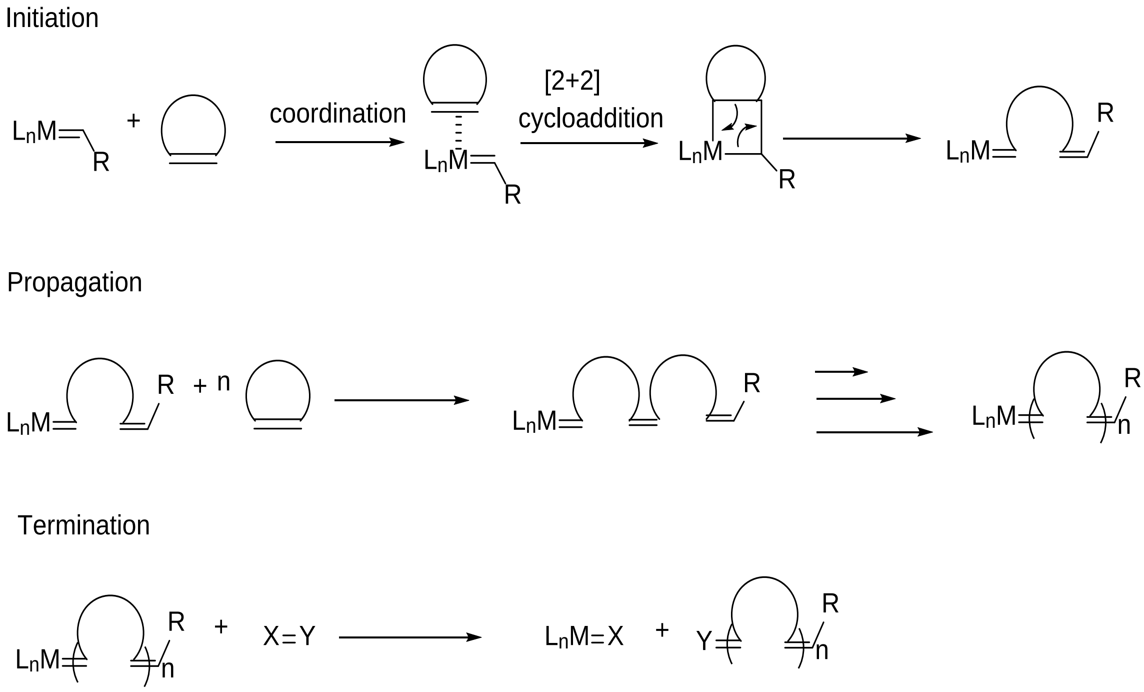

Figure **1-4:** Mechanism of ROMP.

The mechanism of ROMP is shown in Figure 1-4. Firstly, the cycloalkene monomer coordinates with the metal alkylidene complex, followed by a [2+2] cycloaddition to form the four-membered metallacyclobutane intermediate which undergoes ring opening to form a new metal alkylidene. Notably, in this process, the cycloalkene monomer undergoes ring opening and is inserted between the metal and the original alkylidene. The cycloalkene monomer would continue to be inserted into the metal alkylidene complex, as propagation proceeds and polymer is formed. The polymerization can terminated by a type of specialized reagent (such as ethyl vinyl ether) that can react with the transition metal and remove it from the end of the growing polymer chain.[2]

The driving force of ROMP is the relief of ring strain in cyclic olefins. Cyclic olefin monomer with higher ring strain promotes a higher yield of polymers. For example, cyclobutene, cyclopentene, cis-cyclooctene and norbornene derivatives are the most common monomers used for ROMP (Figure1-5).[21]

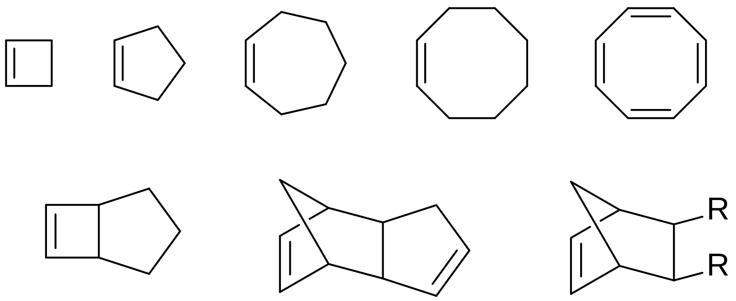

Figure **1-5:** Example of ROMP monomers.[2]

Most ROMP polymers are not degradable. Recently there have been some demonstrations of degradable ROMP polymers, enabled by the corporation of a cleavable group in the cyclic olefin monomer.[22] Despite the developments, there have not been examples of photodegradable ROMP polymers. We reasoned that a photodegradable ROMP system can leverage the advantages of both ROMP and photodegradation. Hence, in our project “Photodegradable ROMP Polymers”, we designed a photodegradable ROMP monomer by incorporating o-NB moiety in a cyclic olefin. Successful ROMP was achieved with the designed monomer and a photodegradation study of the resulting polymer was conducted.

CHAPTER II

Experiment

2.1 Synthesis of *o*-nitrobenzyl dioxocin monomer

In order to obtain this type of photodegradable ROMP polymers, we aim to utilize the *o*-nitrobenzyl functional group as a part of eight-member ring so that we can get a ROMP monomer with photodegradable properties. Figure 2-1 is the synthesis routine of our monomer.

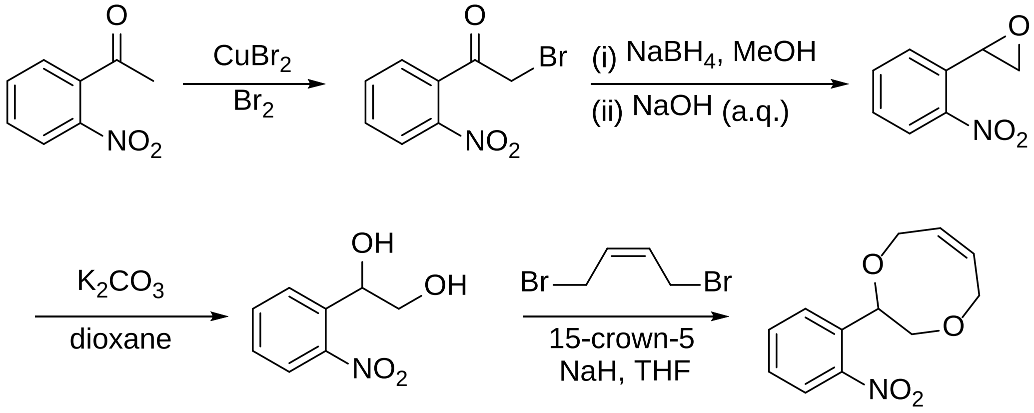

Figure **2-1**: Synthesis routine of *o*-nitrobenzyl dioxocin monomer.

First step is the bromination of ketone. In a single-neck flask 1-(2-nitrophenyl)ethanone (5.43g, 32.8mmol) and $CuBr_2$ (14.12g, 63.2mmol) are added into EA/$CHCl_3$ (v:v = 1:1, 50ml) solvent. Then several drops of Br_2 are added to activate the reaction. The reaction mixture is stirred overnight at 80 ℃. The color of mixture changes from red to green and there are some white precipitate forms during the reaction. After reaction, the mixture is cooled to room temperture and extracted by EA for three times, washed with brine and dried over with Na_2SO_4. After working up, run a column to purfiy the crude product. After purfication, we get 2-bromo-1-(2-nitrophenyl)ethanone (Figure 2-2).

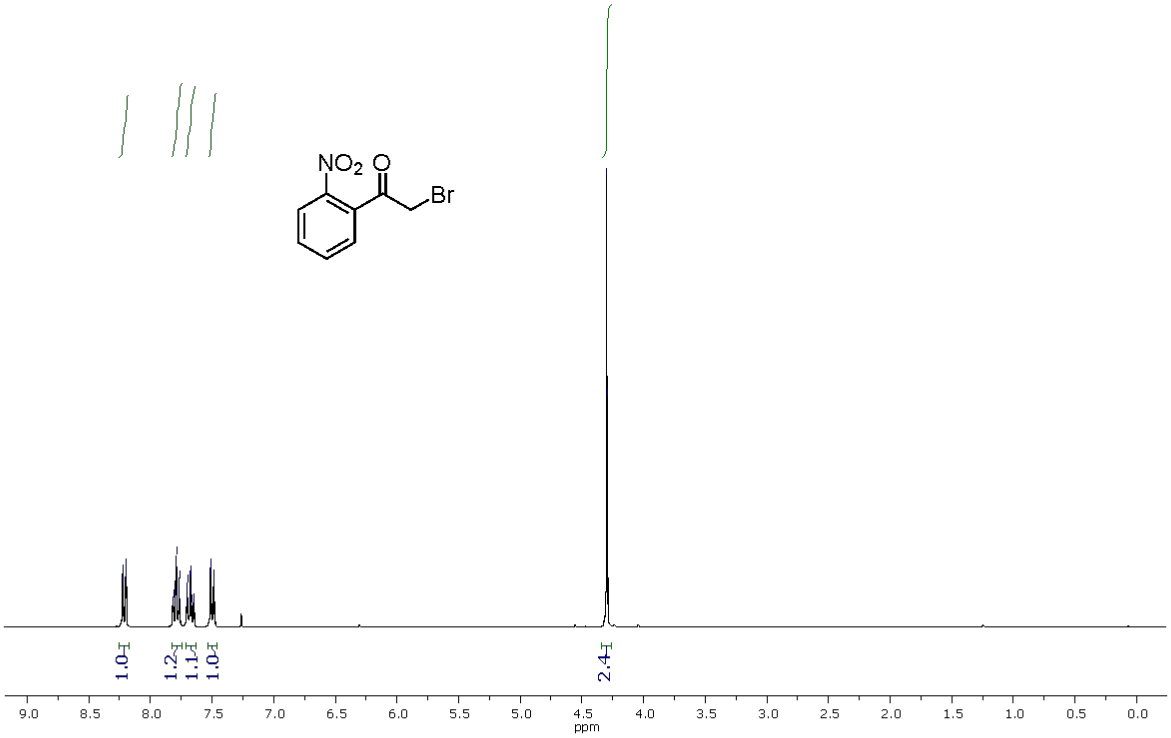

Figure **2-2**: ^1H NMR (300 MHz/$CDCl_3$) spectrum of 2-bromo-1-(2-nitrophenyl)ethanone.

The second step is using 2-bromo-1-(2-nitrophenyl)ethanone to get 2-(2-nitrophenyl)oxirane. Firstly, the 2-bromo-1-(2-nitrophenyl)ethanone (4.93g, 20.2mmol) is dissolved in dioxane (40ml) then $NaBH_4$ (2.29g, 60.6mmol) and MeOH (24ml) are added slowly into solution at 0 ℃. Warm to room temperature and using TLC plate to monitor the reaction process. After 2h reaction, NaOH solution (10%) is added into system at 0 ℃ reacts for 0.5-1h. Then the mixture is extracted by Et_2O for three times and dried over with Na_2SO_4. After filteration, the solvent is removed by rotary evaporation and the crude product is purified by column to get 2-(2-nitrophenyl)oxirane (Figure 2-3).

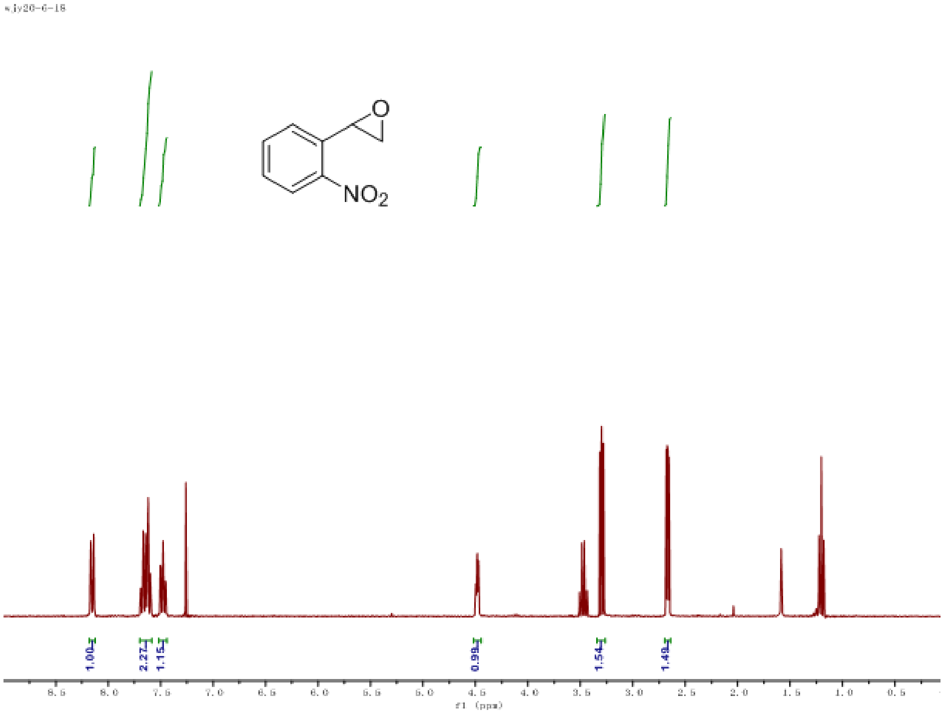

Figure **2-3**: ^{1}H NMR (300 MHz/$CDCl_3$) spectrum of 2-(2-nitrophenyl)oxirane.

The third step is from 2-(2-nitrophenyl)oxirane to get 1-(2-nitrophenyl)-1,2-ethanediol. In a single-neck flask with a stir bar, 2-(2-nitrophenyl)oxirane (2.41g, 14.5mmol) is added into dioxane (100ml). Then K_2CO_3 (100ml, 10 wt%) is added into the solution and the mixture is heated to 110 ℃, refluxed overnight. After reacting overnight, cool to room temperature and using HCl to adjust pH value of the mixture to 5.0. Then the mixture is extracted by ether for three times and dried over with Na_2SO_4. After filteration and concentration, purifing the crude product through column. Get 0.7g pure product (yellow solid) (Figure 2-4).

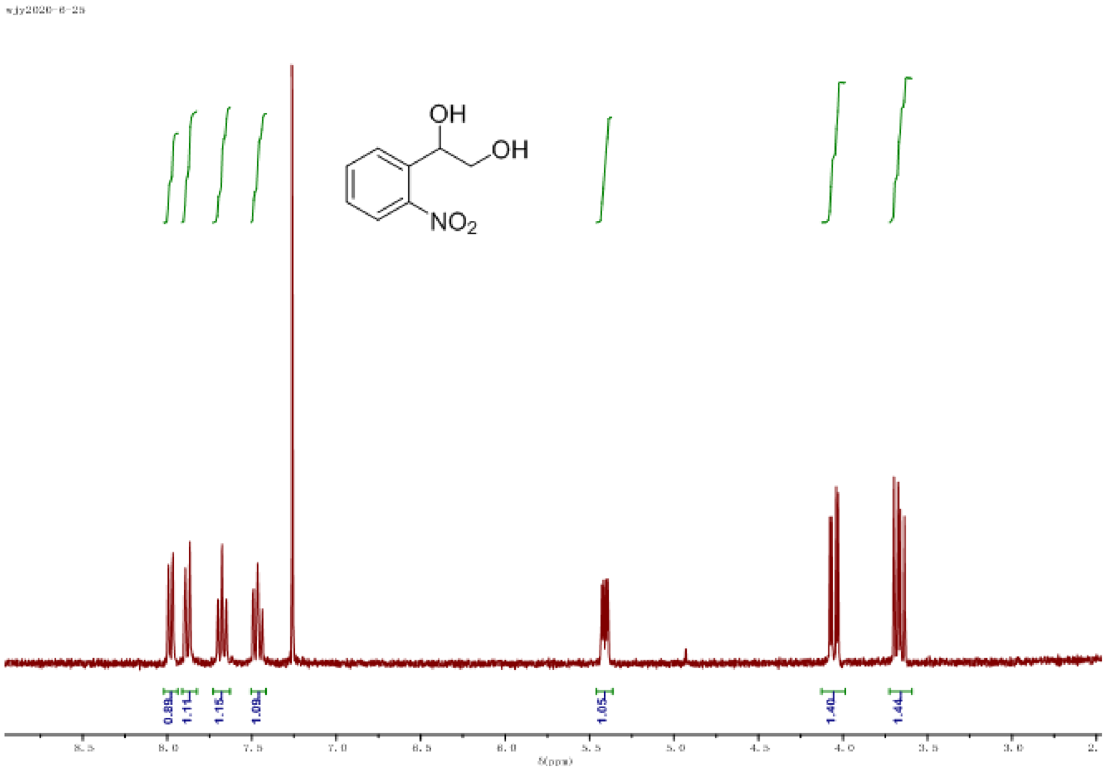

Figure **2-4**: ^{1}H NMR (300 MHz/$CDCl_3$) spectrum of 1-(2-nitrophenyl)-1,2-ethanediol.

The last step to synthesize our monomer is through 1-(2-nitrophenyl)-1,2-ethanediol reacts with (Z)-1,4-dibromobutene to get *o*-nitrobenzyl dioxocin. In a double-neck flask, NaH (0.09g, 3.74mmol) and 1-(2-nitrophenyl)-1,2-ethanediol (0.171g, 0.935mmol) are dissolved in dry THF (40ml). Then 15-crown-5 (0.412g, 1.787mmol) is added and stirred for 1.5h. After stirring 1.5h, (Z)-1,4-dibromobutene (0.20g, 0.935mmol) in dry THF (55ml) is added into the mixture and reacts overnight. Finishing the reaction, remove THF by rotary evaporation then run a column to purify the crude product. Get 0.0312g pure product (Figure 2-5).

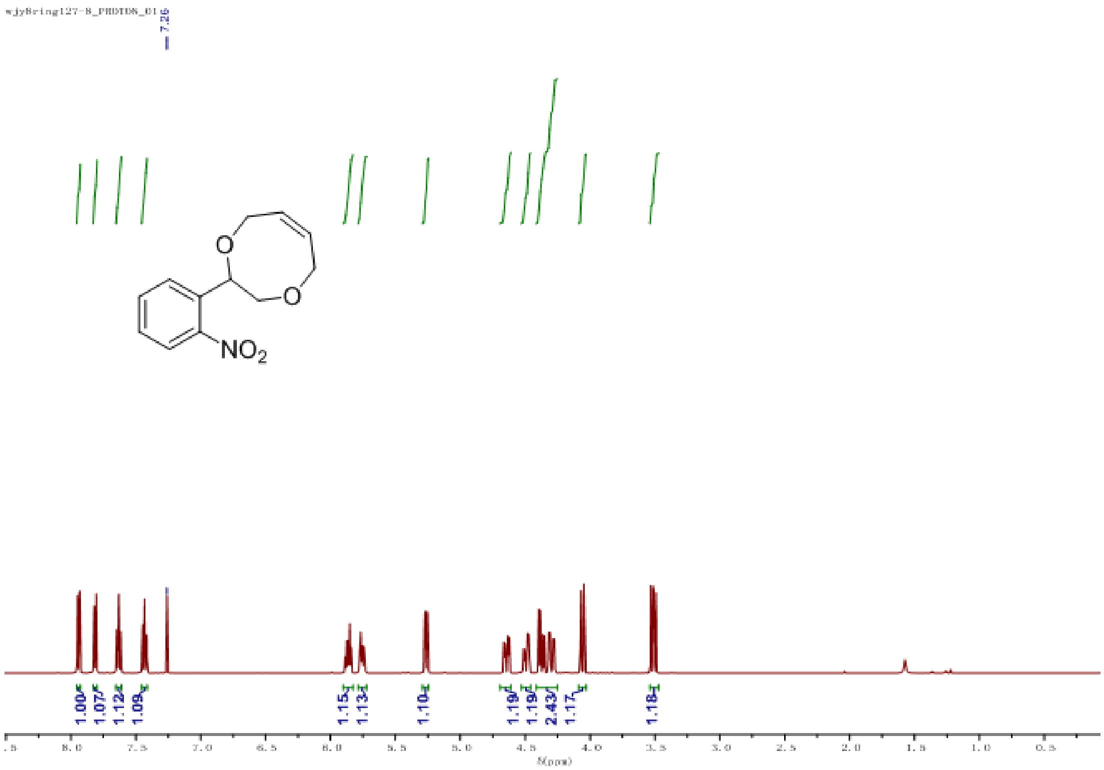

Figure **2-5**: ^{1}H NMR (500 MHz/$CDCl_3$) spectrum of *o*-nitrobenzyl dioxocin monomer.

2.2 Synthesis of *o*-nitrobenzyl dioxocin polymer

After we successfully synthesize the o-nitrobenzyl dioxocin monomer, the following step is through ROMP to synthesize the o-nitrobenzyl dioxocin polymer with second-generation Grubbs catalysts. Figure 2-6 is our synthesis routine.

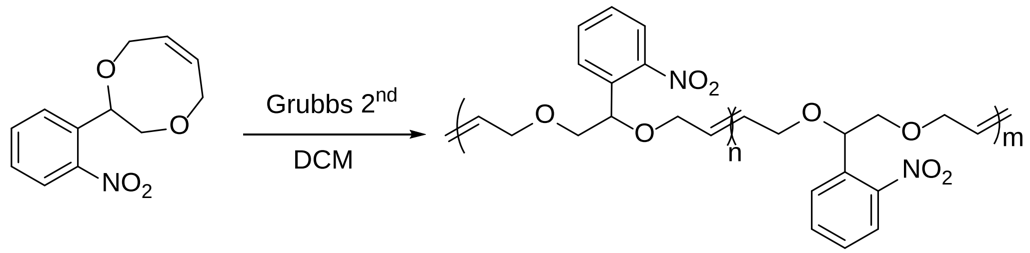

Figure **2-6**: Polymerization of *o*-nitrobenzyl dioxocin monomer.

o-Nitrobenzyl dioxocin monomer (26.4 mg, 0.11 mmol, 1 eq.) and 2nd Grubbs catalyst (0.29 mg, 0.34 µmol, 0.003 eq.) are dissolved in 50 µL DCM with a stir bar. The polymerization is stirred overnight. After reaction, the crude product is seperated with prep-GPC to get the pure product. Yielding green/yellow liquid then dry it under vacuum. Due to the regioselectivity of our monomer, there are three types of polymer can be formed: head-to-head, head-to-tail and tail-to tail. Figure 2-7 is the ^{1}H NMR spectrum of o-nitrobenzyl dioxocin polymer.

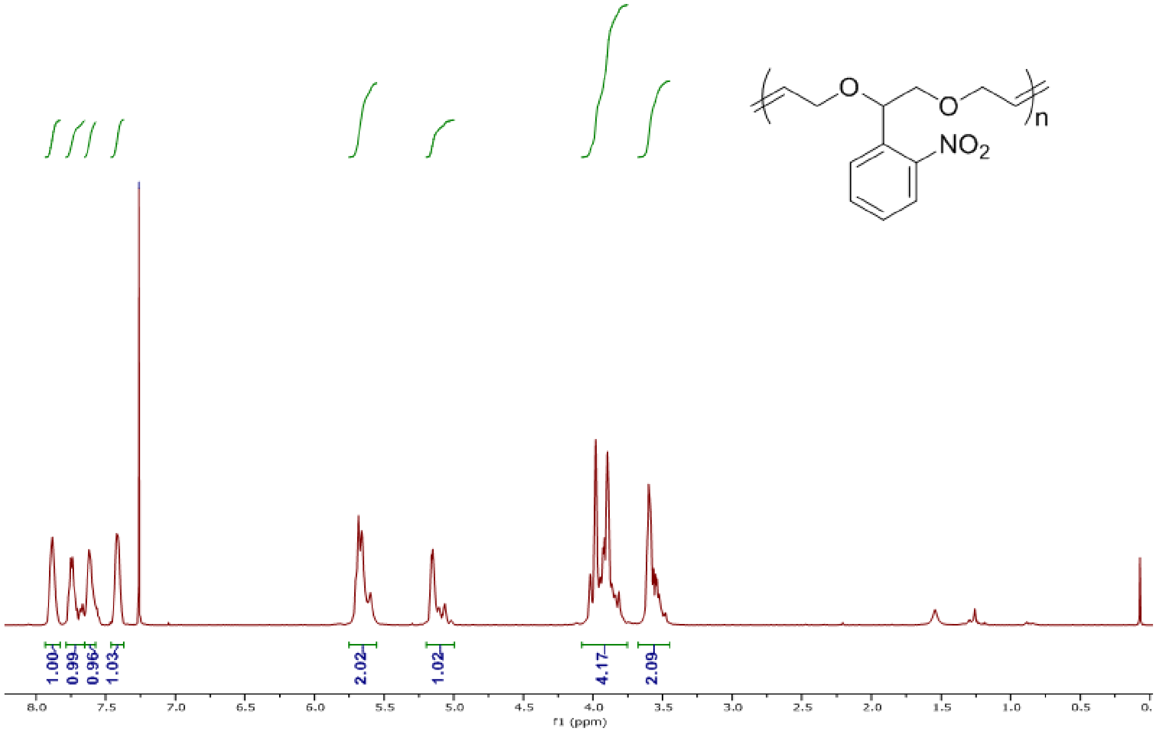

Figure **2-7**: ^{1}H NMR (500 MHz/CDCl$_3$) spectrum of *o*-nitrobenzyl dioxocin polymer.

2.3 Degradation of poly(*o*-Nitrobenzyl dioxocin)

The polymer can be degraded under 365 nm UV light irradiation (Figure 2-8). During degradation, the nitro group will transform into nitroso group, form ketone group and get a non-toxic product with (E)-butene-1,4-diol. Poly(*o*-Nitrobenzyl dioxocin) (7 mg) is dissolved in CDCl$_3$ (700 mL) in a NMR tube, put it under 365 nm UV light (light intersity: 20 mW/cm^2) to see its ^{1}H NMR spectrum under different irradiation time.

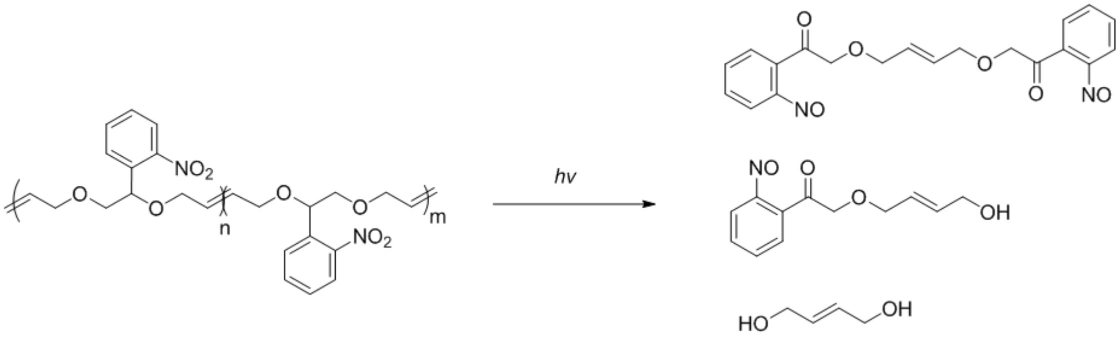

Figure **2-8**: Degradation of poly(o-nitrobenzyl dioxocin).

CHAPTER III

Results and discussions

3.1 Degradation process of poly(o-nitrobenzyl dioxocin)

To proof the photodegradability of poly(o-nitrobenzyl dioxocin), the polymer is dissolved in $CDCl_3$ under 365 nm UV light and be irradiated for 5 min, 15 min, 30 min, 60 min and 90 min. Through ^1H NMR spectrum of different irradiation time, we can get the information that polymer has changed after UV light irradiation. The ^1H NMR spectrum of degradation shows on Figure 3-1.

We can see from Figure 3-1; 0 min is the ^1H NMR spectrum of polymer before irradiation. Begin irradiation, some new signals at following chemical shifts appear such as 4.13 ppm, 4.18 ppm, 4.25 ppm, 4.56 ppm, 5.00 ppm, 5.78 ppm, 5.89 ppm, 6.40 ppm, 5.90 ppm, 9.62 ppm and some signals disappear like 3.5 ppm, 4.0 ppm, 5.23 ppm and 5.65 ppm during the irradiation process. Also, from the degradation process, our polymer has changed after UV light irradiation. But its degradability still needs to further verify.

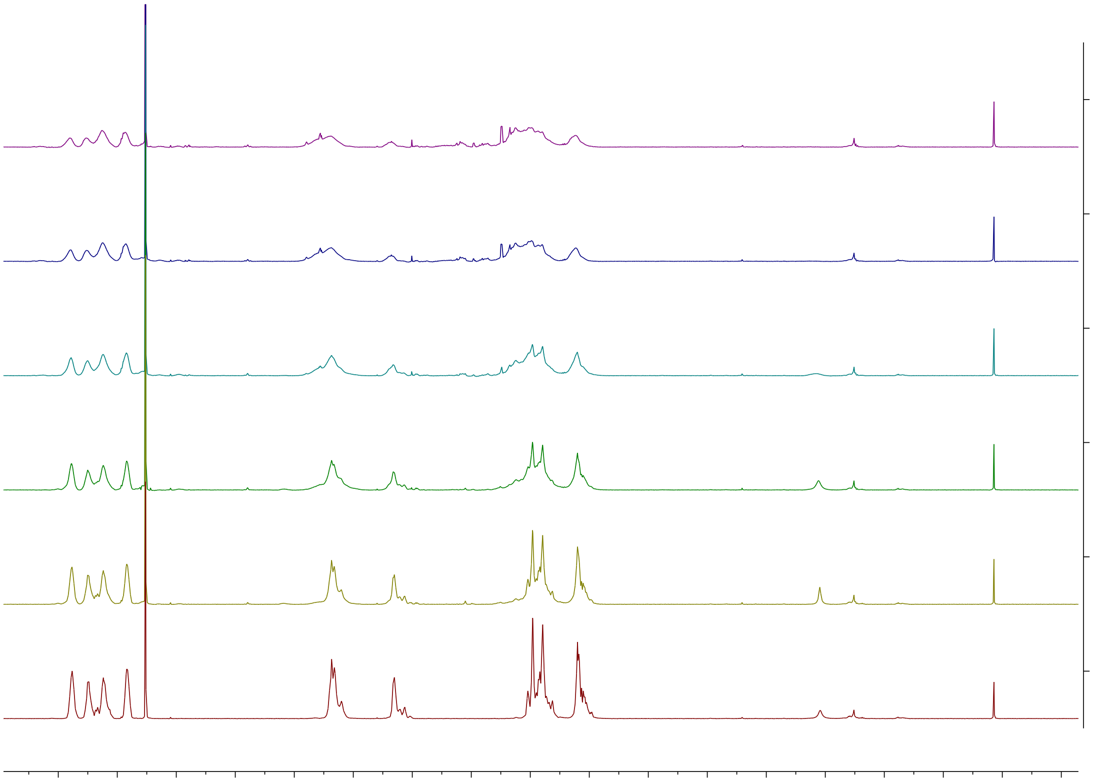

Figure **3-1**: ^{1}H NMR (500 MHz/CDCl$_3$) spectra of poly(o-nitrobenzyl dioxocin) under different UV light irradiation time.

3.2 GPC spectrum of before and after irradiation

Successfully changed under UV light irradiation indicate that the *o*-nitrobenzyl group can be cleaved under irradiation. Then we dissolved our crude polymer (polymer without purification) and the product after irradiation in THF solvent to go through the GPC. Figure 3-2 is the GPC curve before and after UV light irradiation for poly(o-nitrobenzyl dioxocin) and Table 3-1 is the molecular weights and dispersity change before and after irradiation.

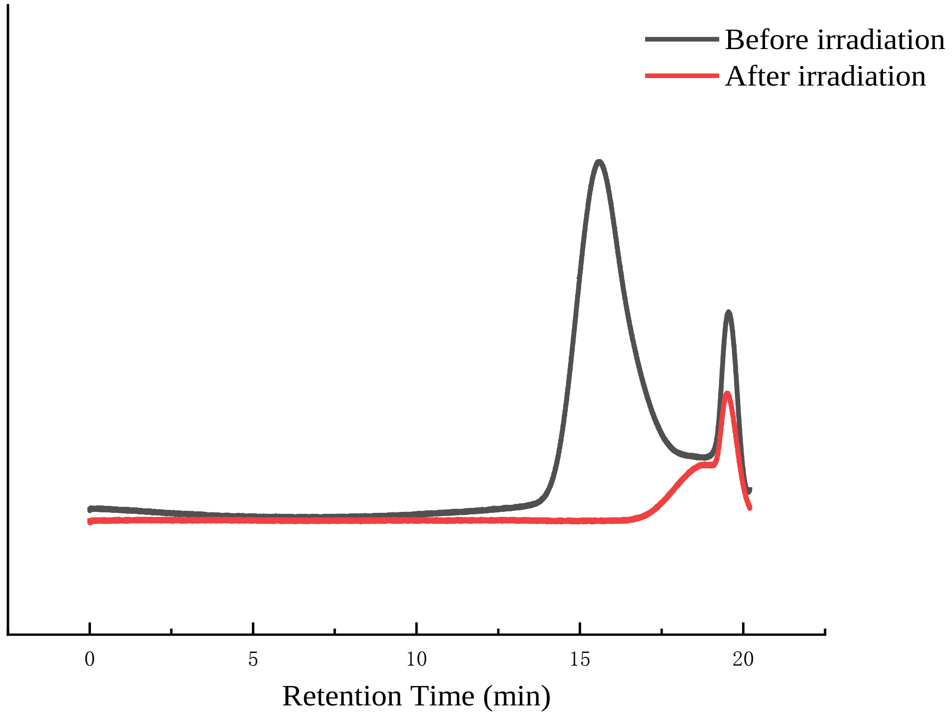

Figure **3-2**: GPC trace of poly(*o*-nitrobenzyl dioxocin) before and after UV light irradiation.

	Before irradiation	**After irradiation**
M_n	12.6 kDa	448 Da
M_w	23.6 kDa	810 Da
PDI	1.87	1.81

Table **3-1**: Molecular weights and dispersity of poly(*o*-nitrobenzyl dioxocin) before and after UV light irradiation.

From GPC curve, the peak around 16 mins disappeared after irradiation which indicate that the polymer degraded into monomers and oligmers. The Mn of polymer before irradiation is 12.6kDa, Mw is 23.6kDa and PDI is 1.87. The Mn after irradiation is 448Da, Mw is 810Da. From Table 3-1, the Mn, Mw are significantly reduced which verified the polymer has been degraded after UV light irradiation.

3.3 UV-vis spectrum of before and after irradiation

To double verify the photodegradable properties of poly(o-nitrobenzyl dioxocin), we use UV-vis spectroscopy to check. Figure 3-3 is the UV-vis curve.

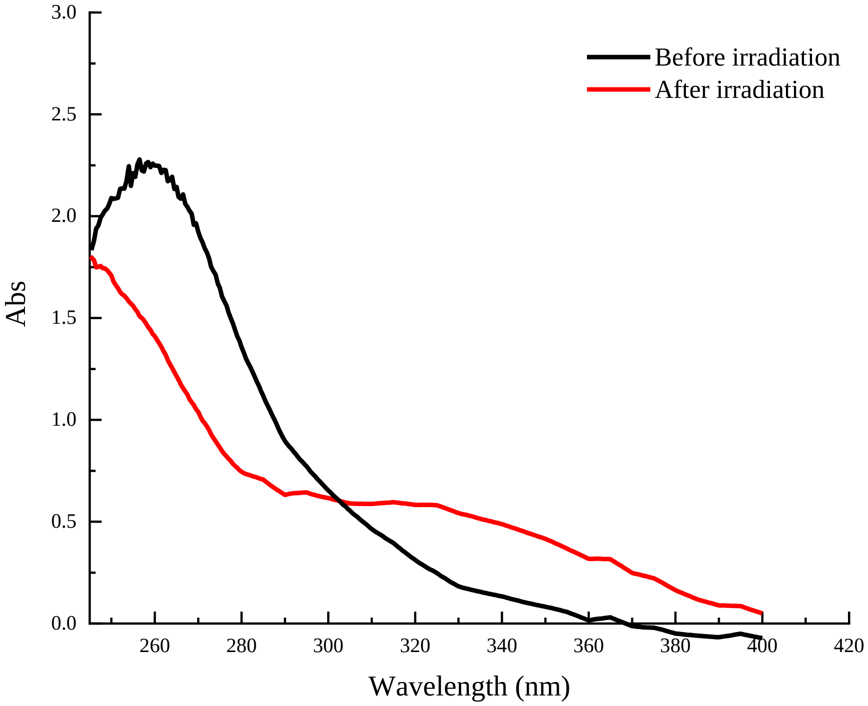

Figure **3-3**: UV-vis spectrum of poly(*o*-nitrobenzyl dioxocin) before and after UV light irradiation.

The UV-vis curve shows that a sharp peak around 260nm decreases and a broad peak around 330nm increases which also confirmed about the degradation of poly(o-nitrobenzyl dioxocin). Also, absorption at smaller wavelength suggests that 260 nm lamp could accelerate the degradation process of poly(o-nitrobenzyl dioxocin).

CHAPTER IV

Conclusion

Degradable polymers can be broken down into unharmful substances after use and can effectively reduce the pressure on our environment. We incorporate o-NB group as a part of eight-member ring to design a monomer which can be polymerized through chain-growth and have photodegradable properties that are satisfied with the principle of green chemistry.

We have also characterized this photodegradable ROMP polymer through ^{1}H NMR, GPC and UV-vis spectrum. In addition, photodegradation study shows the polymer can be degraded under UV irradiation.

CHAPTER V

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