ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

WHITE LED INDUCED DEGRADATION OF POLYACRYLATES AS A GREEN ALTERNATIVE FOR POLYMER RECYCLING

M.Sc. THESIS

Yüsra Bahar ÇAKIR

Department of Chemistry

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JUNE 2023

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

POLİMER GERİ DÖNÜŞÜMÜNDE YEŞİL BİR ALTERNATİF OLARAK POLİAKRİLATLARIN BEYAZ LED IŞIĞI ALTINDA BOZUNMASI

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HAZİRAN 2023

Yüsra Bahar Çakır, a M.Sc. student of İTU Graduate School student ID 509211277, successfully defended the thesis/dissertation entitled "Whıte Led Light Induced Degradation of Polyacrylates as a Green Alternative for Polymer Recycling", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 24 May 2023
Date of Defense : 19 June 2023

To my loved ones,

FOREWORD

Firstly, I would like to thank Prof. Dr. Yusuf Yağcı and remember him with love. It was truly an honor for me to begin my academic life with his mentorship. He was a remarkable scientist. His passing deeply affected me. I am filled with immense sadness and a sense of loss. My academic journey will be difficult without his guidance and enjoyable personality. I will do my best to carry on his legacy and continue my journey with his teachings. He will always remain an important role model and a source of inspiration for me. May his soul rest in peace.

I would secondly like to thank Prof. Dr. Barış Kışkan. I am thankful to him for enabling me to continue my work under his supervision. Without his guidance, I would not have been able to complete this thesis. He guided me throughout my thesis with the best way and kindness.

I would like to thank my teacher, my colleague Hüseyin Cem Kılıçlar. I am grateful for what he has taught me during this study, the advice regarding academic life, and the support he has provided me in every difficulty. Whenever I needed help, he approached me like a big brother and guided me with his experience.

I would like to thank my family for the opportunities they provided me during my education and for their endless support throughout my childhood and my entire life.

I also thank my past and present coworkers at Yağcı Group especially, Zeynep Deliballı, Cansu Aydoğan, Zeynep Arslan, Emirhan Gençosman, Kerem Kaya, Ragıp Talha Uzun, Gizem Güngör, Zehra Gül Çoban Ayaztekin, Azra Kocaarslan Ahmetali, Sevinç Gülyüz, Emine Yılmaz, Cansın Birsen Buldum, Tuğberk Tabak, Ahmet Şefizade, Büşra Nakipoğlu Bölücü for their help during my experiments. We had a great time in the laboratory and they were very helpful in teaching me about the laboratory.

I present my gratitude to the Scientific Research Projects Coordination Unit of Istanbul Technical University for their financial support to this project (Project Number: TYL-2022-44200). Also, I would like to thank The Scientific and Technological Research Council of Turkey (TUBITAK) (220N159) project for financial support.

June 2023

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ABBREVIATIONS

AIBN : 2,2'-azobis(isobutyronitrile)
ATRP : Atom Transfer Radical Polymerization
CRP : Controlled Radical Polymerization
CT : Charge Transfer
CTA : Chain Transfer Agent
DSC : Differential Scanning Calorimetry
EBA : Ethyl cis-3 Bromoacrylate
ErB : Erythrosin B
EY : Eosin Y
FT-IR : Fourier-Transform Infrared Spectroscopy
GPC : Gel Permeation Chromatography
^{1}H NMR : Proton Nuclear Magnetic Resonance Spectroscopy
LED : Light-emitting Diode
LS-MS : Liquid Chromatography/ Mass Spectrometry
MCA : Methyl α-chloroacrylate
MMA : Methyl Methacrylate
NMP : Nitroxide Mediated Polymerization
PMDETA : N,N,N,N,N-pentamethyldiethylenetriamine
PMMA : Polymethylmethacrylate
PPT : 10- Phenylphenothiazine
PS : Polystyrene
PVC : Polyvinyl Chloride
RAFT : Reversible Addition-Fragmentation Chain Transfer
RDRP : Reversible Deactivation Radical Polymerization
TGA : Thermal Gravimetric Analysis
UV-vis : UV-visible Spectrophotometer

SYMBOLS

β	**:** Beta
^{o}C	**:** Degree Celcius
Đ	**:** Dispersity
$[M]_{eq}$	**:** Monomer Concentration at Equilibrium
µL	**:**Microliter
M_n	**:** The number average molecular weight
M_w	**:** The weight average molecular weight
k_p	**:** Rate Constant for Propagation
k_{dp}	**:** Rate Constant for Depropagation
K_{eq}	**:** Equilibrium Constant
T_c	**:** Ceiling Temperature
ΔG	**:** Gibbs Free Energy
ΔG^{o}	**:** Gibbs Free Energy Under Standard Conditions
ΔH	**:** Enthalpy Change
ΔS	**:** Entropy Change

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WHITE LED INDUCED DEGRADATION OF POLYACRYLATES AS A GREEN ALTERNATIVE FOR POLYMER RECYCLING

SUMMARY

In today's world, plastic materials are used almost every day due to their advantageous properties. However, widespread use of plastics has resulted in serious environmental issues, such as the buildup of plastic waste and its damaging effects on ecosystems. Efforts are underway to find effective recycling methods for widely used polymers as part of the journey towards a greener and more sustainable world, aiming to reduce this dependence. The topic of enhancing the sustainability of polymers is at the forefront of the discipline of polymer science and engineering, and it includes a variety of strategies, from mechanical recycling to degradation and chemical recycling. Poly(methyl methacrylate) (PMMA) is a polymer that holds great significance within the realm of materials due to its remarkable combination of high-impact strength, optical clarity, and lightweight characteristics. Various applications of PMMA have resulted in considerable consumption and generation of noticeable amounts of waste. By 2027, it is projected that the consumption of polymers will reach a level of 4 million tons per year and as the years pass, it could further increase. Since PMMA does not have a hydrolysable main chain, depolymerization or degradation requires advanced recycling methods. These methods involve some requirements that are both economically and environmentally harmful, such as high temperatures and heavy toxic metal catalysts. Despite the challenging conditions, the research conducted contributes to polymer recycling. However, replacing these requirements with some green alternatives is highly appealing. Photochemical reactions, with advantages such as being environmentally friendly and low energy consumption, have gained attention both in industry and academia. The idea of adapting light-induced reactions to this field and using a catalyst other than metal-based catalysts, which are another environmental pollutant factor, shed light on this study.

In this study, we take advantage of the efficient properties of light in the field of degradation. We present a novel approach utilizing a white LED light source and a metal-free method for the degradation of PMMA derivatives that contain halogen in the main chain. A copolymerization incorporated PMMA derivatives containing light-triggerable halogen atoms into the main chain. The Reversible Addition-Fragmentation Chain Transfer (RAFT) controlled polymerization technique was employed for the synthesis of methyl methacrylate-methyl α-chloroacrylate and methyl methacrylate-ethyl cis-3 bromoacrylate copolymers. In the presence of organodyes (metal-free catalysts) the synthesized copolymers undergo efficient degradation into low molecular weight oligomers when irradiated with visible light. This study serves as a realistic approach to polymer recycling and leading to the development of more sustainable recycling methods for polymers.

POLİMER GERİ DÖNÜŞÜMÜNDE YEŞİL BİR ALTERNATİF OLARAK POLİAKRİLATLARIN BEYAZ LED IŞIĞI ALTINDA BOZUNMASI

ÖZET

Günümüzde, plastik malzemeler avantajlı özellikleri nedeniyle neredeyse her gün yaygın bir şekilde kullanıldığı görülmektedir. Ancak, plastiklerin yaygın kullanımı çevresel sorunlara yol açmıştır. Plastik atıkların birikmesi, doğal ekosistemlere ve biyoçeşitliliğe zarar veren önemli bir sorundur. Daha sürdürülebilir ve yeşil bir dünya için plastiklere olan bağımlılığın azaltılması ve plastik atıkların etkili bir şekilde yönetilmesi hedeflenmektedir. Bu amaçla, polimer bilimi ve mühendisliği alanında, mekanik geri dönüşümden polimerlerin bozunması ve kimyasal geri dönüşüme kadar çeşitli stratejiler geliştirilmektedir. Polimetil metakrilat (PMMA), yüksek darbe dayanıklılığı, optik berraklık ve hafiflik gibi dikkate değer özellikleriyle malzemeler alanında büyük öneme sahip olan bir polimerdir. Bu özellikler sayesinde PMMA, birçok farklı uygulama alanında kullanılmaktadır. Ancak, PMMA'nın yaygın kullanımı, önemli miktarda atık oluşmasına sebep olmuştur. Öngörülere göre, 2027 yılına kadar polimer tüketimi yıllık 4 milyon ton seviyesine ulaşacak ve yıllar ilerledikçe bu miktarın daha da artma eğilimi gösterecektir. Bu durum, plastik atıklarının artan bir sorun haline gelmesine yol açmaktadır. PMMA, hidroliz edilebilir bir ana zincire sahip olmadığından, geleneksel geri dönüşüm yöntemleriyle kolayca geri dönüştürülememektedir. Bu nedenle, ileri düzeyde geri dönüşüm yöntemlerinin kullanılması gerekmektedir. Ancak, bu yöntemlerin uygulanması ekonomik ve çevresel açıdan zararlı bazı gereksinimleri beraberinde getirmektedir. Yüksek sıcaklıkların kullanılması, enerji tüketimini artırırken çevresel etkileri de olumsuz yönde etkileyebilmektedir. Ayrıca, ağır toksik metal katalizörlerin kullanımı da çevre kirliliği potansiyeli taşımaktadır. Bu zorlayıcı koşullara rağmen, yapılan araştırmalar polimer geri dönüşümüne katkı sağlamaktadır. Ancak, bu gereksinimleri çevre dostu alternatiflerle değiştirmek oldukça ilgi çekici bir konumdadır. Özellikle fotokimyasal reaksiyonlar, çevre dostu olması ve düşük enerji tüketimi gibi avantajlara sahip olması nedeniyle endüstri ve akademide büyük ilgi görmektedir. Işıkla tetiklenen reaksiyonların polimer geri dönüşümü alanında kullanılması, verimli ve çevre dostu bir yöntem olarak öne çıkmaktadır. Bu çalışmanın ana fikri, fotoreaksiyonları bu alana uyarlamak ve başka bir çevre kirliliği faktörü olan metal bazlı katalizörler yerine zararsız bir katalizör kullanmaktır.Bu çalışmada, polimerlerin bozunma alanında ışığın etkili özelliklerinden faydalanıyoruz. PMMA türevlerinin ana zincirinde bulunan halojenin bozunması için beyaz bir LED ışık kaynağı ve metal içermeyen katalizörler kullanarak yeni bir yaklaşım sunuyoruz. Işığa duyarlı halojen atomlarını (klor atomları) içeren PMMA türevleri, kopolimerizasyon yoluyla ana zincire dahil edilmiştir. Metil metakrilat-metil α-kloroakrilat (MCA) ve metil metakrilat-etil cis-3 bromoakrilat (EBA) kopolimerlerinin sentezi için Tersinir Katkı-Fragmentasyon Zincir Transferi (RAFT) kontrollü polimerizasyon tekniği kullanılmıştır. Metal içermeyen organik boyar maddelerin (katalizörlerin) varlığında, sentezlenen kopolimerler, görünür bölge dalga boyunda verimli bir şekilde düşük molekül ağırlıklı

polimer zincirlerine bozunmuştur. Sentezlenen kopolimerlerin fiziksel özellikleri ve yöntemin kinetiği DSC, TGA, ^{1}H-NMR ve GPC analizleriyle araştırılmıştır. Ortam sıcaklığında %80'e kadar bozunma gözlemlenmiştir. Bu çalışma, polimer geri dönüşümü için gerçekçi bir yaklaşımdır ve polimerler için daha sürdürülebilir geri dönüşüm yöntemlerinin geliştirilmesine öncülük etmektedir.

1. INTRODUCTION

Polymer recycling is the process of recovering used or waste polymers and transforming them into new materials. Managing waste made of polymer has become a major concern for society due to the extensive use of polymer materials in many industries.[1] Some of the polymeric structures are not biodegradable. As such, they remain in the environment for hundreds of years. Due to their non-biodegradable nature, they pose a significant threat to the environment. Several kinds of environmental issues, including pollution of land and oceans, can result from improper management of solid polymer waste.[2] Furthermore, it may cause landfills to release harmful gases like methane and carbon dioxide, which will exacerbate climate change. Thus, proper management of solid polymer waste can help minimize the harmful effects of plastic waste on the environment.[3] In addition to the environmental impact, solid polymer waste also affects public health.[4] Improper disposal of plastic waste can lead to the accumulation of waste in public spaces, causing aesthetic problems, and becoming a breeding ground for disease-carrying pests. Besides, burning plastic waste, which is a common practice in some areas, can release toxic fumes that can be harmful to human health. Overall, managing solid polymer waste properly not only helps the environment but also promotes public health.[5] The recycling of polymers is important for eliminating some of the problems mentioned above. There are three types of recycling of polymers: mechanical, energy, and chemical.[6] First, mechanical recycling involves the sorting and cleaning of plastic waste to produce pellets or flakes, which can be used to make new plastic products. Although this method is well-known and quite simple, it is limited by the fact that it can only be used to recycle specific types of plastics. [7] The second one, energy recycling, involves the conversion of plastic waste into energy through processes such as incineration or gasification. While this method can help to reduce waste, it can also release harmful emissions into the atmosphere. The last polymer recycling technique, chemical recycling, use chemical reactions to break down polymer molecules into their constituent smaller parts.[8, 9] Chemical recycling has the benefit of being able to

recycle plastics that are difficult to recycle mechanically. It also has the potential to reduce the amount of plastic waste that ends up in landfills or the sea.This process is still in its early stages of development but has the ability to recycle a much wider amount of polymers than the other alternatives.

Currently, the reduction of plastic usage is a important focus as we moving towards a greener and more sustainable world, particularly given the increasing dependence on conventional plastics in our daily lives. Despite ongoing efforts to develop degradable alternatives for the majority of plastics, there are serious challenges in scaling up production and the dependency on conventional plastics continues to increase.[10] Therefore, there have been efforts to study the degradation and depolymerization reactions of the most commonly used polymers, such as polyvinyl chloride (PVC), polystyrene (PS), and polymethylmethacrylate (PMMA). [11-13]

Various research groups worldwide are currently working on developing new and improved methods to degrade or depolymerize well-known polymers under milder conditions. Depolymerization has the advantage of enabling research teams to gain the monomers used in waste polymers. [14] On the other hand, degradation may utilize similar catalytic systems, but it may require functionalized polymer chains to produce oligomers by breaking down the initial polymer chains.[15]Generally, the methods used to achieve depolymerization or degradation involve the adaptaition of controlled radical polymerization techniques such as RAFT and atom transfer radical polymerization (ATRP) into the subject area.[16]. When we take a look at the notable studies of some research groups, we see that some challenging conditions are required such as high temperature, toxic metal catalysts, and long reaction times. Achieving good degradation and depolymerization yields through a more environmentally friendly and economical approach seems quite interesting. The schematic representation of depolymerization and degradation is shown in Figure 1.1.

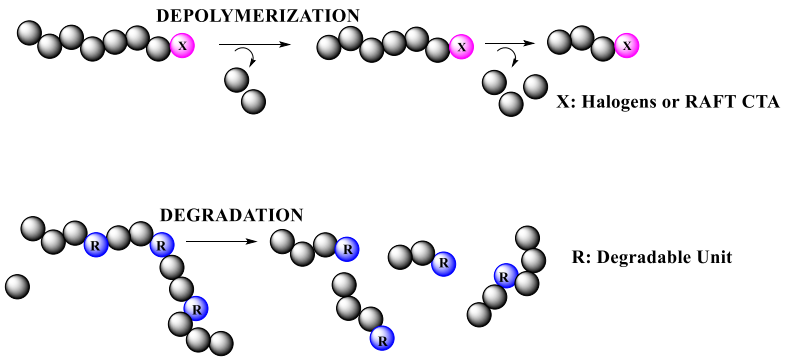

Figure 1.1 : Schematic illustration of depolymerization (a), and degradation (b).

Photochemical approaches were extensively utilized by our research group to synthesize several polymers such as polyethers, polyamides, polyesters, polycarbazoles, polydopamines, polythiophene derivatives, and poly(phenylene methylenes).[17-25] Our research group has also previously applied this approach to the field of degradation/depolymerization reactions due to fast reaction time, high conversion rates, and the environmentally friendly nature of photopolymerization reactions.[26, 27] In addition to this advantageous approach, the manganese decacarbonyl ($Mn_2(CO)_{10}$) catalyst, which is known for halogen abstraction and homolytically cleave ability with irradiation, [28, 29] has been used for catalyzing degradation and depolymerization reactions. Even at room temperature, this technique achieved good degradation yields. However, heat was needed to catalyze the depolymerization. When we examine other reported studies, we can see that toxic and metal-containing catalysts like copper, iron complexes and ruthenium are used to catalyze depolymerization and degradation. (studies will be discussed in detail in the theoretical part). In this thesis, we contemplated on how we could achieve polymer recycling, which is a current problem, by taking a more environmentally friendly approach.

In this thesis, broadband white LED (450 nm-800 nm) and 400 nm blue led were used in combination with eosin y (EY), erythrosin B (ErB) and 10-phenylphenothiazine (PPT) in the novel photodegradation system to overcome the requirement of heat and metal catalysts.The reactions between organo-dyes and tertiary amines in the excited state, known as charge transfer (CT) reactions, is widely known and established. In order to obtain polymers which can be degraded by visible light at room temperature and possess comparable physical properties with PMMA, two copolymers consisting of methyl methacrylate (MMA), methyl α-chloroacrylate (MCA), and ethyl cis-3 bromoacrylate (EBA) were synthesized by RAFT. Synthesized PMMA copolymers ((PMMA-*co*-PMCA) and PMMA-*co*-PEBA)) are degraded to low molecular weights by white light and organo photocatalysts. This promising method could trigger the development of more environmentally friendly recycling techniques in the near future.

2. THEORETICAL PART

The major concern of this thesis is to degrade the commonly used PMMA derivatives, which synthesized by the controlled polymerization method (RAFT), into smaller chains using non-toxic catalysts (organodyes) at ambient conditions.

2.1 Reversibility of Polymerization

Reversibility and thermodynamics are fundamental concepts in polymerization processes. Although it has been known that polymerization reactions can be reversible since the beginning of the polymer chemistry, Dainton and Ivin's article (1948) provided the first complete thermodynamic explanation of the reversibility of polymerization.[14, 30] Polymerization refers to the chemical reaction in which monomers join together to form a polymer chain. Reversibility in polymerization refers to the ability of the polymerization reaction to proceed in both the forward (polymerization) and reverse (depolymerization) directions. A negative Gibbs free energy value (ΔG) denotes a preference for polymerization, whereas a positive ΔG value denotes a preference for depolymerization. The ceiling temperature, T_c, is the temperature at which $\Delta G = 0$. When $\Delta G = 0$, the forward (polymerization) and reverse (depolymerization) reactions are in equilibrium, meaning that the rate of polymerization is equal to the rate of depolymerization. Heating a polymer above its ceiling temperature (T_c) can induce depolymerization due to the general trend of negative enthalpy (ΔH) and negative entropy change ($-T\Delta S$) in polymerizations. This leads to the conclusion that by heating the polymer, the equilibrium is shifted towards depolymerization, causing the monomer to be removed from the system until no polymer remains.[14, 31-34] The equations of ΔG (equation 1), ΔG^o (Gibbs free energy under standard conditions (equation 2), and equilibrium constant (K_{eq}) (equation 3) (where k_p represents the rate constant for propagation, k_{dp} represents the rate constant for depropagation, and $[M]_{eq}$ represents the monomer concentration at equilibrium) are provided below.

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

$$\Delta G^{\circ} = -RT\ln K_{eq} \quad (2)$$

$$K_{eq} = k_p / k_{dp} = 1/[M]_{eq} \quad (3)$$

2.1.1 Depolymerization from controlled polymerization methods

Controlled radical polymerization (CRP), also known as reversible deactivation radical polymerization, has revolutionized the field of polymer chemistry by offering the ability to produce well-defined polymers with adjustable molecular weight, molar mass distributions, block sequence, and structure.[35-38] In addition to polymerization, these two methods also hold significant importance in depolymerization.

2.1.1.1 Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is a type of polymerization known as reversible deactivation radical polymerization (RDRP). It was discovered independently by Matyjaszewski and Sawamoto in 1995.[39, 40] This technique enables the production of controlled polymers with specific molecular weights and tighter molecular weight distribution ($M_w/M_n < 1.5$), surpassing the outcomes achieved with conventional free radical polymerization. ATRP involves the use of a transition metal catalyst, typically a copper or iron complex, and a halogen-containing initiator or dormant species. The catalyst facilitates the transfer of a halogen atom between the dormant species and the growing polymer chain, enabling controlled growth of the polymer. Traditional ATRP relies on a transition metal complex with a low oxidation state, often CuX/L (copper is commonly employed, although other metals such as iron, ruthenium, and nickel are also frequently utilized in ATRP, whereas X = Cl or Br, L = ligand), in combination with a suitable alkyl halide, denoted as R-X. The initiation process involves a rapid equilibrium between CuX and R-X, resulting in the reversible formation of CuX_2 and R•. In this dynamic state, monomers can react with the alkyl radical, leading to dormant chains through halogen abstraction, yielding CuX and Pn-X. This equilibrium favors the reverse reaction, producing chains with R as the α-chain and halide as the ω-chain-end functionalities. The fast initiation and the reversibility of halide abstraction-donation steps allow for the production of polymers with desired molecular weights and narrow molecular weight distributions.[41, 42] Methacrylic-

type monomers, which have polymeric side chains (referred to as macromonomers) or large groups, have played a crucial role in the advancement of depolymerization techniques for ATRP.[43] A simple ATRP mechanism is depicted in Figure 2.1, which includes some conditions for polymerization and depolymerization.

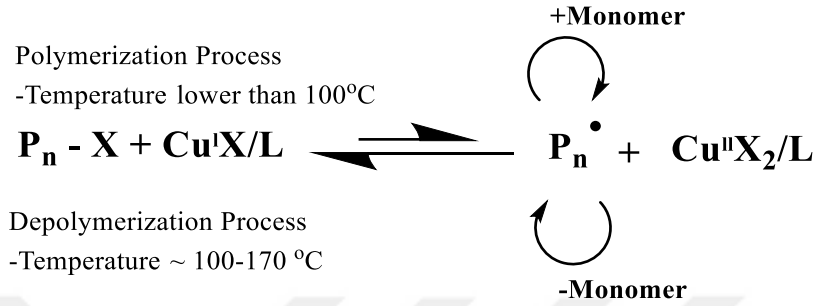

Figure 2.1 : Brief ATRP mechanism highlighting the conditions for polymerization and depolymerization.

2.1.1.2 Reversible addition/fragmentation chain transfer polymerization.

Reversible Addition/Fragmentation Chain Transfer (RAFT) polymerization is considered one of the most efficient techniques to introduce living characteristics into radical polymerization by employing a reversible deactivation process. The first report on RAFT (Reversible Addition/Fragmentation Chain Transfer) polymerization was published in 1998 by Moad, Rizzardo, Thang, and co-workers[43]. The mechanism of RAFT polymerization is significantly different from other controlled polymerization methods (such as ATRP and NMP).[44, 45] RAFT polymerization follows the mechanism as demonstrated in Figure 2.2. In RAFT, the reversible deactivation of polymer chains is caused by reversible chain-transfer events rather than reversible termination. Nonetheless, this method is highly efficient in generating precisely defined polymers and can be considered one of the most resilient techniques for controlled radical polymerization, particularly in terms of its ability to accommodate various monomer functionalities. Usually, the chain-transfer agent (CTA) used in RAFT polymerization is a compound with a thiocarbonylthio (Z–C(═S)S–R) structure. The Z-group plays a significant role in determining the reactivity of the C═S bond towards radicals and the stability of the intermediate radical formed. On the other hand, the R-group acts as a suitable leaving group with sufficient reactivity to initiate the propagation of new polymer chains. Similar to depolymerization systems that are based on ATRP, RAFT polymethacrylates provide the capability to control and access

chain-end radicals as needed. When thermodynamically favorable conditions are met, these radicals undergo depropagation to produce monomers.[46]

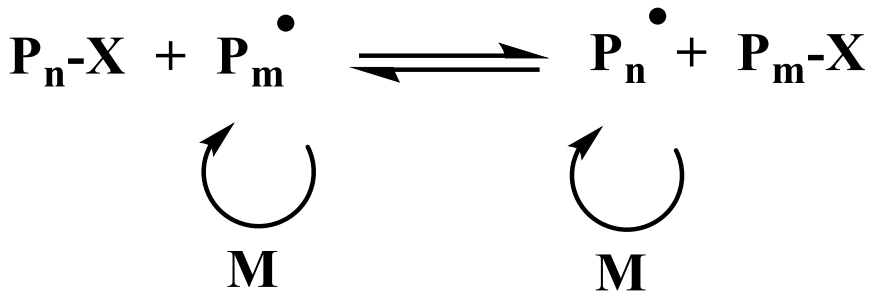

Figure 2.2 : Mechanism of reversible addition/fragmentation chain transfer (RAFT).

2.2 Polymer Degradation

Polymer degradation is a term that refers to the modifications of polymer properties, including tensile strength, color, shape, and molecular weight, as well as the properties of products made from polymers. This alteration occurs due to some factors such as heat, light, chemicals, etc.[47-49] While the importance of developing sustainable polymer materials that can be recycled or disposed of without causing harm to the environment is increasing, polymer degradation has attracted attention for the polymer design, because it could allow on-demand degradation after use while the material stability is ensured. These factors might not be suitable for the degradation of every polymer. The polymer stability of high-volume polymers stems from the strong carbon-carbon bonds present in the polymer backbone.This degradation preventive state in polymer backbones can facilitate degradation through the presence of certain groups that are triggered by heat or light. The presence of these triggerable groups provides a mechanism for controlled or on-demand degradation, allowing the polymer to retain its stability during normal usage but undergo controlled degradation when subjected to specific environmental conditions. A common occurrence in the degradation of polymers involves the generation of radicals on the polymer backbone, which is then followed by the breaking of bonds via β-scission.[50-52] β-scission refers to the cleavage of a bond adjacent to a carbon atom in the polymer backbone. This bond cleavage occurs between the carbon atom and an adjacent atom or group, leading to the formation of two free radicals or other reactive species. Generally, these reactions are often initiated by the presence of radicals or high-energy stimuli such as heat or light. These reactions play a significant role in the degradation of polymers.

2.3 Poly(methylmethacrylate) (PMMA)

PMMA is a synthetic polymer from the methyl methacrylate monomer that belongs to the acrylic family of polymers.[53] PMMA was first identified in the early 1930s by British chemists Rowland Hill and John Crawford. Soon after, in 1934, German chemist Otto Rohm utilized PMMA for its initial practical application. [54] PMMA is renowned for its exceptional transparency, high impact resistance, and weather resistance, making it a popular alternative to glass in various applications. PMMA is preferred in many industries,such as optical lenses, automotive components, and medical devices, due to its exceptional properties.[55-57] PMMA can be synthesized from its monomer utilizing by different methods of polymerization such as free radical and anionic initiations in bulk, solution, suspension, and emulsion techniques.[31, 58] In addition, there are several techniques and variations of polymerization methods used to control polymer properties including molecular weight, and molecular weight distribution. Some of these polymerization techniques involve controlled radical polymerization methods like ATRP, RAFT, and NMP.[40, 59, 60]

PMMA has been widely used in various fields due to its superior properties. By 2027, it is anticipated that the consumption will escalate to approximately 4 million tons per year. This significant increase in consumption raises concerns about the potential for excessive waste generation, emphasizing the urgent need for recycling. However, recycling has persistently posed challenges due to the scarcity of environmentally friendly approaches. PMMA cannot be easily depolymerized/degraded by hydrolysis or transesterification due to the presence of carbon-carbon bonds along the polymer chain. However, recent studies have focused on the depolymerization of polymethacrylate derivatives, which require high temperatures of approximately 300°C and the use of toxic chemicals. One of the goals of scientists in the near future is to degrade or depolymerize PMMA without the need for heat and using environmentally friendly chemicals, considering its widespread use and the need for sustainable waste management strategies in the polymer industry.

2.3.1 Degradation/Depolymerization of PMMA

Conventional methods of degradation/depolymerization of polymers usually involve cleavage of covalent bonds in the main chain that contains hetero atoms like acetal, ester, and carbonate.[61-63] However, depolymerization/ degradation of some

polymers which formed by acrylic monomers is more difficult due to the fact that the carbon-carbon bond is non-hydrolazable. Therefore, a hydrolyzable group is needed either at the end of the polymer chain or at the main chain in order to depolymerize or degrade such polymers. There are more examples in the literature regarding the thermal depolymerization and degradation of PMMA, but there are very few studies conducted using light assistance. In this field, several renowned research groups have reported detailed studies. These studies will be examined in sequence.

Ouchi initially conducted efforts to degrade and depolymerize modified PMMA derivatives using catalysts based on ruthenium. [64] Firstly, they demonstrated the depolymerization of chlorine-terminated poly(methyl methacrylate) (PMMA–Cl),which was synthesized using the ATRP technique, with the assistance of metal catalysts (ruthenium). In this case, the carbon-halogen bond played a pivotal tole as a triggering factor for depolymerization. Methylmethacrylate (MMA) monomer was gradually produced as a result of depolymerization using the PMMA-Cl/ruthenium catalyst/tributylamine system in a under reduced pressure system at 100 ^{o}C. The evidence for monomer formation was obtained by observing the peaks of olefinic protons in the ^{1}H NMR spectrum immediately after the reaction mixture was heated (Figure 2.3). Furthermore, the gradual increase in the intensity of these peaks throughout the reaction time strengthened this notion. This study contributes to advancing our understanding of depolymerization mechanisms of functionalized PMMA derivatives and also presented the first demonstration of depolymerizing a pre-synthesized and purified polymethacrylate that was synthesized using ATRP.

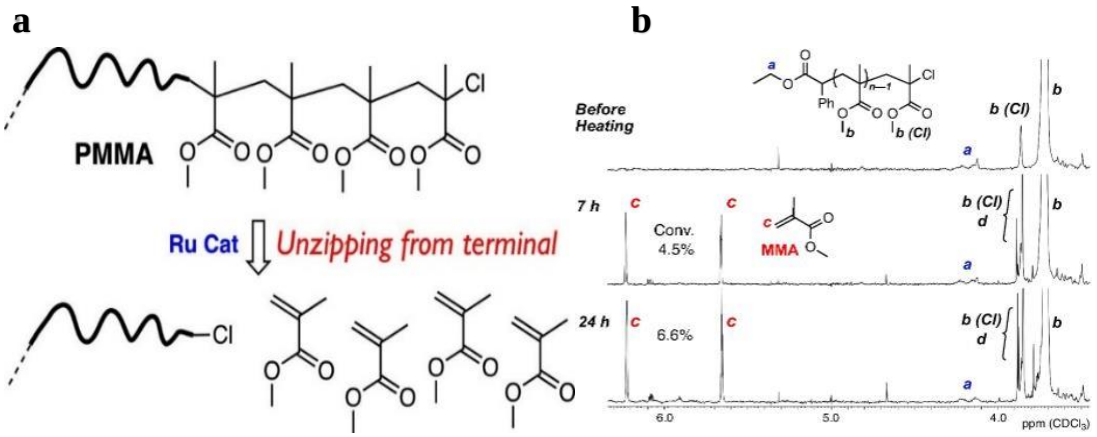

Figure 2.3 : Depolymerization illustration of PMMA-Cl (a), ^{1}H-NMR spectra for characterization of monomer generation (b) [64].

After demonstrating in their depolymerization publication that the C-halogen bond plays a triggering role in depolymerization, Ouchi hypothesized that this bond would have the same effect on the polymer chain and published a paper on degradation. [65] In this study, the importance of incorporating trigger units into the polymer chain for degradation and depolymerization has been emphasized. Then, a copolymer of (MMA/MCA) was synthesized through RAFT copolymerization where the alpha substituent of the PMMA backbone was partially changed with chlorine. For degradation, polymers with different molecular weights, monomer, and comonomer ratios were reacted with a ruthenium complex and amine structure (*n*-Bu_3N) at 100 ^oC for 4 hours. The degradation efficiency was monitored by GPC (Gel Permeation Chromatography), and significant shifts toward low molecular weight regions were observed. Additionally, several control experiments were conducted, including subjecting a straight PMMA chain to the same reaction. As a result, no change in molecular weight was observed. The GPC results for this study are shown in Figure 2.4.

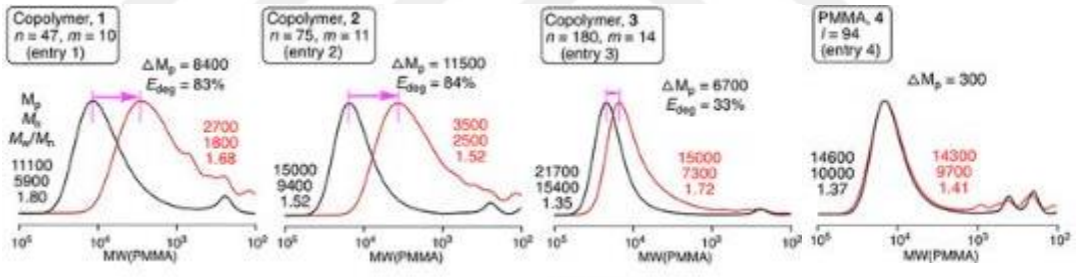

Figure 2.4 : GPC chromatograms of (MMA-MCA) copolymers, namely copolymer 1, copolymer 2, copolymer 3, and PMMA before degradation (black line), after degradation (red line) [65].

After, Matyjaszewski's research group made additional advancements and explored the potential of employing iron complexes, which are more environmentally friendly, as catalysts for depolymerization.[66] The iron catalysts utilized in this study consist of $FeCl_2$ combined with tetra(ethylene glycol) dimethyl ether serving as both a solvent and ligand. However, at the high temperature, the catalysts exhibited enough activity to effectively reduce the alkyl chlorine chain-end functionality, resulting in the depolymerization of chlorine-capped poly(*n*-butyl methacrylate) (PBMA-Cl) and poly(methyl methacrylate) (PMMA-Cl) macroinitiators with a conversion rate of over 70% in less than 15 minutes. The proposed mechanism is shown in Figure 2.5. These

iron catalysts used by Matyjaszewski are more economical and environmentally friendly compared to previously reported metal catalysts used in the depolymerization of polymethacrylates.

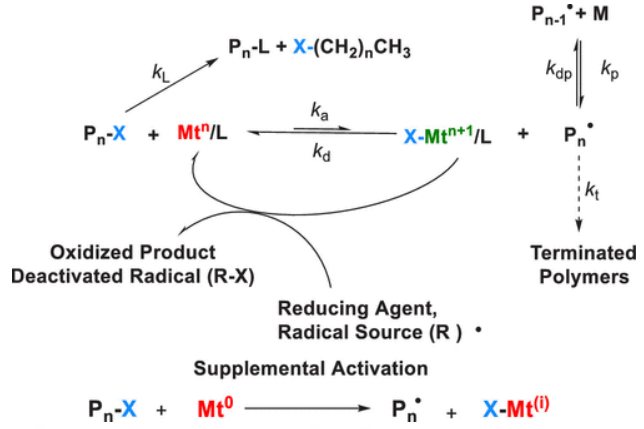

Figure 2.5 : Proposed mechanism involving ATRP with reversible propagation, activator regeneration, supplemental activation of the alkyl halide, and lactonization of the chain-end [66].

Sumerlin and co-workers investigated a depolymerization strategy for polymethacrylate that involved light assistance.[13] This approach differs from the thermal method employed by Ouchi. They aimed to enable depolymerization at lower temperatures by utilizing both heat and light. In this strategy, radicals are generated through direct photolysis of the chain transfer agent (CTA) chain-end, resembling a photoiniferter polymerization process. Evaluating the depolymerization efficiencies of certain PMMA derivatives synthesized via RAFT, it was found that PMMA with trithiocarbonate, dithiocarbamate, and *p*-substituted dithiobenzoate end groups exhibited higher depolymerization efficiencies at a lower wavelength. As can be seen from the graphical abstract presented in Figure 2.6, the depolymerization process was completed with approximately 70% yield within one hour, a relatively low temperature of 100 ^{o}C was sufficient.

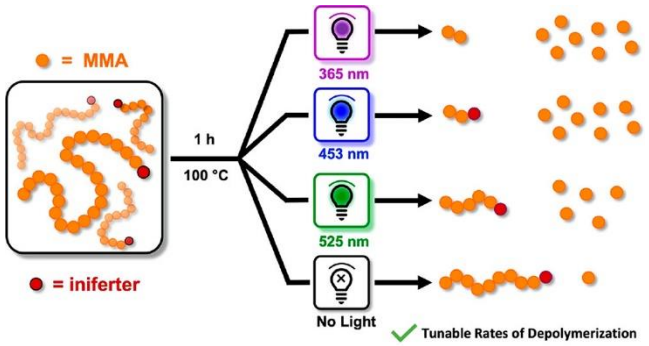

Figure 2.6 : Graphical abstract of Sumerlin's photo-assisted depolymerization [13].

Finally, Anastasaki et al. reported a depolymerization technique without a catalyst, achieving nearly complete depolymerization for both bulky and non-bulky polymethacrylates, as well as for insoluble gel-like substances synthesized through RAFT.[10] Approximately 92% depolymerization was accomplished using a dithiobenzoate end-group at 120 °C in dioxane. The interesting aspect of this process is the ability to reuse the RAFT agent after depolymerization, allowing a controlled RAFT polymerization of the regenerated monomer at 70 °C in the presence of a free radical initiator.

3. EXPERIMENTAL PART

3.1 Materials and Chemicals

Methyl methacrylate (MMA; Merck, 99%)	: used after filtration through basic alumina to remove the inhibitor and stored in the fridge.
Methyl α-chloroacrylate (MCA; Thermo Scientific™, 98+%)	:used after filtration through basic alumina to remove the inhibitor and stored in the fridge.
Ethyl cis-3 bromoacrylate (EBA; Aldrich, ≥99.0%)	:used after filtration through basic alumina to remove the inhibitor and stored in the fridge.
Toluene (Aldrich, 99.7%)	:dried and purified before use.
N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA; Aldrich, 99%)	:dried and purified before use.
Hexane (Aldrich, 98%)	:dried and purified before use.
2-cyano-2-propyl dodecyl trithiocarbonate (RAFT Agent; Aldrich, 97% HPLC)	:used as received and stored in the fridge.
10-phenylphenothiazine (PPT; Aldrich, ≥95%)	:used as received and stored in the dark.
Eosin Y (EY; Merck, 99%)	:used as received and stored in dark.
Erythrosin B (ErB; Merck, 99%)	:used as received and stored in dark.
2,2'-azobis(isobutyronitrile) (AIBN; Wako, 98%)	:used as received.

3.2 Equipments

3.2.1 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained on a TOSOH EcoSEC GPC system equipped with an autosampler system, a temperature-controlled

pump, a column oven, a refractive index (RI) detector, a purge, and degasser unit and TSK gel superhZ2000, 4.6mm ID x 15 cm x 2cm column. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 $mL.min^{-1}$ at 40°C. RI detector was calibrated with polystyrene standard, and all the data were analyzed by the Eco-SEC Analysis software.

3.2.2 ^{1}H Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of the P(MMA-*co*-MCA) and its degradation products were recorded at room temperature at 500 MHz on an Agilent VNMRS 500 spectrometer in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard.

3.2.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on a PerkinElmer Diamond DSC. A typical DSC sample was prepared 2–5 mg in a 30 μL aluminum pan.

3.2.4 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was performed on a PerkinElmer Diamond TA/TGA with a heating rate of 10 $^{o}C\ min^{-1}$ under nitrogen flow (200 $mL.min^{-1}$).

3.2.5 Liquid chromatography/ Mass spectrometry (LS/MS)

High-resolution LC/MS analysis was performed using an Agilent Technologies Q-TOF LC/MS System equipped with a HiP sampler, binary pump, and column comp. and Q-TOF. TOF/Q-TOF Acquisition parameters are: a dual ESI ion source, gas temp 300 °C, gas flow 10 L min^{-1} and nebulizer 40 psig.

3.2.6 UV-visible spectrophotometer (UV-vis)

UV−vis analyses were performed with a Shimadzu UV-1601 double-beam spectrometer sporting a deuterium lamp and a 50 W halogen lamp with a light emission spectrum of 190 - 1100 nm.

3.2.7 Infrared spectrophotometer (IR)

Fourier-transform infrared (FT-IR) analyses were performed on a Perkin-Elmer FTIR Spectrum One B spectrometer.

3.3 Preparation Methods

3.3.1 Synthesis of copolymers

3.3.1.1 Synthesis of P(MMA-*co*-MCA) by RAFT

P(MMA-*co*-MCA) was synthesized by RAFT. Methyl α-chloroacrylate (0.2 mL, 1.97 mmol), methyl methacrylate (2.03 mL, 19 mmol), 2-cyano-2-propyl dodecyl trithiocarbonate (34.8 µL, 0.097 mmol), toluene (7.7 mL), AIBN (3.1 mg, 0.018 mmol) were placed into a dried Schlenk tube under the nitrogen ambient. The reaction mixture was degassed by three freeze-pump thaw cycles to remove oxygen from the reaction media, sealed off, and placed in an oil bath. Polymerization was held at 85 ℃ for 6 hours. At the end of copolymerization, polymers were precipitated in hexane and dried under reduced pressure for further use.

3.3.1.2 Synthesis of P(MMA-*co*-MCA) by free radical polymerization

Methyl α-chloroacrylate (0.2 mL, 1.97 mmol), methyl methacrylate (2.03 mL, 19 mmol) toluene (7.7 mL), AIBN (3.1 mg, 0.018 mmol) were placed into a dried Schlenk tube under the nitrogen atmosphere. Polymerization was held at 85oC for 6 hours in an oil bath. The obtained mixture was precipitated in hexane and dried under low pressure.

3.3.1.3 Synthesis of P(MMA-*co*-EBA) by RAFT

The Schlenk tube was equipped with a magnetic stirrer and heated in vacuo with the heat gun. When the tube cooled down, it was charged with MMA (2.03 mL, 19 mmol), ethyl cis-3 bromoacrylate (0.2 mL, 1.73 mmol), 2-cyano-2-propyl dodecyl trithiocarbonate (34.8 µL, 0.097 mmol), 7.7 mL toluene and AIBN (3.1 mg, 0.018 mmol). After 12 h of mixing at 90 oC, the obtained polymer was precipitated in hexane and then dried under reduced pressure

3.3.2 Degradation procedure

3.3.2.1 Degradation of P(MMA-*co*-MCA)

P(MMA-*co*-MCA) was degraded with 10-phenylphenothiazine and dyes, namely, eosin y and erythrosin b, under visible light at room temperature. For this purpose, P(MMA-*co*-MCA) (10 mg, 0.0013 mmol), PMDETA (19 µL, 0.09 mmol), 8 mL

toluene, ErB (8.79 mg, 0.1 mmol) or EY (6.91 mg, 0.1 mmol or PPT (2.75 mg, 0.1 mmol) were added to screw capped glass. tube. The reaction mixture was bubbled with dry nitrogen gas. After 6 hours of irradiation, the whole solvent was evaporated and the degradation products dried under vacuum at room temperature.

3.3.2.2 Degradation of P(MMA-*co*-EBA)

The copolymer was degraded with PPT, ErB, and EY under ambient conditions. Firstly, P(MMA-*co*-EBA) (10 mg, 0.0013 mmol), PMDETA (19 μL, 0.09 mmol), 8 mL toluene, ErB (8.79 mg, 0.01 mmol) or EY (6.91 mg, 0.01 mmol) or PPT (2.75 mg, 0.01 mmol) were added to the tube. After nitrogen bubbling for 5 min, the reaction tube was tightly sealed and irradiated for 6 hours. The solvent, toluene, was evaporated by a rotary evaporator, and the degraded polymer was left in a vacuum for drying.

4. RESULTS AND DISCUSSION

Two different acrylate derivatives, namely, methyl α-chloroacrylate (MCA) and ethyl 3-bromoacrylate (EBA) were employed in order to obtain degradable PMMA alternatives. The MCA and EBA monomers were separately copolymerized with methylmethacrylate (MMA) using conventional RAFT method to better observe the degradation benefiting from narrow dispersity ($Đ$). The polymerization conditions and physical properties of the resulting copolymers, P(MMA-co-MCA) and P(MMA-co-EBA), were recorded in Table 4.1. Furthermore, the proposed degradation mechanisms were depicted in Figure 4.1. According to the table, two copolymers with comparable molecular weights and nearly identical dispersities have been obtained. ^{1}H-NMR and FT-IR spectra of the obtained polymers are observable at Figure A.1 and A.2

Table 4.1 : Copolymerization of MMA MCA EBA monomers to obtain degradable PMMA derivatives.[a]

Monomer	Reaction Time (h)	M_n[b] kg mol^{-1}	$Đ$[a]	Polymer
[MMA]:[MCA]	6	11.4	1.4	P(MMA-*co*-MCA)
[MMA]:[EBA]	12	8.1	1.4	P(MMA-*co*-EBA)

a- [MMA]:[Comonomer]:[Raft Agent]:[AIBN]=1000:100:5:1, at 90°C.

b- Determined by GPC

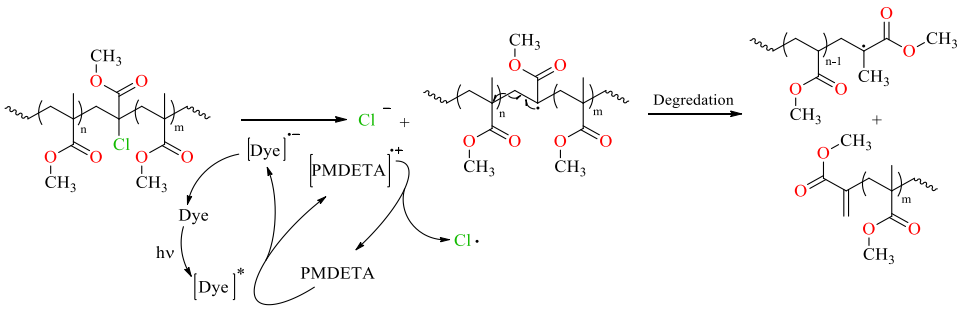

Figure 4.1 : White LED induced degradation mechanism of poly (methylmethacrylate), methyl α-chloroacrylate copolymer using organodyes as photocatalyst.

Degradation reactions of eosin Y (EY) and erythrosin B (ErB) were conducted under white LED irradiation in toluene solvent. For 10-phenylphenothiazine (PPT), the same experimental conditions were used, but a 400 nm LED light was chosen to accommodate its specific absorption characteristics. UV-Vis spectra of the reaction mixtures are presented in Figure 4.2.

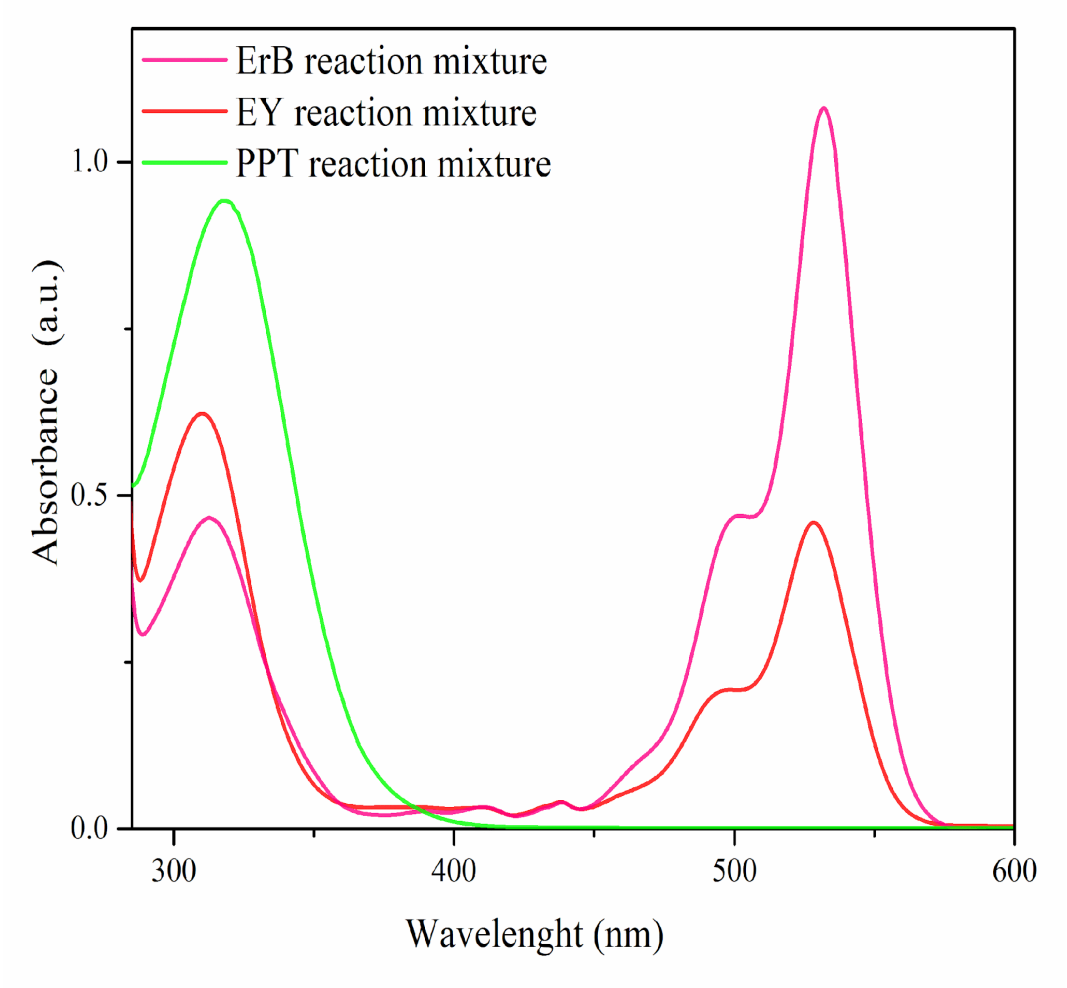

Figure 4.2 : UV-Vis spectra of reaction medias using EY, ErB and PPT.

To prevent the loss of degraded products with low molecular weights, the solvent was evaporated under vacuum at room temperature after 6 hours of irradiation. The molecular weight changes of the degraded products were analyzed using GPC. The weight average molecular weight (M_w) of the P(MMA-*co*-MCA) copolymer was decreased from 15.96 kg mol^{-1} to 8.3 kg mol^{-1}, 10.8 kg mol^{-1} and 1.8 kg mol^{-1} when using ErB, EY or PPT as photocatalyst respectively. The number average molecular weight (M_n) and weight average molecular weight (M_w) decreases were noted as molecular weight change percentage in Figure 4.3.

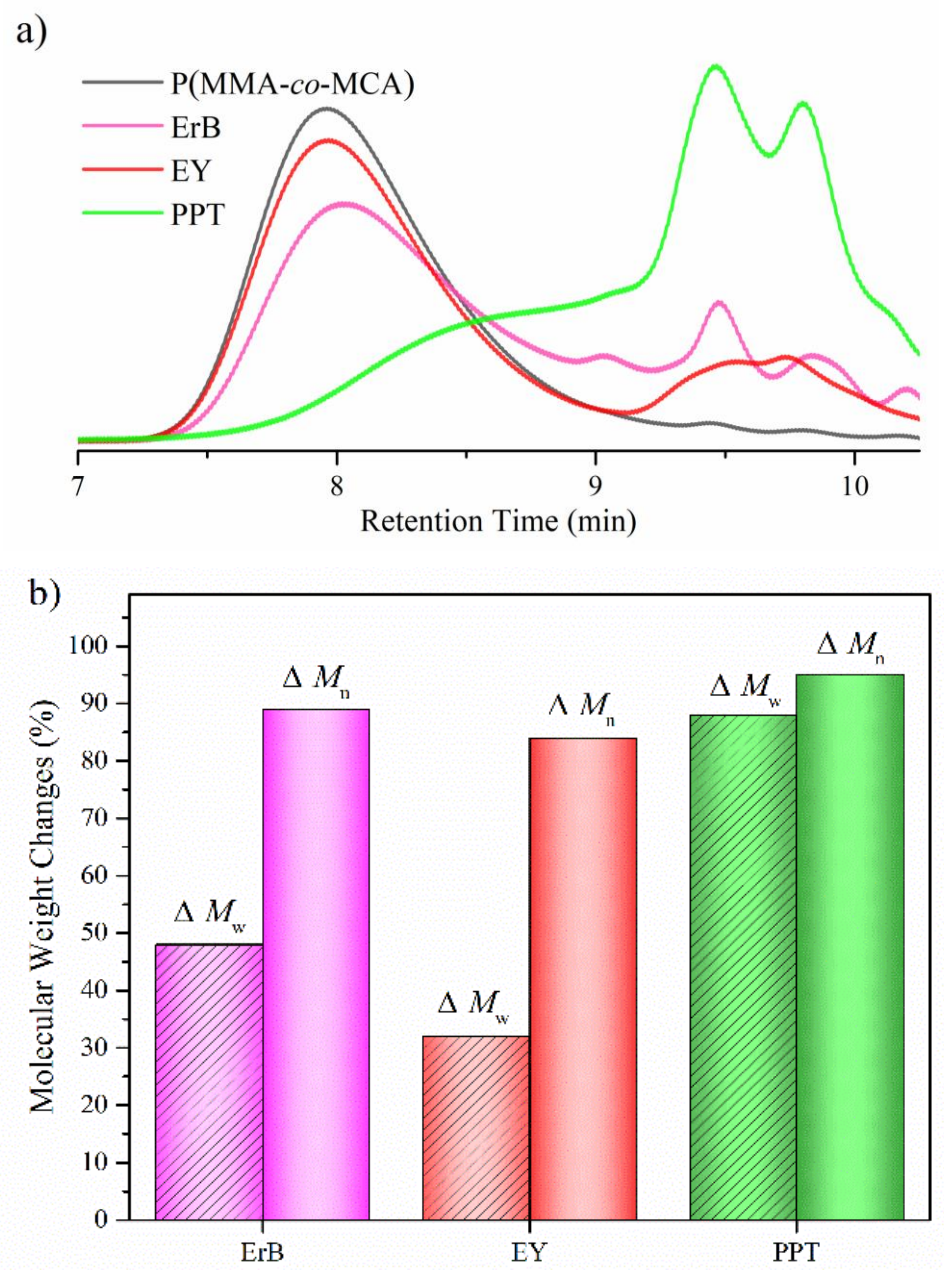

Figure 4.3 : (a) GPC chromatograms of degraded samples of P(MMA-*co*-MCA) using EY, ErB and PPT and (b) overall molecular weight changes (6h).

PPT demonstrated remarkable results in degradation when compared to ErB and EY photocatalysts, which exhibited comparable levels of efficiency after 6 hours of irradiation. In the GPC results, a significant shift towards lower molecular weight is observed. The LC-MS results indicated the existence of oligomers possessing molecular weights below 800 g mol-1. (Figure 4.5) Control experiments were conducted in the absence of PMDETA and using different light sources and dark conditions. Results were tabulated in Table 4.2 and GPC chromatograms were presented in Figure 4.4.

Table 4.2 : Control experiments on the photodegradation process.

PC	Initial Properties of P(MMA-*co*-MCA)		w/o Light		w/o PMDETA		Different Wavelenghts[b]	
	M_w[a] (kg mol^{-1})	$Đ$[a]	M_w[a] (kg mol^{-1})	$Đ$[a]	M_w[a] (kg mol^{-1})	$Đ$[a]	M_w[a] (kg mol^{-1})	$Đ$[a]
EY	10.9	1.6	14.7	4.0	17.4	3.8	17.8	3.7
ErB	10.9	1.6	14.7	4.4	13.6	5.3	17.6	3.4
PPT	10.9	1.6	18.1	3.8	17.5	4.4	9.9	7.1

[a]- Determined by GPC

[b]- 400 nm for PPT, broad white LED for EY and ErB.

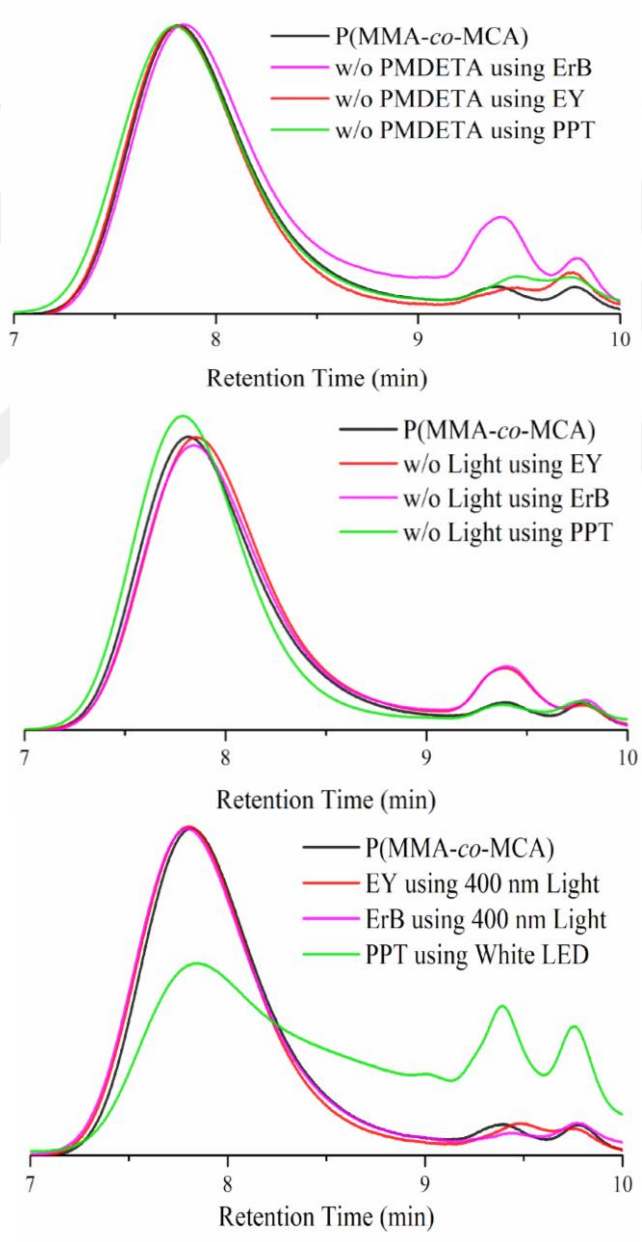

Figure 4.4 : GPC chromatograms of control experiments using EY, ErB and PPT.

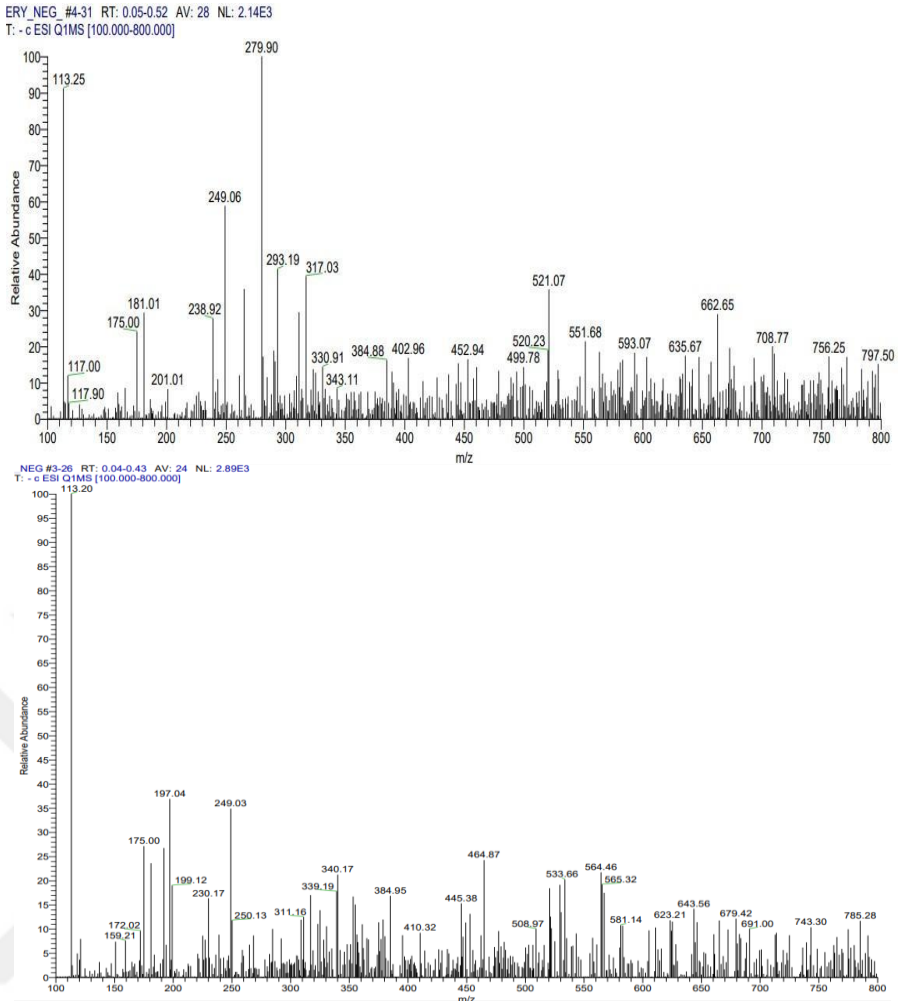

Figure 4.5 : LC-MS spectra of degraded a) P(MMA-*co*-MCA) using PPT and b) P(MMA-*co*-EBA) using ErB.

To determine the most suitable time for achieving complete degradation, the photodegradation kinetics were examined by periodically collecting samples from the reaction media at different time intervals. Subsequently, all samples were analyzed using GPC. Molecular weight and dispersity changes of PPT-catalyzed degradation of P(MMA-*co*-MCA) are tabulated in Table 4.3 and chromatograms can be seen in Figure 4.6a. GPC chromatograms displayed a significant decrease in molecular weight between 6 to 9 hours, indicating substantial degradation. Within 24 hours, nearly all polymers had transformed into oligomers.The kinetics analysis of the EY method showed promising results, despite the fact that with a slower degradation rate compared to PPT. The kinetics of EY-catalyzed degradation are tabulated in Table 4.3 and GPC chromatograms are observable in Figure 4.6b. Although both sets of chromatograms indicated degradation, the PPT-catalyzed method demonstrated greater efficiency compared to the EY-catalyzed degradation.

Table 4.3 : Photodegradation kinetics of the copolymers using PPT,ErB and EY.

Irradiation Time (h)	P(MMA-*co*-MCA)		P(MMA- *co*-MCA)		P(MMA-*co*-EBA)	
	Using PPT[b]		Using EY[c]		Using ErB[c]	
	M_n[a] (kg mol^{-1})	M_w[a] (kg mol^{-1})	M_n[a] (kg mol^{-1})	M_w[a] (kg mol^{-1})	M_n[a] (kg mol^{-1})	M_w[a] (kg mol^{-1})
0	11.4	16.0	11.4	16.0	7.6	11.4
0.5	2.3	10.4	1.6	10.1	2.3	10.1
1	1.8	9.0	1.9	10.1	1.8	9.0
2	1.8	8.5	1.6	9.4	1.9	9.1
4	2.0	10.4	1.8	10.4	1.4	7.7
6	2.1	8.2	1.3	10.1	1.5	8.3
9	1.2	6.8	1.9	10.1	-	-
24	0.7	2.7	-	-	-	-

a- Determined by GPC.

b- [Copolymer]:[PPT]:[PMDETA]=[0.013]:[1]:[1] under 400 nm visible light irradiation.

c- [Copolymer]:[ErB or EY]:[PMDETA]=[0.013]:[1]:[1] under 400 nm LED light irradiation.

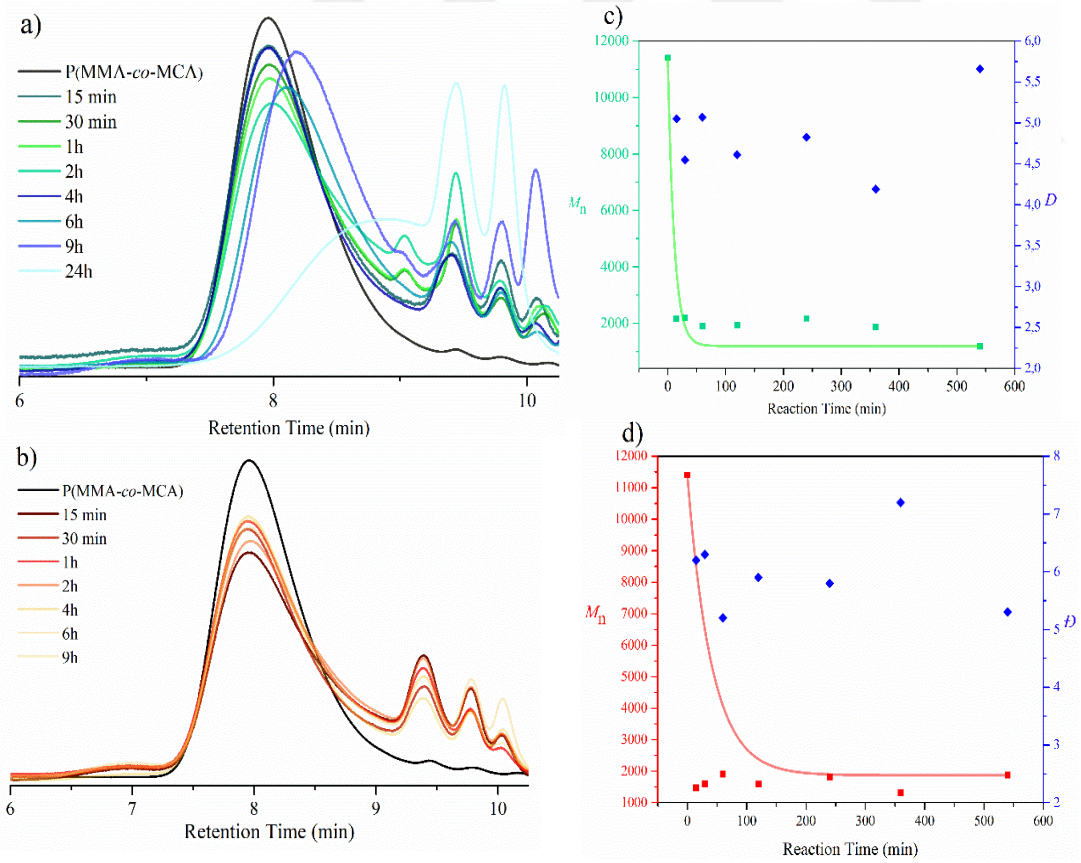

Figure 4.6 : GPC chromatograms of P(MMA-*co*-MCA) degradation kinetics experiment via (a)PPT and (b)EY and calculated molecular weight decrease using (c)PPT and (d) EY.

Furthermore, temporal control experiments were conducted to investigate the light-dependency of the degradation process. The initial control experiments demonstrated that degradation does not initiate in the absence of irradiation., (Table 4.2, Figure 4.4) temporal control experiments further confirmed that degradation cannot occur in the absence of light.(Figure 4.7)

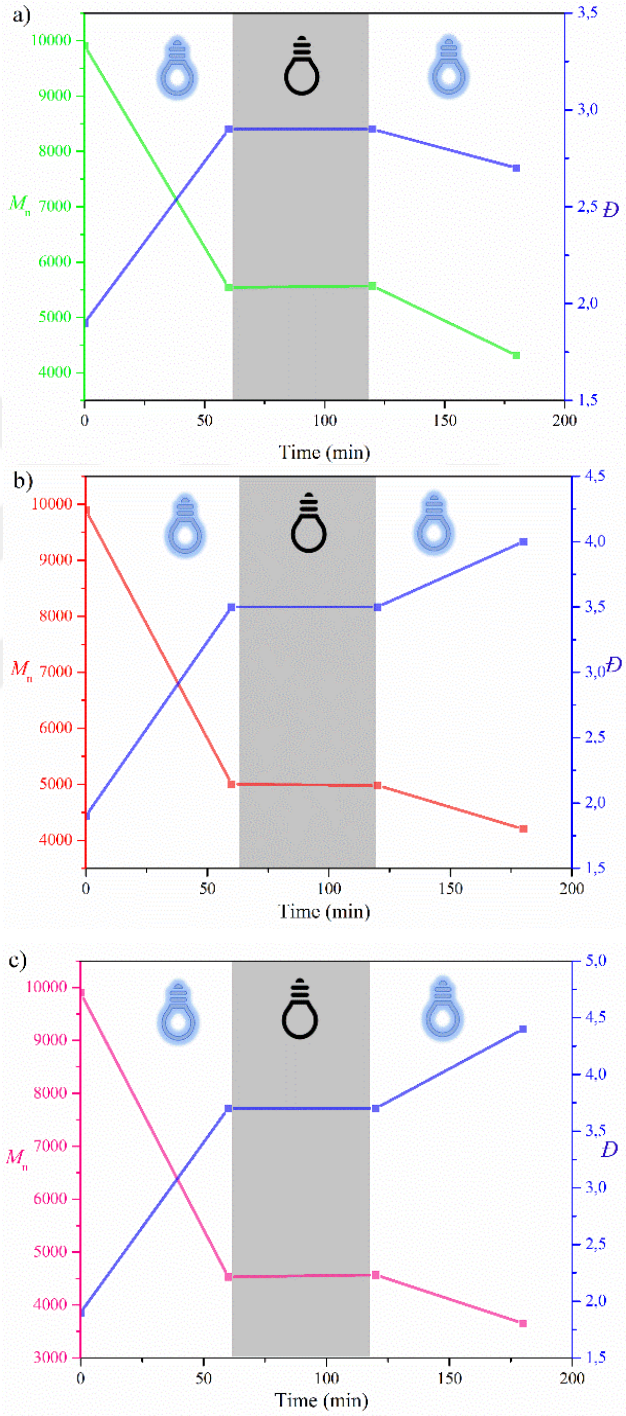

Figure 4.7 : Temporal control experiments of P(MMA-*co*-MCA) degradation using (a) PPT, (b) EY, (c) ErB.

Later on, this approach was further extended to P(MMA-*co*-EBA) copolymer consisting bromine at the adjacent carbon compared to P(MMA-*co*-MCA) to see the effect of the regional presence of the halogens on the main chain. Since the more unstable nature of the formed radical at the beta position to the carbonyl functionality hinders the abstract ability of the halogen, bromine is preferred instead of chlorine to accelerate the homolytic abstraction step. It can be seen in Figure 4.8 that the degradation products share a similar radical character which cannot be delocalized to increase the stability, the overall yield of degradation has been negatively affected when P(MMA-*co*-EBA) polymer was employed for degradation. Also, the chirality of the carbon which is bearing a single electron and the adjacent carbon, decreases the possibilities for elimination arising from stereochemical and conformational positions. For the P(MMA-*co*-MCA) example, four adjacent hydrogen atoms are employable to yield degradation, on the other hand, for P(MMA-*co*-EBA), there are only two adjacent hydrogens that can also more likely to be stereochemically blocked hindering the rate of degradation. The GPC chromatograms of P(MMA-*co*-EBA) after 6 h of irradiation involving PPT, EY, and ErB are depicted in Figure 4.9.

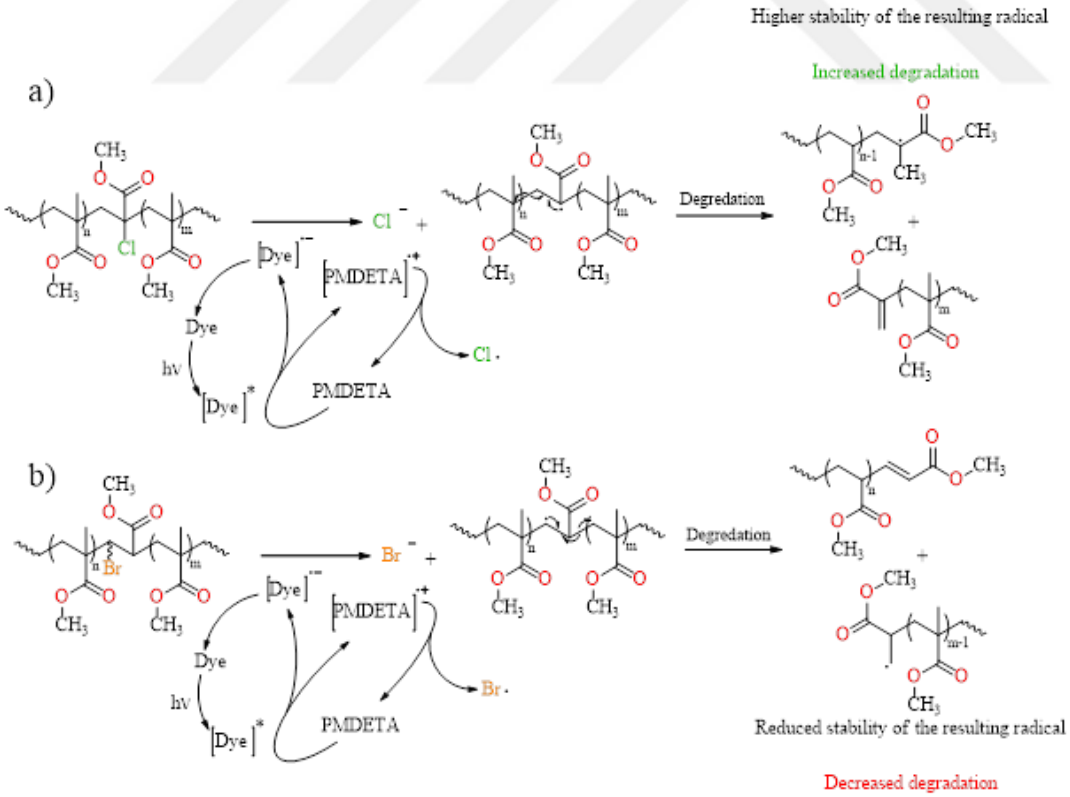

Figure 4.8 : (a)White LED induced degradation mechanism of poly(methylmethacrylate), methyl α-chloro acrylate copolymer, (b) poly(methylmethacrylate), ethyl 3-bromo acrylate copolymer using organodyes as photocatalyst.

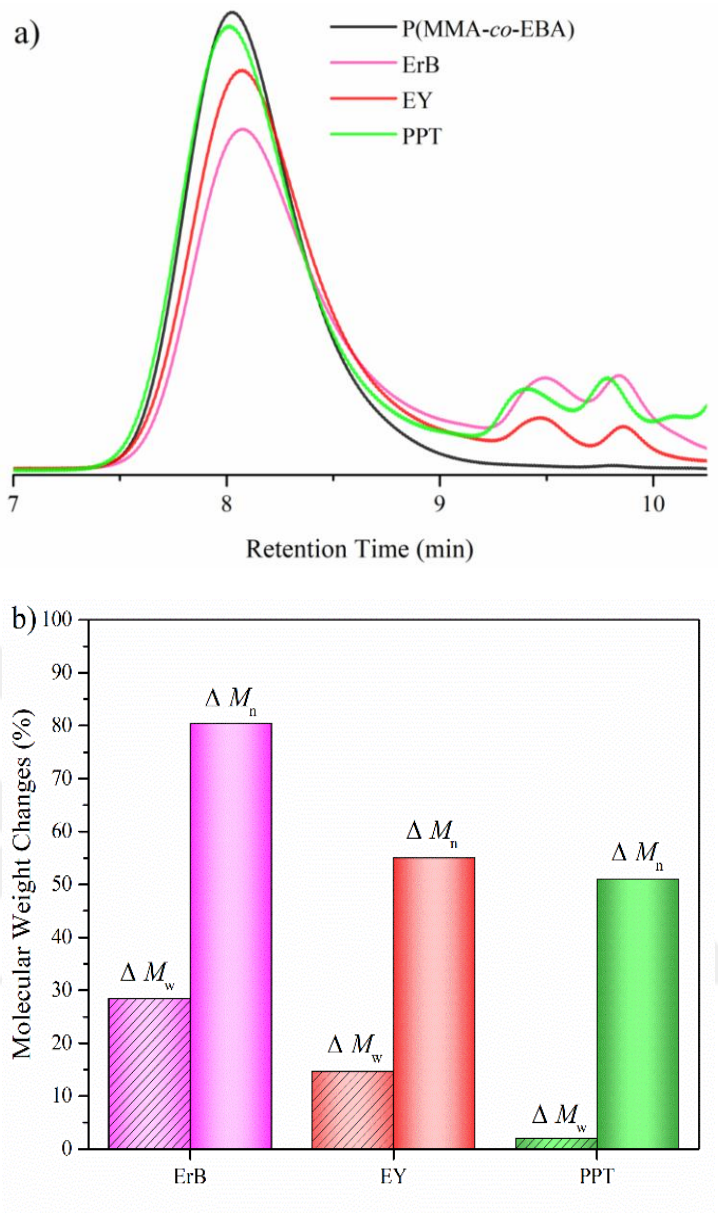

Figure 4.9 : (a) GPC chromatograms of prepolymer and degraded samples of P(MMA-*co*-EBA) using EY, ErB and PPT and (b) overall molecular weight changes.

In Figure 4.9, the degradation experiment with P(MMA-*co*-EBA) and PPT yielded a slight shift towards a higher molecular weight region arising from the rapid abstraction of the halogens in addition to the degradation. PPT is the most efficient catalyst among the organodyes due to its superior capability for halide abstraction. However, the subsequent rise in free radical concentration leads to the initiation of undesired coupling reactions, resulting in the formation of branched structures.

The kinetic analysis of P(MMA-*co*-EBA) degradation using ErB was executed under white LED irradiation increasing degradation over time was observed and the results were depicted in Figure 4.10.

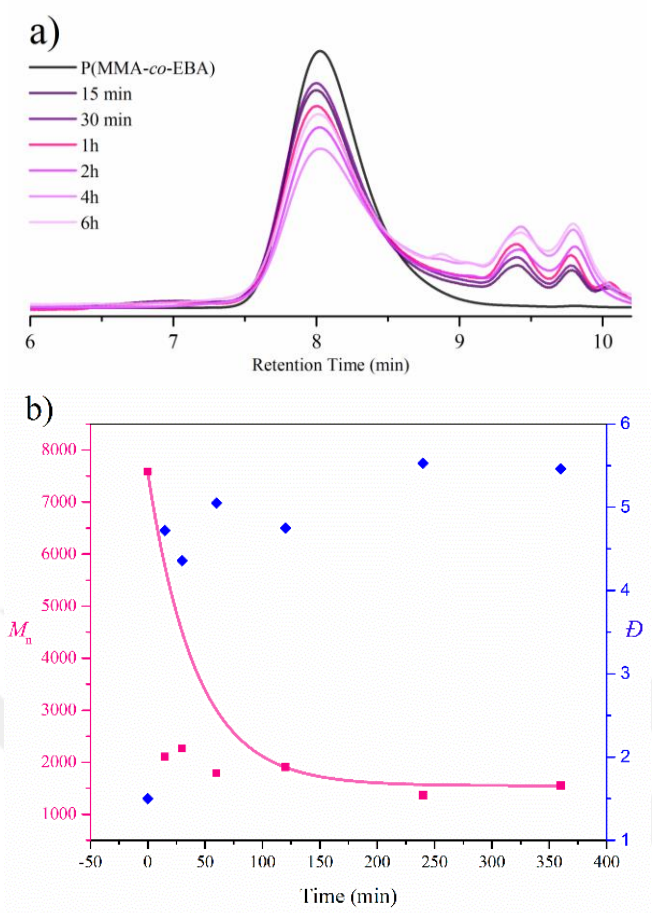

Figure 4.10 : (a) GPC chromatograms and (b) calculated molecular weight decreases of P(MMA-*co*-EBA) degradation kinetics using ErB.

In addition, a batch of P(MMA-*co*-MCA) was synthesized by free radical polymerization, and degraded by the same approaches to observe the effect of the end group. Similar molecular weight decreases were observed by GPC chromatograms of the obtained polymers. (Figure 4.11)

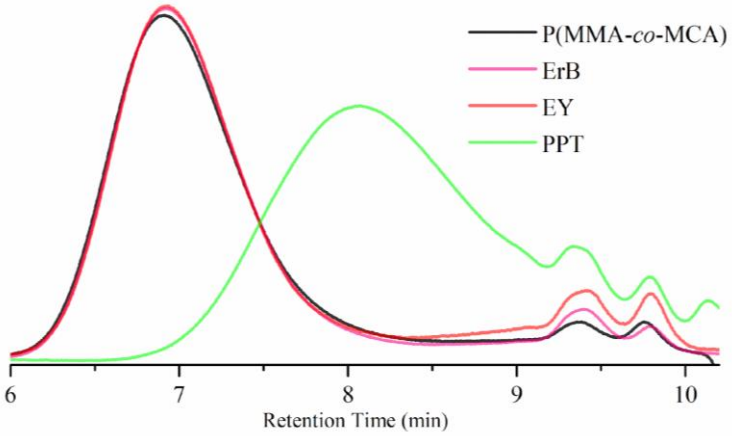

Figure 4.11 : GPC chromatograms of degradation with organodyes using P(MMA-*co*-MCA) obtained by free radical polymerization.

Calorimetry (DSC) and thermogravimetric analyses (TGA) were used to compare the thermal characteristics of the copolymers and PMMA. Lower thermal resistance was observed as expected from copolymers compared to PMMA as the halogens at the main chain make the polymer main chain more susceptible to thermal degradation too (Figure 4.12).

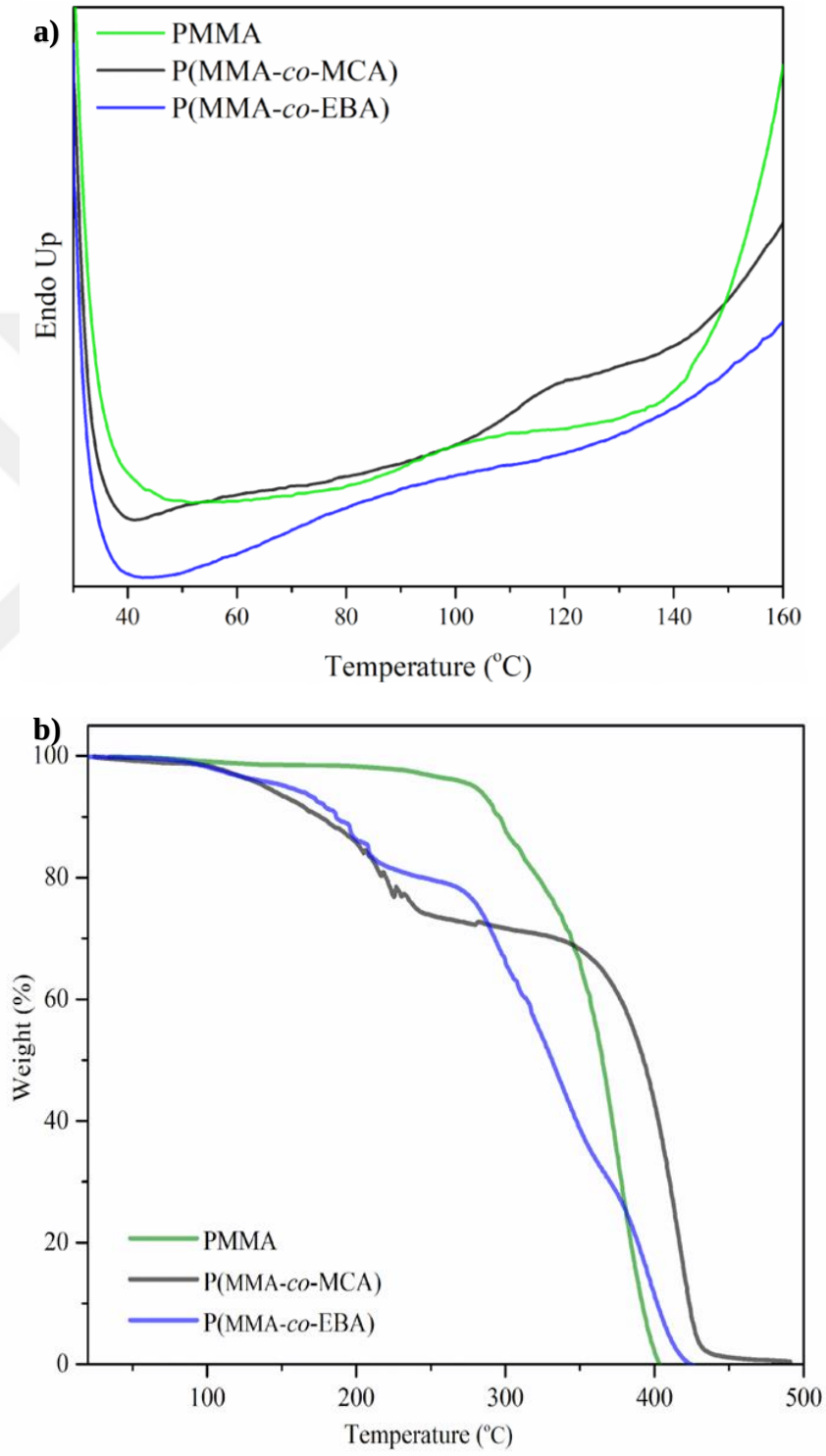

Figure 4.12 : a) DSC thermograms of PMMA, P(MMA-*co*-MCA) and P(MMA-*co*-EBA), b) TGA thermograms of PMMA, P(MMA-*co*-MCA) and P(MMA-*co*-EBA).

5. CONCLUSION

In conclusion, a novel photodegradation system is developed to overcome the need for heat and metal catalysts in degradation with broadband white LED irradiation (400 nm-800 nm) and blue LED irradiation (400 nm) in combination with EY, ErB dyes, or PPT. In order to detect ideal conditions for the subsequent degradation process, two variations of halogen-containing PMMA derivatives have been synthesized. Remarkably low molecular weights were achieved through the degradation of P(MMA-co-MCA) using visible light in the presence of organo photocatalysts. Temporal control and the kinetics experiments of the novel degradation system were examined by taking aliquot samples from reaction media and performing GPC analyses. The thermal properties of the copolymers were also examined by DSC and TGA to outline their potential as a substitute for PMMA in commercial use.

REFERENCES

[1] **Freinkel, S.** (2011). *Plastic: a toxic love story*. Retrieved from https://www.google.com.tr/books/edition/Plastic/ZO5auQEACAAJ?hl=tr (Original work published 2011)

[2] **Letcher, T. M.** (2020). *Plastic waste and recycling: Environmental impact, societal issues, prevention, and solutions*. Retrieved from https://www.google.com.tr/books/edition/Plastic_Waste_and_Recycling/Ma_SDwAAQBAJ?hl=tr&gbpv=0 (Original work published 2020)

[3] **Tchobanoglous, G.** (1993). *Integrated solid waste managementengineering principles and management issues*. Retrieved from https://books.google.com.tr/books/about/Integrated_Solid_Waste_Management_Engine.html?id=-5JSAAAAMAAJ&redir_esc=y (Original work published 1993)

[4] **Nzediegwu, C. and S. X. Chang.** (2020). Improper solid waste management increases potential for COVID-19 spread in developing countries, *Resources, conservation, and recycling*, ***161***, 104947.

[5] **Kibria, M. G., N. I. Masuk, R. Safayet, H. Q. Nguyen, et al.** (2023). Plastic Waste: Challenges and Opportunities to Mitigate Pollution and Effective Management, *International Journal of Environmental Research*, ***17***(1), 20.

[6] **Garcia, J. M. and M. L. Robertson.** (2017). The future of plastics recycling, *Science*, ***358***(6365), 870-872.

[7] **Ragaert, K., L. Delva , and K. Van Geem.** (2017). Mechanical and chemical recycling of solid plastic waste, *Waste management*, ***69***, 24-58.

[8] **Coates, G. W. and Y. D. Getzler.** (2020). Chemical recycling to monomer for an ideal, circular polymer economy, *Nature Reviews Materials*, ***5***(7), 501-516.

[9] **Hong, M. and E. Y.-X. Chen.** (2017). Chemically recyclable polymers: a circular economy approach to sustainability, *Green Chemistry*, ***19***(16), 3692-3706.

[10] **Worch, J. C. and A. P. Dove.** (2020). 100th anniversary of macromolecular science viewpoint: toward catalytic chemical recycling of waste (and future) plastics, *ACS Macro Letters*, ***9***(11), 1494-1506.

[11] **Yu, J., L. Sun, C. Ma, Y. Qiao, et al.** (2016). Thermal degradation of PVC: A review, *Waste management*, ***48***, 300-314.

[12] **Balema, V. P., I. Z. Hlova, S. L. Carnahan, M. Seyedi, et al.** (2021). Depolymerization of polystyrene under ambient conditions, *New Journal of Chemistry*, ***45***(6), 2935-2938.

[13] **Young, J. B., J. I. Bowman, C. B. Eades, A. J. Wong, et al.** (2022). Photoassisted Radical Depolymerization, *ACS Macro Letters*, ***11***(12), 1390-1395.

[14] **Dainton, F. and K. Ivin.** (1948). Reversibility of the propagation reaction in polymerization processes and its manifestation in the phenomenon of a 'Ceiling Temperature', *Nature*, ***162***(4122), 705-707.

[15] **Pesenti, T. and J. Nicolas.** (2020). 100th anniversary of macromolecular science viewpoint: Degradable polymers from radical ring-opening polymerization: Latest advances, new directions, and ongoing challenges, *ACS Macro Letters*, ***9***(12), 1812-1835.

[16] **Jones, G. R., H. S. Wang, K. Parkatzidis, R. Whitfield, et al.** (2023). Reversed Controlled Polymerization (RCP): Depolymerization from Well-Defined Polymers to Monomers, *Journal of the American Chemical Society*.

[17] **Kiliclar, H. C., G. Yilmaz , and Y. Yagci.** (2021). Visible Light Induced Step-Growth Polymerization by Substitution Reactions, *Macromolecular Rapid Communications*, ***42***(7), 2000686.

[18] **Nakipoglu, B., G. Yilmaz , and Y. Yagci.** (2019). Visible light induced radical coupling reactions for the synthesis of conventional polycondensates, *Polymer Chemistry*, ***10***(41), 5652-5658.

[19] **Yurteri, S., I. Cianga, M. Degirmenci , and Y. Yagci.** (2004). Synthesis and characterization of poly (p-phenylene)-graft-poly (ε-caprolactone) copolymers by combined ring-opening polymerization and cross-coupling processes, *Polymer international*, ***53***(9), 1219-1225.

[20] **Sari, E., G. Yilmaz, S. Koyuncu , and Y. Yagci.** (2018). Photoinduced step-growth polymerization of N-ethylcarbazole, *Journal of the American Chemical Society*, ***140***(40), 12728-12731.

[21] **Kaya, K., S. Koyuncu , and Y. Yagci.** (2019). Photoinduced synthesis of poly (N-ethylcarbazole) from phenacylium salt without conventional catalyst and/or monomer, *Chemical Communications*, ***55***(77), 11531-11534.

[22] **Kiliclar, H. C., E. Gencosman , and Y. Yagci.** (2022). Visible Light Induced Conventional Step-Growth and Chain-Growth Condensation Polymerizations by Electrophilic Aromatic Substitution, *Macromolecular Rapid Communications*, ***43***(1), 2100584.

[23] **Kiliclar, H. C., C. Altinkok, G. Yilmaz , and Y. Yagci.** (2021). Visible light induced step-growth polymerization by electrophilic aromatic substitution reactions, *Chemical Communications*, ***57***(44), 5398-5401.

[24] **Kaya, K., S. Jockusch , and Y. Yagci.** (2021). Mussel-inspired coatings by photoinduced electron-transfer reactions: photopolymerization of dopamine under UV, visible, and daylight under oxygen-free conditions, *Macromolecules*, ***54***(13), 5991-5999.

[25] **Kaya, K., H. C. Kiliclar , and Y. Yagci.** (2023). Photochemically generated ionic species for cationic and step-growth polymerizations, *European Polymer Journal*, ***190***, 112000.

[26] **Arslan, Z., H. C. Kiliclar , and Y. Yagci.** (2022). Dimanganese decacarbonyl catalyzed visible light induced ambient temperature depolymerization of poly (methyl methacrylate), *Designed Monomers and Polymers*, ***25***(1), 271-276.

[27] **Arslan, Z., H. C. Kiliclar , and Y. Yagci.** (2023). Visible light Induced Degradation of Poly (methyl methacrylate-co-methyl α-chloro acrylate)

Copolymer at Ambient Temperature, *Macromolecular Rapid Communications*, 2300066.

[28] **Bamford, C. H., P. Crowe , and R. Wayne.** (1965). Studies in polymerization-XV. The photosensitized initiation of vinyl polymerization by manganese carbonyl, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, ***284***(1399), 455-468.

[29] **Bamford, C. and R. Denyer.** (1968). Initiation of free radical polymerization by manganese carbonyl and carbon tetrachloride, *Nature*, ***217***, 59-60.

[30] **Ivin, K.** (1973). Thermodynamics of addition polymerization processes, *Angewandte Chemie International Edition in English*, ***12***(6), 487-494.

[31] **Odian, G.** (2004). *Principles of polymerization*. Retrieved from https://onlinelibrary.wiley.com/doi/book/10.1002/047147875X (Original work published 2004)

[32] **Young, R. J. and P. A. Lovell.** (2011). *Introduction to polymers*. Retrieved from. https://www.google.com.tr/books/edition/Introduction_to_Polymers_Third_Edition/ImQg2MK8NtkC?hl=tr&gbpv=0 (Original work published 2011)

[33] **Roberts, D. E.** (1950). Heats of polymerization. A summary of published values and their relation to structure, *J. Res. Natl. Bur. Stand*, ***44***, 221-232.

[34] **Snow, R. and F. Frey.** (1943). The reaction of sulfur dioxide with olefins: the ceiling temperature phenomenon, *Journal of the American Chemical Society*, ***65***(12), 2417-2418.

[35] **De Neve, J., J. J. Haven, L. Maes , and T. Junkers.** (2018). Sequence-definition from controlled polymerization: the next generation of materials, *Polymer Chemistry*, ***9***(38), 4692-4705.

[36] **Gody, G., T. Maschmeyer, P. B. Zetterlund , and S. Perrier.** (2013). Rapid and quantitative one-pot synthesis of sequence-controlled polymers by radical polymerization, *Nature communications*, ***4***(1), 2505.

[37] **Parkatzidis, K., H. S. Wang, N. P. Truong , and A. Anastasaki.** (2020). Recent developments and future challenges in controlled radical polymerization: a 2020 update, *Chem*, ***6***(7), 1575-1588.

[38] **Gentekos, D. T., R. J. Sifri , and B. P. Fors.** (2019). Controlling polymer properties through the shape of the molecular-weight distribution, *Nature Reviews Materials*, ***4***(12), 761-774.

[39] **Kato, M., M. Kamigaito, M. Sawamoto , and T. Higashimura.** (1995). Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris- (triphenylphosphine ruthenium (II)/methylal uminum bis (2, 6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization, *Macromolecules*, ***28***(5), 1721-1723.

[40] **Wang, J.-S. and K. Matyjaszewski.** (1995). Controlled/" living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes, *Journal of the American Chemical Society*, ***117***(20), 5614-5615.

[41] **Lorandi, F., M. Fantin , and K. Matyjaszewski.** (2022). Atom Transfer Radical Polymerization: A Mechanistic Perspective, *Journal of the American Chemical Society*, ***144***(34), 15413-15430.

[42] **Matyjaszewski, K. and J. Xia.** (2001). Atom transfer radical polymerization, *Chemical reviews*, ***101***(9), 2921-2990.

[43] **Raus, V., E. Cadova, L. Starovoytova , and M. Janata.** (2014). ATRP of POSS monomers revisited: Toward high-molecular weight methacrylate–POSS (co) polymers, *Macromolecules*, ***47***(21), 7311-7320.

[44] **Truong, N. P., G. R. Jones, K. G. Bradford, D. Konkolewicz, et al.** (2021). A comparison of RAFT and ATRP methods for controlled radical polymerization, *Nature Reviews Chemistry*, ***5***(12), 859-869.

[45] **Hill, M. R., R. N. Carmean , and B. S. Sumerlin.** (2015). Expanding the scope of RAFT polymerization: recent advances and new horizons, *Macromolecules*, ***48***(16), 5459-5469.

[46] **Flanders, M. J. and W. M. Gramlich.** (2018). Reversible-addition fragmentation chain transfer (RAFT) mediated depolymerization of brush polymers, *Polymer Chemistry*, ***9***(17), 2328-2335.

[47] **Hawkins, W. L.**, (1984). *Polymer degradation, in Polymer degradation and stabilization.* Retrieved from https://www.google.com.tr/books/edition/Polymer_Degradation_and_Stabilization/Q_vsCAAAQBAJ?hl=tr&gbpv=1&dq=Polymer+degradation,+in+Polymer+degradation+and+stabilization&printsec=frontcove (Original work published 1984)

[48] **Göpferich, A.** (1996). *The biomaterials: silver jubilee compendium*. Retrieved from https://www.google.com.tr/books/edition/The_Biomaterials_Silver_Jubilee_Compendi/yyvdg8dMdk4C?hl=tr&gbpv=1&dq=The+biomaterials:+silver+jubilee+compendium&printsec=frontcover (Original work published 1996)

[49] **Hamid, S. H.** (2000). *Handbook of polymer degradation*. Retrieved from https://www.google.com.tr/books/edition/Handbook_of_Polymer_Degradation_Second_E/khIL2x6uKaMC?hl=tr (Original work published 2000)

[50] **Triacca, V., P. Gloor, S. Zhu, A. Hrymak, et al.** (1993). Free radical degradation of polypropylene: random chain scission, *Polymer Engineering & Science*, ***33***(8), 445-454.

[51] **Ueno, T., E. Nakashima , and K. Takeda.** (2010). Quantitative analysis of random scission and chain-end scission in the thermal degradation of polyethylene, *Polymer degradation and stability*, ***95***(9), 1862-1869.

[52] **Kruse, T. M., O. S. Woo , and L. J. Broadbelt.** (2001). Detailed mechanistic modeling of polymer degradation: application to polystyrene, *Chemical engineering science*, ***56***(3), 971-979.

[53] **Ali, U., K. J. B. A. Karim , and N. A. Buang.** (2015). A review of the properties and applications of poly (methyl methacrylate)(PMMA), *Polymer Reviews*, ***55***(4), 678-705.

[54] **Henri, L.** (2007). Thermohygroelastic properties of polymethylmethacrylate, (*Technical Note PR-TN*) ***440***.

[55] **Henry, A. C., T. J. Tutt, M. Galloway, Y. Y. Davidson, et al.** (2000). Surface modification of poly (methyl methacrylate) used in the fabrication of microanalytical devices, *Analytical chemistry*, ***72***(21), 5331-5337.

[56] **Adhikari, B. and S. Majumdar.** (2004). Polymers in sensor applications, *Progress in polymer science*, ***29***(7), 699-766.

[57] **Lee, L.-H. and W.-C. Chen.** (2001). High-refractive-index thin films prepared from trialkoxysilane-capped poly (methyl methacrylate)− titania materials, *Chemistry of materials*, ***13***(3), 1137-1142.

[58] **Mishra, M. and Y. Yagci.** (2016). *Handbook of vinyl polymers: radical polymerization, process, and technology*. Boca Raton, FL.: CRC Press

[59] **Perrier, S., T. P. Davis, A. J. Carmichael , and D. M. Haddleton.** (2002). First report of reversible addition–fragmentation chain transfer (RAFT) polymerisation in room temperature ionic liquids, *Chemical Communications*, (19), 2226-2227.

[60] **Guillaneuf, Y., D. Gigmes, S. R. Marque, P. Astolfi, et al.** (2007). First effective nitroxide-mediated polymerization of methyl methacrylate, *Macromolecules*, ***40***(9), 3108-3114.

[61] **Seo, W. and S. T. Phillips.** (2010). Patterned plastics that change physical structure in response to applied chemical signals, *Journal of the American Chemical Society*, ***132***(27), 9234-9235.

[62] **Tsuji, H., T. Saeki, T. Tsukegi, H. Daimon, et al.** (2008). Comparative study on hydrolytic degradation and monomer recovery of poly (L-lactic acid) in the solid and in the melt, *Polymer Degradation and Stability*, ***93***(10), 1956-1963.

[63] **Zhang, H. and M. W. Grinstaff.** (2013). Synthesis of atactic and isotactic poly (1, 2-glycerol carbonate) s: degradable polymers for biomedical and pharmaceutical applications, *Journal of the American Chemical Society*, ***135***(18), 6806-6809.

[64] **Sano, Y., T. Konishi, M. Sawamoto , and M. Ouchi.** (2019). Controlled radical depolymerization of chlorine-capped PMMA via reversible activation of the terminal group by ruthenium catalyst, *European Polymer Journal*, ***120***, 109181.

[65] **Kimura, T., K. Kuroda, H. Kubota , and M. Ouchi.** (2021). Metal-Catalyzed Switching Degradation of Vinyl Polymers via Introduction of an "In-Chain" Carbon–Halogen Bond as the Trigger, *ACS Macro Letters*, ***10***(12), 1535-1539.

[66] **Martinez, M. R., D. Schild, F. De Luca Bossa , and K. Matyjaszewski.** (2022). Depolymerization of Polymethacrylates by Iron ATRP, *Macromolecules*, ***55***(23), 10590-10599.

APPENDICES

APPENDIX A: ^{1}H NMR and FT-IR spectra

APPENDIX A

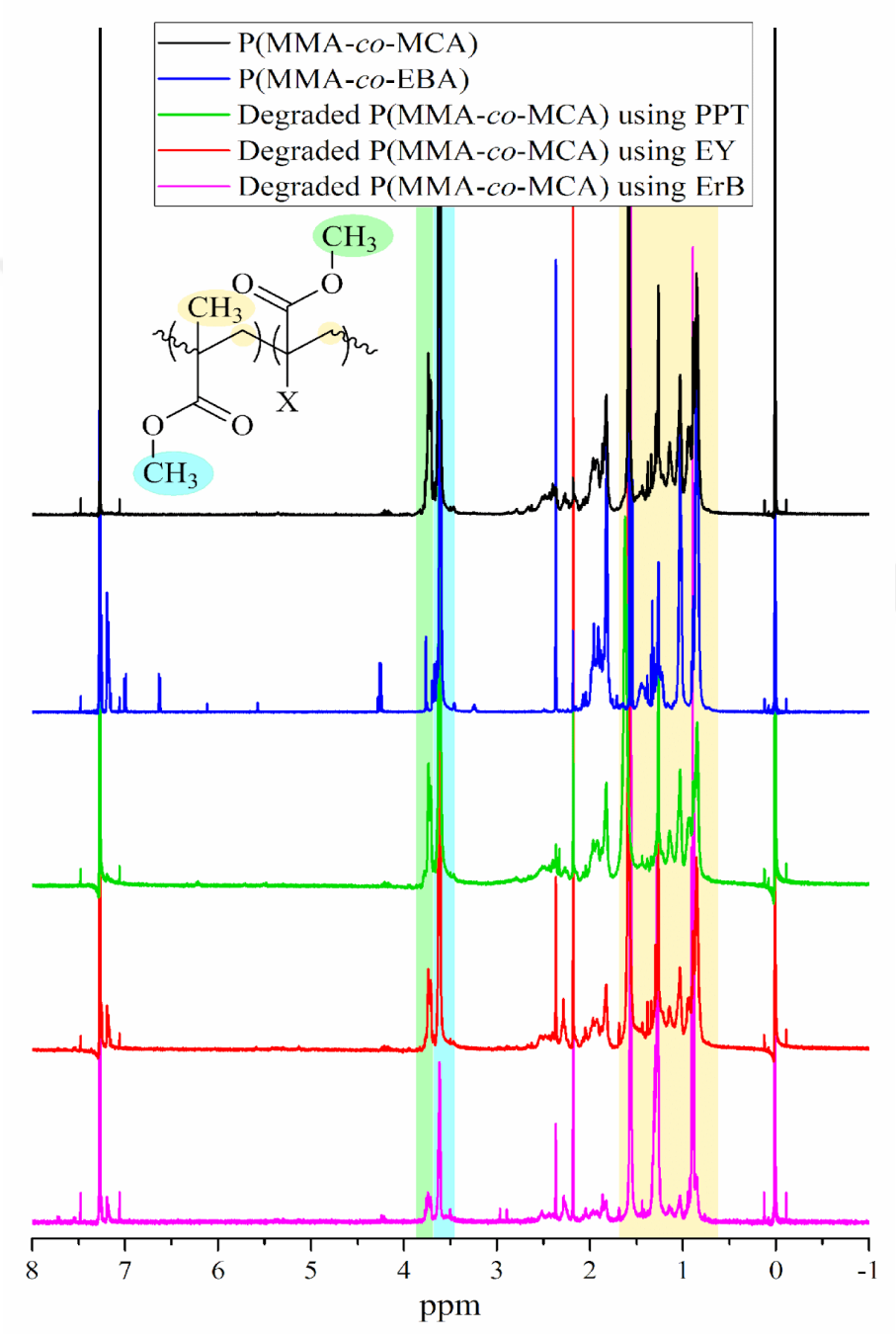

Figure A.1 : ^{1}H-NMR spectra of P(MMA-*co*-MCA), P(MMA-*co*-EBA) and degraded samples of P(MMA-*co*-MCA) using PPT, EY and ErB.

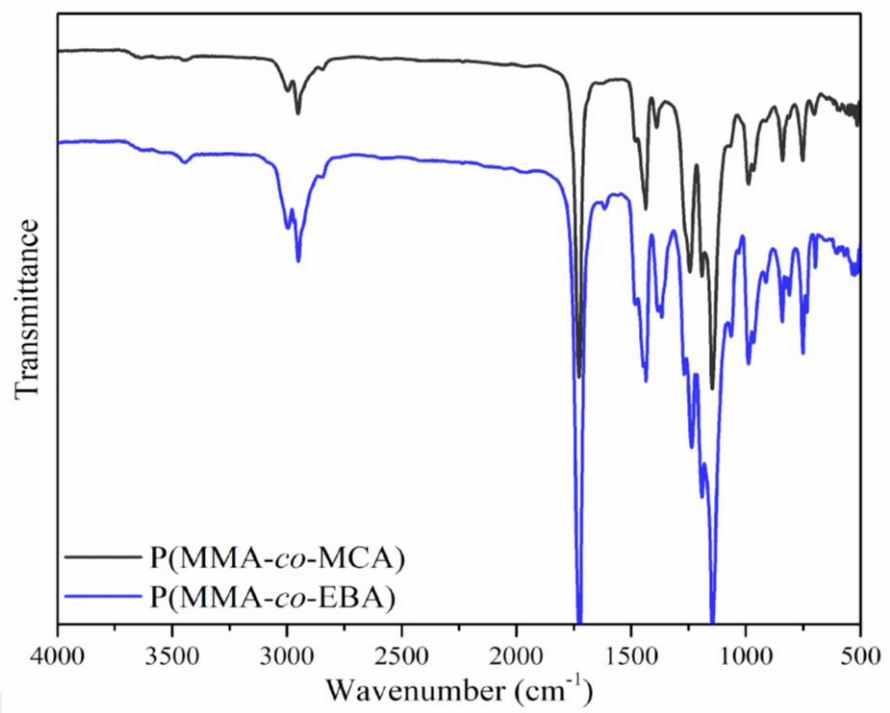

Figure A.2 : FT-IR spectra of P(MMA-*co*-MCA) and P(MMA-*co*-EBA).

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- **Cakir Y. B., Kiliclar H.C., Yagci Y**. 2023: White LED Light Induced Degradation of Polyacrylates as a Green Alternative for Polymer Recycling. Advanced Polymer of Macromolecular Engineering 2023 (APME'23), Paris, Fransa (Poster Presentation)
- **Kiliclar H.C., Arslan Z., Cakir Y. B.**, **Uzun R.T., Yagci Y.** 2023: New Advances on Visible Light Induced Ambient Temperature Photodegradation and Photopolymerizations. Advanced Polymer of Macromolecular Engineering 2023 (APME'23), Paris, Fransa (Oral Presentation)