

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL**

**DIMANGANESEDECACARBONYL CATALYZED VISIBLE LIGHT  
INDUCED AMBIENT TEMPERATURE DEPOLYMERIZATION OF  
POLY(METHYL METHACRYLATE)**



**M.Sc. THESIS**

**Zeynep ARSLAN TANGÜLER**

**Department of Chemistry**

**Chemistry Programme**

**MARCH 2024**



**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL**

**DIMANGANESEDECACARBONYL CATALYZED VISIBLE LIGHT  
INDUCED AMBIENT TEMPERATURE DEPOLYMERIZATION OF POLY  
(METHYL METHACRYLATE)**

**M.Sc. THESIS**

**Zeynep ARSLAN TANGÜLER  
(509211279)**

**Department of Chemistry**

**Chemistry Programme**

**Thesis Advisor: Prof. Dr. Barış KIŞKAN**

**MARCH 2024**



**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ**

**DİMANANEZDEKAKARBONİL KATALİZLİ GÖRÜNÜR IŞIK  
BÖLGESİNDE VE ODA SICAKLIĞINDA POLİ(METİLMETAKRİLAT)  
DEPOLİMERİZASYONU**

**YÜKSEK LİSANS TEZİ**

**Zeynep ARSLAN TANGÜLER  
(509211279)**

**Kimya Anabilim Dalı**

**Kimya Programı**

**Tez Danışmanı: Prof. Dr. Barış KIŞKAN**

**MART 2024**



Zeynep Arslan Tangüler, a M.Sc. student of İTÜ Graduate School student ID 509211279, successfully defended the thesis entitled “DIMANGANESEDECACARBONYL CATALYZED VISIBLE LIGHT INDUCED AMBIENT TEMPERATURE DEPOLYMERIZATION OF POLY (METHYL METHACRYLATE)”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

**Thesis Advisor :**     **Prof. Dr. Barış KIŞKAN** .....  
İstanbul Technical University

**Jury Members :**     **Doç. Dr. Cüneyt Hüseyin ÜNLÜ** .....  
İstanbul Technical University

**Prof. Dr. Aydan DAĞ** .....  
Bezmialem Vakıf University

**Date of Submission : 04 February 2024**

**Date of Defense : 18 March 2024**





*To my loved ones,*



## FOREWORD

First and foremost, I would like to express my heartfelt gratitude to my late supervisor, Prof. Dr. Yusuf Yağcı, for letting me to work with him and for providing me with invaluable guidance throughout my academic journey. His vast knowledge and mentorship not only allowed me to broaden my horizons in chemistry but also all aspects of life. His recent death was a great loss to the scientific community, and I will always remember his remarkable contributions to the science and his enjoyable personality for the rest of my life.

I am fortunate to be able to continue my research with Prof. Dr. Barış Kışkan, who has taken over as my advisor. I would secondly like to thank to him, who has an extensive knowledge and experience in the field of chemistry, for his contribution to my research and kindness. He supported the development of my research during my thesis and guided me with his knowledge.

I also would like to express my special gratitude, my colleague Hüseyin Cem Kılıçlar, who helped me tremendously during my experimental work in the lab and taught me how to conduct experiments. He always guided me with as much as he can and supported everytime when I need help.

I am honored to have had the opportunity to work with such talented and dedicated team for their friendship and support. I want to thank each past and present member at Yağcı Lab, in particular, Zeynep Deliballı, Yüstra Bahar Çakır, Cansu Aydoğan, Gizem Güngör, Emine Yılmaz, Kerem Kaya, Emirhan Gençosman, Ahmet Şefizade, Büşra Nakipoğlu Bölücü, Tuğberk Tabak, Cansın Birsen Buldum, Azra Kocaarslan Ahmetali, Sevinç Gülyüz and Ragıp Talha Uzun.

I would like to thank to my family, friends and my beloved husband Caner. Their infinite support and encouragement provided me to achieve my academic goals throughout my entire life.

I also want to thank to the TUBITAK (The Scientific and Technical Research Council of Turkey) Project number 120C121 and Istanbul Technical University Research Fund Project no. TYL-2022-44203. Moreover for financial support, I would like to thank The Scientific and Technological Research Council of Turkey (TUBITAK (2211-A))

February 2024

Zeynep Arslan Tangüler  
(Chemist)



## TABLE OF CONTENTS

	<u>Page</u>
<b>FOREWORD</b> .....	<b>ix</b>
<b>TABLE OF CONTENTS</b> .....	<b>xi</b>
<b>ABBREVIATIONS</b> .....	<b>xiii</b>
<b>SYMBOLS</b> .....	<b>xv</b>
<b>LIST OF TABLES</b> .....	<b>xvii</b>
<b>LIST OF FIGURES</b> .....	<b>xix</b>
<b>SUMMARY</b> .....	<b>xxi</b>
<b>ÖZET</b> .....	<b>xxiii</b>
<b>1. INTRODUCTION</b> .....	<b>1</b>
<b>2. THEORETICAL PART</b> .....	<b>3</b>
2.1 Environmental Related Plastic Waste.....	3
2.2 Recycle.....	4
2.3 PMMA as a Commercial Plastic.....	5
2.3.1 Synthesis of PMMA.....	5
2.3.2 Atom transfer radical polymerization (ATRP).....	7
2.3.2.1 Mechanisms and kinetics of ATRP.....	7
2.3.2.2 Components used in ATRP.....	8
2.3.3 Nitroxide-mediated free radical polymerization (NMRP, NMP).....	9
2.3.4 Reversible addition / fragmentation chain transfer (RAFT).....	10
2.4 Photochemistry.....	11
2.4.1 Mn <sub>2</sub> Co <sub>10</sub> chemistry.....	11
2.5 Depolymerization / Degradation.....	12
2.5.1 Photodepolymerization.....	18
<b>3. EXPERIMENTAL PART</b> .....	<b>21</b>
3.1 Materials and Chemicals.....	21
3.2 Equipments.....	21
3.2.1 GPC.....	21
3.2.2 NMR.....	22
3.2.3 Light-source.....	22
3.3 Preparation Methods.....	22
3.3.1 Using ATRP to synthesize PMMA-Cl <sup>1</sup> .....	22
3.3.2 Using ATRP to synthesize PMMA-Cl <sup>2</sup> .....	22
3.3.3 Using ATRP to synthesize PMMA-Br.....	23
3.3.4 Using ATRP to synthesize PMMA-co-PGMA-Cl.....	23
3.4 Photodepolymerization.....	23
<b>4. RESULT AND DISCUSSION</b> .....	<b>25</b>
<b>5. CONCLUSIONS AND RECOMMENDATIONS</b> .....	<b>31</b>
<b>REFERENCES</b> .....	<b>33</b>
<b>APPENDICES</b> .....	<b>41</b>
<b>CURRICULUM VITAE</b> .....	<b>45</b>



## ABBREVIATIONS

<b>ATRP</b>	: Atom Transfer Radical Polymerization
<b>CRP</b>	: Controlled Radical Polymerization
<b>GPC</b>	: Gel Permeation Chromatography
<b><sup>1</sup>H NMR</b>	: Proton Nuclear Magnetic Resonance Spectroscopy
<b>MMA</b>	: Methyl Methacrylate
<b>Mn<sub>2</sub>(CO)<sub>10</sub></b>	: Dimanganese Decacarbonyl
<b>NMP</b>	: Nitroxide Mediated Polymerization
<b>PMDETA</b>	: N,N,N,N,N-pentamethyldiethylenetriamine
<b>PMMA</b>	: Polymethylmethacrylate
<b>RAFT</b>	: Reversible Addition-Fragmentation Chain-Transfer Polymerization
<b>TEMPO</b>	: 2,2,6,6-tetramethylpiperidine 1-oxyl
<b>UV</b>	: Ultraviolet
<b>Vis.</b>	: Visible



## SYMBOLS

$^{\circ}\text{C}$	: Degree Celcius
$\mathcal{D}$	: Polydispersity index
$M_n$	: The number average molecular weight
$M_w$	: The weight average molecular weight
$\lambda$	: Wavelength





## LIST OF TABLES

	<u>Page</u>
<b>Table 4.1</b> : Molecular weight characteristics of PMMA-Cl1, PMMA-Br and PMMA-co-PGMA-Cl before and after visible light irradiation (a).....	27
<b>Table 4.2</b> : Molecular weight characteristics of PMMA-Cl before and after visible light irradiation (a). .....	28
<b>Table A.1</b> : Molecular weight decrease caused by depolymerization.....	44
<b>Table A.2</b> : Visible light induced depolymerization of different polymers. ....	44





## LIST OF FIGURES

	<u>Page</u>
<b>Figure 2.1</b> : Brief representation of ATRP mechanism [70].	7
<b>Figure 2.2</b> : Nitroxide-Mediated polymerization mechanism [72].	9
<b>Figure 2.3</b> : Steps of Reversible Addition/Fragmentation Chain Transfer polymerization mechanism [75].	10
<b>Figure 2.4</b> : $Mn_2(CO)_{10}$ -induced photochemical reaction of terminal halide groups for block copolymer generation [80].	12
<b>Figure 2.5</b> : Depolymerization illustration of PMMA-Cl [33].	13
<b>Figure 2.6</b> : (a) Degradation illustration of copolymers, (b) GPC chromatograms of copolymers (MMA-MCA) (1–3,5) and PMMA (4) before (black line) and after degradation (red line) in the presence or absence of catalyst (RuInd) or cocatalyst (n-Bu <sub>3</sub> N) [85].	14
<b>Figure 2.7</b> : Illustration of catalyzed depolymerization of poly(n-butyl methacrylate) (PBMA) macroinitiator with terminal chlorine chain-end functionality via $CuCl_2/TPMA$ [34].	15
<b>Figure 2.8</b> : (a) Illustration of depolymerization via iron catalysts, (b) Proposed mechanism of ATRP with Reversible Propagation, Activator Regeneration, Supplemental Activation of the Alkyl Halide, and Lactonization of the Chain-End [86,87].	16
<b>Figure 2.9</b> : Illustration of light assisted thermal depolymerization system [87].	17
<b>Figure 2.10</b> : Illustration of catalyst-free depolymerization of various materials by reversible-addition-fragmentation chain-transfer (RAFT) technique [88].	17
<b>Figure 2.11</b> : Visual representation of depolymerization system through short-path distillation setup [89].	18
<b>Figure 4.1</b> : Photoinitiated unzipping type depropagation of PMMA-Cl with $Mn_2(CO)_{10}$ at 400 nm.	25
<b>Figure 4.2</b> : GPC analysis of a) PMMA-Cl and depolymerized PMMA-Cl b) PMMA-Br and depolymerized PMMA-Br c) PMMA-co-PGMA-Cl and depolymerized PMMA-co-PGMA-Cl.	27
<b>Figure 4.3</b> : GPC analysis of PMMA-Cl and depolymerized PMMA-Cl under 400 nm visible light and a) 23°C b) 90°C c) 170°C.	27
<b>Figure 4.4</b> : The effect of temperature on the $M_n$ and $\bar{M}_w$ values obtained through gel permeation chromatography.	28
<b>Figure 4.5</b> : <sup>1</sup> H-NMR spectra of Bz-PMMA-Cl before (red) and after depolymerized (blue).	29
<b>Figure A.1</b> : <sup>1</sup> H-NMR spectrum of depolymerized Bz-PMMA- Cl.	42
<b>Figure A.2</b> : Peak analysis of <sup>1</sup> H-NMR spectra of depolymerized Bz-PMMA- Cl to separate the integration values of $CHCl_3$ and aromatic hydrogen peaks.	43
<b>Figure A.3</b> : <sup>1</sup> H-NMR spectrum of initial Bz-PMMA- Cl	43



# **DIMANGANESEDECACARBONYL CATALYZED VISIBLE LIGHT INDUCED AMBIENT TEMPERATURE DEPOLYMERIZATION OF POLY (METHYL METHACRYLATE)**

## **SUMMARY**

Photochemistry is known to be one of the subbranch of chemistry that studies the light induced chemical reactions. In photochemistry light is significantly essential, since it provides the energy to initiate the chemical reactions. The growing importance of photochemistry in recent years is not unexpected as it provides a big support for the development of sustainable resources of energy through its environmentally friendly approach to green chemistry and lower energy requirements for sustainability. Currently, photochemistry offers prominent benefits and advantages over the conventional techniques, such as precise spatial-temporal control and cost-efficiency. Furthermore, as the demand for the green chemistry approach increases, so does the necessity for photochemical methods in today's world.

One of the most promising application of photochemistry is depolymerization, which could be defined as the process of breaking down polymers into their constituent monomers or reverse of the polymerization mechanism. Hence, photoinduced depolymerization, which is particularly beneficial for recycling, serves as a crucial answer to address the recycling problem. Thus this novel concept named as "photodepolymerization", combines light and depolymerization together which will be a key to overcome the environmental concerns, such as limits the potential usage of harmful chemicals in industrial applications and reducing non-renewable resource use.

Polymethyl methacrylate (PMMA), usually referred to as plexiglass, is a widely utilized rigid and transparent plastic material belonging to the synthetic polymer family. Additionally, this polymer is highly adaptable and finds application across several various industries due to its unique properties including robustness, weather resistance, and transparency. Thanks to its excellent UV resistance, optical clarity and other prominent characteristics, PMMA is widely used in the field of architecture, construction, automotive, electronics, furniture and medical field. Hence, the process of depolymerizing the commonly employed PMMA polymer into its constituent monomer units by the utilization of light holds great potential as an eco-friendly solution for promoting sustainable development and addressing environmental issues related to plastic recycling. It could be emphasized that within the field of green chemistry, photodepolymerization technique has significant promise in minimizing the harmful environmental effects and providing substantial benefits.

This thesis presents a study on the synthesis of polymethylmethacrylate (PMMA) derivatives with different halogen chain ends using Atom Transfer Radical Polymerization (ATRP) technique and subsequent depolymerization through visible light irradiation using dimanganese decacarbonyl ( $Mn_2(CO)_{10}$ ) as a photoinitiator. The effects of irradiation time and temperature on the depolymerization process were investigated. This study highlights that ambient temperature is sufficient for the photodepolymerization process. As a result, gel permeation chromatography (GPC)

analysis results shows a noticeable decrease in molecular weight with an increase in polydispersity index. Overall, this work emphasizes the potential and importance of the visible light-induced depolymerization technique for PMMA derivatives.



## **DİMANGANEZDEKAKARBONİL KATALİZLİ GÖRÜNÜR İŞİK BÖLGESİNDE VE ODA SICAKLIĞINDA POLİ(METİLMETAKRİLAT) DEPOLİMERİZASYONU**

### **ÖZET**

Fotokimya, ışığın absorpsiyonu sonucu meydana gelen kimyasal reaksiyonları inceleyen kimya alt disiplini olarak adlandırılabilir. Bu reaksiyonlar ise fotokimyasal reaksiyonlar olarak isimlendirilip ultraviyole, görünür ışık veya kızılötesi ışımaya bölgesinde gerçekleşebilir. Fotokimyadaki temel bileşen olan ışık, kimyasal reaksiyonları başlatmak için gereken enerjiyi sağlar. Son yirmi yılda çevre dostu yaklaşımlara olan ihtiyacın ve ilginin artmasıyla fotokimyanın önemi giderek artmaktadır. Fotokimya, geleneksel termal işlemlere göre birçok avantaj sunar. Örneğin, mekansal ve zamansal kontrol edilebilirliği, maliyet üzerindeki olumlu etkisi, düşük sıcaklıkta çalışma olanağı ve çevre dostu olması bunlardan birkaçıdır. Fotokimya öne çıkan bu özellikleri sayesinde son zamanlarda yapılan çalışmaların ilgi odağı olarak üzerinde araştırmacılar tarafından yoğunlaşılacak bir disiplin haline gelmiştir.

Son zamanlarda, ışık ve depolimerizasyonun birleştiği yeni bir konsept ortaya çıkmıştır ve "fotodepolimerizasyon" olarak adlandırılmaktadır. Bu konsept, düşük enerji tüketimiyle depolimerizasyon için bir çözüm sunarak istenmeyen atıkları yönetmeye, yenilenemeyen kaynakların kullanımını azaltmaya ve üretim sürecinde toksik kimyasalların kullanımını sınırlamaya yardımcı olarak günümüz çevresel sorunlarına umut vaat etmektedir. Ayrıca enerji bağımlılığına olan ihtiyacın azaltılmasıyla beraber ekonomik açıdan da birçok endüstriyel uygulama adına faydalı olmaktadır. Fotodepolimerizasyon kullanarak araştırmacılar, çevresel sorunları ele alabilir ve çeşitli alanlarda daha çevre dostu yaklaşımların geliştirilmesine katkıda bulunabilirler.

Plastik endüstrisinde en yaygın kullanılan genel ticari plastik malzemelerden biri polimetilmetakrilat (PMMA) veya diğer adıyla akrilik camdır. PMMA, yüksek ışık geçirgenliği, kimyasallara karşı gösterdiği güçlü direnç, sert hava koşullarına dayanıklılık ve yüksek yüzey sertliği gibi özellikleri nedeniyle farklı endüstrilerde çeşitli uygulamalara sahip bir termoplastik polimerdir. Optik bileşenlerin, elektroniklerin, endüstriyel lambaların, uçak camlarının ve otomobil parçalarının üretiminde oldukça sık kullanılır. Her geçen yıl daha farklı sektörlerde de endüstriyel ölçekteki PMMA kullanımının artmasıyla beraber pazarda yoğun bir talep haline gelmiştir. Gelişen ihtiyaç doğrultusunda üretimine yönelik ilgi artmış ve plastik pazarında önemli bir konuma ulaşmıştır. Bu nedenle, PMMA'nın geri dönüşümü sürdürülebilirlik açısından önemli bir konu haline gelmiştir. Fotodepolimerizasyon tekniğinin kullanımı ise bu alanda umut vaat eden bir çözüm sunar. Atıkların çevresel kötü etkisinin azaltılmasında, plastik üretiminin kısıtlanmasında ve genel olarak atık yönetiminin çok daha sistematik bir şekilde ele alınıp sürdürülebilir bir yaklaşımı teşvik etmesinde kullanılabilir. Bu çalışmada ise çevre kirliliğine bağlı olarak gelişen

geri kazanım ve yeniden kullanma akımları üzerine fotokimyasal reaksiyonlar ilk defa depolimerizasyon sistemlerine adapte edilmiştir.

PMMA sentezi için kullanılabilecek çeşitli yöntemler mevcuttur. Bunlardan biri olan yığın polimerizasyon yöntemi ile endüstriyel ölçekte uygun maliyetli, basit ve yüksek kalitede polimerler elde etmek mümkündür. Yığın polimerizasyon yönteminde monomer, zincir transfer ajanları ve başlatıcı kullanılarak reaksiyon karışımı hazırlanır ve polimerizasyon termal olarak gerçekleşir. Süspansiyon polimerizasyon tekniği ise yığın polimerizasyona göre belli avantajlar sunar. Daha az enerji gereksinimine ihtiyaç duyan bu yöntem asılı halde bulunan küçük MMA damlacıklarının PMMA oluşturmasını sağlar. Emülsiyon polimerizasyon yöntemi ile PMMA eldesinde ise MMA monomerleri uygun bir yüzey aktif madde veya emülgatör ile tek faz içinde sulu ortamda tutularak radikal olarak polimerizasyon başlatılır. Elde edilen PMMA filtrasyon veya santrifüjleme yoluyla emülsiyondan ayrılır ve kurutulur. PMMA'yı yüksek saflıkta ve istenen moleküler ağırlıkta elde etmek için bir başka yöntem de çözelti polimerizasyonudur. Bu yöntemde MMA monomeri bir çözücü içinde çözülür, ardından serbest radikal başlatıcı ile polimerizasyon başlatılır. Çözelti polimerizasyonu diğer polimerizasyon tekniklerine kıyasla daha pahalı ve zaman alıcı olsa da bu yöntemle de PMMA eldesi mümkündür. Son olarak geleneksel yöntemlere göre üstün avantajlara sahip bir başka polimerizasyon grubu olan kontrollü radikal polimerizasyon yöntemleri ile istenilen mimariye ve moleküler ağırlığına sahip polimerler elde etmek mümkündür. Bu yöntemlerden en çok kullanılan Atom Transfer Radikal Polimerizasyonu (ATRP) ve Tersinir Katılma Ayrılma Zincir Transfer polimerizasyon (RAFT) tekniğidir. ATRP ve RAFT arasındaki en temel farklardan biri ATRP'de sürekli ve bir denge halinde aktivasyon ve deaktivasyon basamakları bulunurken RAFT metotunda sürekli ve tersinir bir zincir transfer prosesi bulunur. ATRP de sıklıkla kullanılan monomerler metakrilatlar, akrilatlar, akrilonitriller, metakrilamitler ve stirenlerdir. Monomer çeşitliliği sayesinde oldukça kapsamlı endüstriyel kullanım alanına sahiptir. Örnek olarak biyobozunur malzemeler, otomotiv parçaları, optoelektronik malzemeler ve ilaç salınım sistemleri verilebilir. RAFT yöntemi ise pek çok monomer için tersinir bir deaktivasyon radikal polimerizasyon tekniği olarak tanımlanabilir. Zincir transfer ajanı olarak ditiyoesterler, tritiyokarbonatlar ve ksantatlar kullanılarak zincir transfer mekanizma aşaması başlatılır ve yıldız, blok, dallanmış veya hiper dallanmış polimerler elde edilebilir.

Bu çalışma, ATRP ile sentezlenen PMMA türevlerinin dimanganez dekarbonil ( $Mn_2CO_{10}$ ) fotobaşlatıcısı ile oda sıcaklığında görünür ışık bölgesinde depolimerizasyonunu ele almıştır. Dimanganez dekarbonil bileşiği metal-metal bağı olan Mn-Mn bağı ve her mangan atomu ile koordinasyon halinde olan on karbonmonoksit (CO) ligandına sahip bir organometalik komplekstir.  $Mn_2CO_{10}$  ultraviyole (UV) ışığına maruz kaldığında moleküldeki elektronların daha düşük enerjili orbitallerden daha yüksek enerjili orbitallere geçiş yapmasını yol açarak elektronik uyarılmaları tetikler ve molekülde kimyasal değişimlere yol açabilir. Bu radikal üretebilme yeteneği sebebiyle polimerizasyon reaksiyonlarında fotobaşlatıcı olarak görev alır.

Bu çalışmada polimerizasyon karışımı  $Mn_2CO_{10}$  fotobaşlatıcısı kullanılarak görünür bölge ışığı ile aydınlatılmış ve aydınlatılma sonucu  $MnCO_5$  metaloradikallerini oluşturmuştur. Oluşan radikaller ATRP ile sentezlenmiş olan PMMA-Cl polimerinin uç kısmındaki halojen olan klor atomunu kopararak radikal oluşturur ve depolimerizasyon reaksiyonunu başlatır. Fotodepolimerizasyon mekanizması çalışmada fermuar modeline benzetilmiştir ve polimerin en ucundan başlayarak

polimer zinciri boyunca devam eder. Böylece polimerden ayrılan her bir MMA monomeri polimerin kendi molekül ağırlığının azalmasını yol açar. Bu sayede jel geçirgenlik kromatografisi (GPC) ile polimerizasyon kinetiği takip edilir ve belli sürelerde reaksiyon karışımından numune alınarak depolimerizasyon için optimal süre belirlenir. Analiz sonuçlarından moleküler ağırlıktaki azalmanın ve polidispersite indeksindeki artışın en verimli olduğu sürenin altı saat olduğuna karar verilmiştir. Farklı halojen atomlarının depolimerizasyon üzerindeki verimini incelemek amacıyla klor uçlu ve brom uçlu olmak üzere iki farklı PMMA türevi ATRP yöntemi ile sentezlenmiştir. Aynı koşullar altında yapılan denemelerde Br uçlu PMMA'nın, bromun hızlı kopması ve ortamdaki radikal konsantrasyonu bir anda artması sonucu istenmeyen birleşme reaksiyonuna yol açtığı gözlemlenmiş ve depolimerizasyon üzerinde verimli olmadığı sonucuna varılmıştır. Klor uçlu PMMA polimerinde ise klorun broma göre daha yavaş kopması sonucu düzenli radikal oluşturduğu tespit edilmiş ve depolimerizasyon kinetiğini katalizleme etkisi olduğu anlaşılmıştır. Bu nedenle çalışma PMMA-Cl üzerinde yapılan denemeler ile devam etmiştir. Sıcaklığın depolimerizasyon verimi üzerindeki arttırıcı etkisinin bilinmesiyle bu çalışmada da sıcaklık değişiminin reaksiyon kinetiğini nasıl etkileceği görmek için denemek istenmiş ve farklı sıcaklıklarda yapılan denemeler ile depolimerizasyon yüzdesindeki artış tespit edilmiştir. Ancak oda sıcaklığındaki sonuçlar hala rekabetçi ve yenilikçi özelliğini korumaktadır. Jel geçirgenlik kromatografisiyle reaksiyon karışımından altı saat sonra alınan numune ile depolimerizasyon verimi %20 olarak hesaplanmıştır. Ayrıca bir diğer analiz yöntemi olan nükleer manyetik rezonans (<sup>1</sup>H-NMR) da çalışmada kullanılmış ve depolimerizasyon verimini kontrol edebilmek için ATRP başlatıcıları olarak benzil bromür ve benzil klorür bu amaçla en başta polimer sentezinde kullanılmıştır. Benzilik zincir ucundan gelen aromatik piklerin ve PMMA'nın metoksi gruplarına karşılık gelen piklerin artan entegrasyon oranının depolimerizasyon reaksiyonunun kanıtı olduğu belirtilerek depolimerizasyon verimi %40 olarak hesaplanmıştır. Ancak Mn<sub>2</sub>CO<sub>10</sub>'un paramanyetik genişleme etkisi nedeniyle <sup>1</sup>H-NMR spektrumunun çok doğru entegrasyon değerleri vermediği tezde belirtilmiştir.

Sonuç olarak, bu çalışma sayede PMMA türevlerinin çevre dostu bir yaklaşım ile tekrar geri kazanımını sağlanmış olup düşük enerji tüketimiyle ısıya gereksinimi yok ederek ışık sayesinde, kontrol edilebilirliği kolay ve pratik olan, kimyasal gereksinimini azaltan çevreye duyarlı bir yöntem literatüre kazandırılmıştır. Yeşil kimya ve sürdürülebilirlik adına fotodepolimerizasyon ve fotodegradasyon konusunda daha ileri çalışmalar devam etmektedir.



## 1. INTRODUCTION

Photoinduced methods encompass a variety of scientific techniques that utilize the interaction between light and matter to induce chemical and physical changes, with applications in fields such as materials science, energy conversion, environmental science, and medicine [1,2]. They have numerous advantages over conventional methods, including spatial and temporal control, cost-effectiveness, the ability to work at low temperatures, last but not least, being environmentally friendly [3–12]. Therefore, in the last two decades there has been a growing interest in the utilization of photochemical processes in a variety of applications. One of the most significant applications of photochemical processes is photoinduced polymerization, which has been used in the production of dental fillings, 3D printing, inks, adhesives, photoresists, coatings, and so on [13–18].

Photochemical reactions provides precise control over the reaction media where it takes place. When photoinduced methods compared with the conventional methods, it enables researches to have a spatial and temporal control to manipulate chemical reactions [5,6]. This level of control has led to the development of 3D printing systems that are capable of producing complex designs, structures and materials. Since light is used as an energy source, the distribution of heat becomes more homogeneous within the reaction environment. This results in a more controlled and safer reaction condition. Moreover, as they require less solvent requirements, photochemical reactions provide a more eco-friendly, cost-effective and environmentally sustainable approach to synthesis [3,4].

The advantages of photochemical reactions have led to its application in diverse fields, particularly the development of photoinduced polymerizations techniques. Several methods, including chain and step-growth polymerizations, cationic, radical, ring-opening, and radical coupling systems, have been used to adapt photoinduced polymerizations [19–32]. As a result, various polymers with different characteristics and applications have been generated.

The development of recycling and reuse attempts have become a significant topic, since the need for environmentally sustainable processes continues to grow. One of the ways that this has been achieved is through the adaptation of photochemical reactions to depolymerization systems. Depolymerization is the process of breaking down polymers into their monomer units so that monomers can be reused to generate new polymers. This is an eco-friendly alternative to traditional methods that using high temperatures and chemical catalysts.

Several groups have adapted photochemical reactions to depolymerization systems, with one of the most notable being the work of Ouchi and colleagues. In their most recent study, they used ruthenium catalysts to depolymerize chlorinated polymethyl methacrylate (PMMA-Cl) at 100°C, but the depolymerization efficiency was found to be low [33]. More recently, Matyjaszewski and colleagues used a copper catalyst (CuCl<sub>2</sub>/tris(2-pyridylmethyl)amine) to depolymerize PMMA-Cl at 170°C [34]. The high-temperature requirements of this method limit its application in terms of environmental sustainability.

In this study, PMMA-Cl synthesized by atom transfer radical polymerization (ATRP) will be depolymerized using Mn<sub>2</sub>(CO)<sub>10</sub> under visible light irradiation [35]. Mn<sub>2</sub>(CO)<sub>10</sub> is a photoactive catalyst that absorbs visible light and undergoes homolytic cleavage to form Mn(CO)<sub>5</sub> radicals [36]. These radicals remove halogens from the end of polymer chains, leading to depolymerization under controlled conditions. The efficiency of the depolymerization process has evaluated by analyzing the resulting products via various characterization techniques, such as nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC).

## **2. THEORETICAL PART**

### **2.1 Environmental Related Plastic Waste**

The problem of environmental plastic waste has become a major problem due to its adverse effects on the environment and human health. Plastic waste originates from a numerous sources, including households, industry, and transportation [37,38]. These plastic waste products are generally improperly disposed. This situation results in pollution in the environment, in particular oceans, rivers, and landfills. Wildlife, especially marine life, is among the group that face the greatest pollution risk, since the plastic waste can be entangled or even consumed by the living beings [37,39]. Additionally, plastic waste can release harmful chemicals into the environment, they contaminate food chains, thus it leads to become a risk to human health [40].

The issue of plastic waste has been taken up with many initiatives over time. Most common ones are the introduction of recycling programs, the production of biodegradable polymers, and stop using the single-use plastics [38,41]. Although these efficient applications and developed recycling programs, there are still many obstacles to be handle. These challenges include insufficient waste management, deficient environmental awareness among the general population of all ages, the need for alternative waste management systems and sustainable production types for plastic derivatives.

Mechanical recycling is one of the most common examples of plastic waste recovery [42]. It involves the procedures of collection, sorting, and processing of plastic waste into new products. Firstly, the plastic waste is collected and sorted according to its type and color. Secondly, it is cleaned and shredded into small pieces or pellets. Then, the pellets are melted down to create new plastic products, such as bottles, containers, and packaging materials. Mechanical recycling conservs natural resources like oil, that are used to produce virgin plastic materials. It helps to reduce the amount of plastic waste that ends up in landfills and the environment. Additionally, the process of mechanical

recycling creates job opportunities in the recycling industry and helps to support the circular economy [41].

## **2.2 Recycle**

Recycling is an essential process of waste management since it helps to reduce environmental impact of waste and protect natural resources. The recycling process involves various stages, including the gathering, separation, treatment, and manufacture of new products using materials that would otherwise be discarded [43]. This procedure not only decreases the volume of waste directed to landfills but also contributes to the conservation of natural resources by diminishing the need for raw materials. One important aspect of recycling is the concept of value-added products. Value-added products in recycling refer to the manufacture of new products with greater economic value than the original material, resulting in a profit for the recycling business [44]. The production of new products from old materials that would otherwise be wasted benefits the economy by creating new industries and job possibilities. Recycled plastic bottles that are transformed into polyester fabrics, or recycled glass that is made into new glass products such as bottles and jars can be given as examples to value added products [45].

One way to create value-added products in recycling is through depolymerization [46]. Depolymerization is the process of breaking down a polymer into its monomer units, which can after be used to create new polymers. This approach can be used to recycle a variety of materials, including polyethylene terephthalate (PET) and polycarbonate (PC) plastics.

Another approach to value-added recycling is through upcycling. Upcycling involves transforming waste materials into products of higher value, with improved properties or functionality [46]. For example, the upcycling of waste plastics into construction materials, such as insulation, can provide a more sustainable alternative to traditional construction materials [39,47,48]. Upcycling can also involve the use of innovative technologies, such as 3D printing, to create new products from recycled materials.

The concept of value-added recycling is closely linked to the circular economy, which aims to reduce waste and promote sustainable resource use [49]. By creating value-

added products from waste materials, we can reduce the environmental impact of waste and help to create a more sustainable future.

### **2.3 PMMA as a Commercial Plastic**

Poly (methyl methacrylate) (PMMA) is a commodity transparent thermoplastic that is also known as plexi glass and acrylic glass. Brand names or trade names could also be used to define PMMA such as Perclax, Crylux, and Lucite [50–52]. It is basically a synthetic polymer that is composed of methyl methacrylate monomer units [53]. Beyond this, it is a notable material that offers various remarkable features such as high light transmittance. Thus it could be utilized in the field of display screens, lenses, and medical equipment where optical clarity is significant and essential at the same time. Also, PMMA is a strong and durable material that has high resistance to impact, weathering, aging, UV radiation, and a variety of chemicals [54–56]. In addition to these properties, it is easy to machine, fabricate, mold and can be easily shaped into different forms to make it versatile for specific usage. Overall, these unique features make it a popular and suitable choice for plenty of applications across several industries, for instance, PMMA is an ideal material to be used in architectural and automotive applications due to its chemical resistance and biocompatibility. Another industry where PMMA finds widespread use through the feature of being resistant to weathering and UV radiation is the manufacturing of electronic devices such as touch screens and other electronic components [13,15,17,53,57,58]. Thus being a preferred and widely used material in many industries, including automotive, construction, electronics, and medical, it is expected to increase the growth of PMMA production on a global scale according to the boosting demand [59,60]. Global PMMA Market Report stated that the PMMA consumption was approximately 4.4 million tons in 2020 [61]. China was the leading consumer of PMMA, with a consumption of approximately 1.5 million tons in the same year, followed by Europe and North America. To sum up all these, the numbers highlight how PMMA plays a major role in various industries and how it is important in the global economy.

#### **2.3.1 Synthesis of PMMA**

There are various techniques that can be used to synthesize PMMA. Bulk polymerization is one of the most common methods since it is cost-effective, simple,

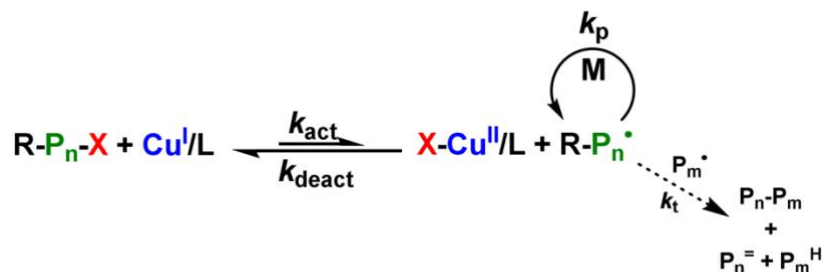
and proper for a scale-up process in industrial applications to obtain a high-quality polymer. In the bulk polymerization technique, the monomer methyl methacrylate (MMA) is mixed with an initiator and other additives, such as chain transfer agents or stabilizers, then the reaction mixture is heated to initiate the polymerization reaction. It continues until the monomer is consumed and a solid polymer, PMMA is formed [62,63]. Another technique to synthesize PMMA is the suspension polymerization method which has several advantages over bulk polymerization, including lower heat requirement, reduced environmental impact, and viscosity. This process takes place in an aqueous media via suspended small MMA droplets containing a dispersant and a free radical initiator. The resulting PMMA polymer particles are separated from the suspension by filtration or centrifugation, then they are washed, and dried respectively [64]. Another method to synthesize PMMA by emulsifying small droplets of MMA monomer in an aqueous medium containing a surfactant and a free radical initiator is emulsion polymerization. The resulting PMMA polymer particles are separated from the emulsion by filtration or centrifugation and then washed and dried. Overall, this technique is another viable alternative to other synthesizing methods to compare in better control over particle size and lower viscosity [62,65,66]. Another method to obtain PMMA via high purity and the desired molecular weight is solution polymerization. In this process, the MMA monomer is dissolved in a solvent, then it is polymerized by a free radical initiator. The resulting PMMA polymer is obtained as a solution and the solvent can be removed by evaporation. Even though solution polymerization is more expensive and time-consuming compared to other polymerization techniques, the choice of utilizing methods depends on the specific requirements of the application [67]. Last but not the least, another class of polymerization process that has unique advantages over conventional methods is CRP (controlled radical polymerization) techniques. This method allows for better control through the polymerization process, such as obtaining polymers with specific properties and structures. There are several CRP techniques, including Atom Transfer Radical Polymerization (ATRP), Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization, and Nitroxide Mediated Polymerization (NMP) [68].

### 2.3.2 Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most widely utilized methods of conducting a controlled radical polymerization, since its versatility it is used to prepare polymers with predetermined molecular weights, narrow molecular weight distributions ( $M_w/M_n$ ), and high degrees of chain end functionalities. This controlled polymerization technique was discovered by Mitsuo Sawamoto and by Krzysztof Matyjaszewski in 1995. Although ATRP provides greater control over the polymerization process, it has significant drawbacks, in particular, the use of an excessive amount of catalyst (typically copper or iron) which is difficult to remove, air sensitivity, and the inability to function in aqueous conditions [69,70].

#### 2.3.2.1 Mechanisms and kinetics of ATRP

In a conventional ATRP reaction, a dormant (macro)alkyl halide ( $P_nX$ ) is activated by a lower oxidation state transition metal catalyst, typically  $Cu^I/L$ , to form a higher oxidation state halide complex ( $XCu^{II}/L$ ) and a radical ( $P_n^\bullet$ ). The radicals propagate, however typically after a single, or several monomer additions, they are deactivated back to reform dormant (macro)alkyl halides. For the ATRP to successfully synthesize polymers with predetermined molecular weight and narrow polydispersity index, quick and effective deactivation is crucial. The much decreased radical concentration in the reaction media greatly suppresses termination reactions. Also, telechelic functional or block copolymer can be generated by reducing the fraction of dead chains and reusing dormant polymer chains as (macro)initiators. In Figure 2.1 brief representation of ATRP mechanism is found.



**Figure 2.1** : Brief representation of ATRP mechanism [70].

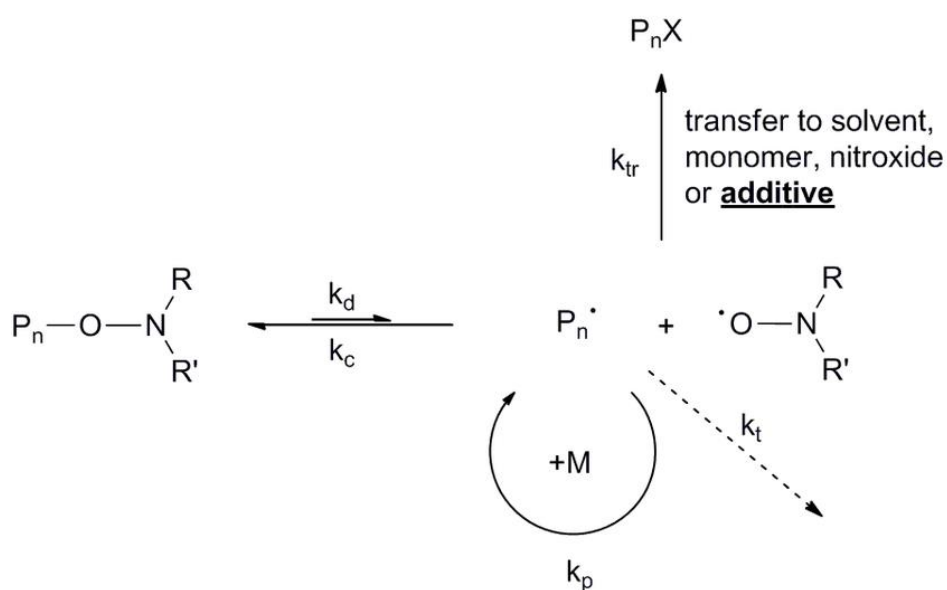
### 2.3.2.2 Components used in ATRP

Atom transfer radical polymerizations have five key variable components, such as monomer, initiator, catalyst, solvent, ligand. Acrylonitriles, (meth)acrylates, (meth)acrylamides, and styrenes are the most commonly utilized as monomers in ATRP. When the concentration of the propagating radical balances the rate of radical termination, ATRP is effective for generating polymers with a significant average MW and low dispersion. The initiator, as the another key component of ATRP, controls the amount of polymer chains will grow. The rate of initiation must be as rapid as, or ideally faster than, the rate of propagation in order to achieve low polydispersity and tightly controlled polymerization. Typically, alkyl halides having frameworks related to the propagating radical are used as initiators. Polymer architecture is affected by the initiator's type as well as structure. For instance, initiators containing several alkyl halide groups on a single core can result in the formation of polymers with a star-like shape. The catalyst, which has the essential role is the most significant component in ATRP, since it controls the equilibrium constant between active and dormant species. The polymerization rate is determined by this equilibrium, for instance a small equilibrium constant may impede or slow polymerization, whereas a large equilibrium constant results in a wide variety of chain lengths. According to the studies, copper-containing catalysts have proven to be the most versatile, with effective polymerizations for a diverse range of monomers. The choice of ligand that is combined with the conventional copper halide catalyst to generate the catalyst complex is one of the most crucial factors in an ATRP process. The primary roles of the ligand are to solubilize the copper halide in the selected solvent and to modify the copper's redox potential. This alters the halogen exchange reaction's kinetics and activity as well as the activation and deactivation of the polymer chains that follow through polymerization. Consequently, this has a significant impact on the kinetics of the process and the level of control over polymerization. In both homogeneous and heterogeneous environments, ATRP can be conducted in bulk, in water, and in organic solvents. Toluene, 1,4-dioxane, xylene, anisole, DMF, DMSO, water, methanol, acetonitrile, or even the monomer itself is frequently employed as a solvent in ATRP.

### 2.3.3 Nitroxide-mediated free radical polymerization (NMRP, NMP)

Nitroxide-mediated free radical polymerization (NMRP, NMP) is one of the most utilized representative free radical polymerization (SFRP) techniques that allow the synthesis of well-defined polymers with predictable molecular mass distribution, narrow polydispersity, and composition. Thus, this technique is suitable to design well-defined polymer architecture such as comb, gradient, and star copolymers including variable functionality, and provides extending polymer chains to synthesize multi-block copolymers via various monomers [71]. Compared to other techniques, this method is relatively easy and simple to perform, since it requires only the addition of an appropriate alkoxyamine to the polymerization reactions, such as TEMPO (2,2,6,6-tetramethyl piperidiny-1-oxy) as an initiator. A typical mechanism is given in Figure 2.2 [72].

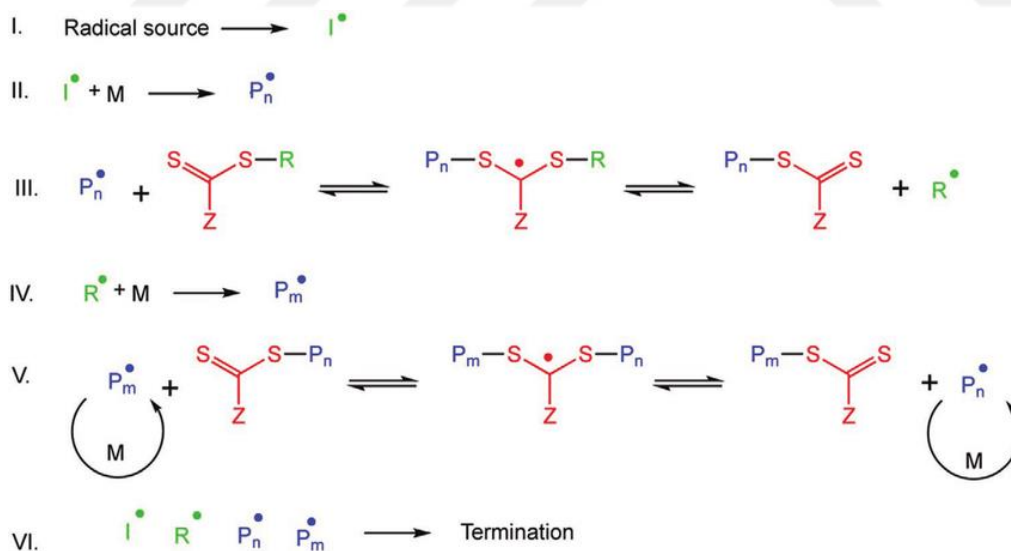
In this mechanism, the propagating species ( $P_n\bullet$ ) combines with a stable radical ( $X\bullet$ ) to generate dormant species ( $P_n\bullet-X$ ), which deactivates the propagating radicals. Thus, the ensuing dormant species can then reversibly cleave, reforming the free radicals. Once formed,  $P_n\bullet$  can either proliferate by reacting with a monomer ( $M$ ) or terminate by reacting with other radicals. As a result, the majority of dormant living chains can grow until the monomer is completely consumed, and polymer chains via reactivable chain end and equal chain lengths can be generated.



**Figure 2.2 :** Nitroxide-Mediated polymerization mechanism [72].

### 2.3.4 Reversible addition / fragmentation chain transfer (RAFT)

RAFT (Reversible Addition/Fragmentation Chain Transfer) is one of the preferred polymerization techniques that it provides living characteristics to radical polymerization via a reversible deactivation process to synthesize various type of polymers, for instance, linear block copolymers, brush polymers, star-shaped polymers, cross-linked networks and so on. In this method, the thiocarbonylthio compounds, including dithioesters, thiocarbamates, and xanthates are used as chain transfer agents to provide pre-chosen molecular weight with the expected low polydispersity index [73,74]. Compared to other known polymerization techniques, a variety of monomers including (meth)acrylates, (meth)acrylamides, styrene, acrylonitrile, N-vinylpyrrolidone, vinyl acetate, butadiene, and derivatives can be suitable to polymerize via RAFT process. Another prominent advantage over ATRP and NMP technique is it has a better tolerance under different reaction conditions such as various impurity levels, wide temperature range, and no need for transition metals. It is also versatile for ease of implementation that polymerization reactions could be carried out in aqueous media or protic media. Lastly, it increases its importance and usage due to being an inexpensive and simple method.



**Figure 2.3 :** Steps of Reversible Addition/Fragmentation Chain Transfer polymerization mechanism [75].

In RAFT mechanism mainly includes these steps, such as initiation, pre-equilibrium, re-initiation, main equilibrium, propagation, and termination. For simplification, it is depicted in Figure 2.3. Firstly, the polymer chain reacts with a RAFT agent which

behaves as a transfer agent to functionalize chain-end characteristics via a RAFT moiety. Then, a new polymer chain is generated with the remaining moiety of the original RAFT agent to react with a RAFT-functionalized polymer chain. Thus a suitable environment is created for polymer chains to alternate between being dormant and active to grow at similar rates. This ideally yields a polymer chain leading to an average chain length that increases linearly with the conversion of monomer into polymer [75].

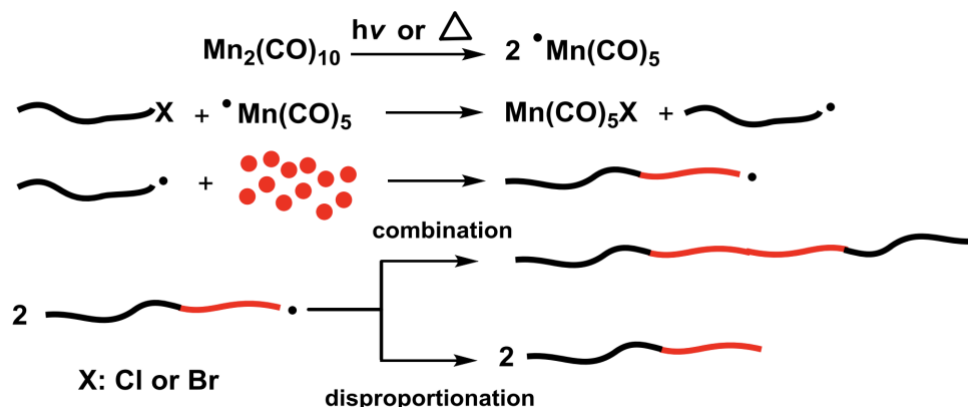
## **2.4 Photochemistry**

Photochemistry is the study of chemical reactions, physical phenomena and isomerizations, that may take place when exposed to visible (400-750 nm) and/or ultraviolet light (100-380 nm). Thus, a photochemical reaction can be described as it is a chemical reaction triggered when light energy is absorbed by a substance's molecules. For instance photoinduced polymerization of PMMA, photodegradation of PVC and photoalkylation reactions can be given as examples of photochemical reactions. Nowadays, photoinduced reactions has become one of the most extensively used technologies since they present the advantages to be simple, clean and relatively inexpensive compared to conventional methods [76].

### **2.4.1 Mn<sub>2</sub>Co<sub>10</sub> chemistry**

Dimanganese decacarbonyl is a binary bimetallic carbonyl complex centered around the first row transition metal manganese compound that have been used for a variety of key processes, including radical generation in the presence of alkyl halides as a homogeneous catalysts [77]. For instance, using Mn<sub>2</sub>Co<sub>10</sub> in light-induced polymerization systems have been mentioned in the literature as an excellent approach for generating block and graft polymers [78–80].

Mn<sub>2</sub>Co<sub>10</sub> is air stable as a crystalline solid that has bond dissociation energies of Mn-Mn ~36 kcal/mol (151 kJ/mol) and Mn-CO ~38 kcal/mol (160 kJ/mol). It generates Mn(CO)<sub>5</sub> metalloradicals with a high quantum yield under the irradiation between 460 to 380 nm, depicted in Figure 2.4.



**Figure 2.4 :**  $\text{Mn}_2(\text{CO})_{10}$ -induced photochemical reaction of terminal halide groups for block copolymer generation [80]

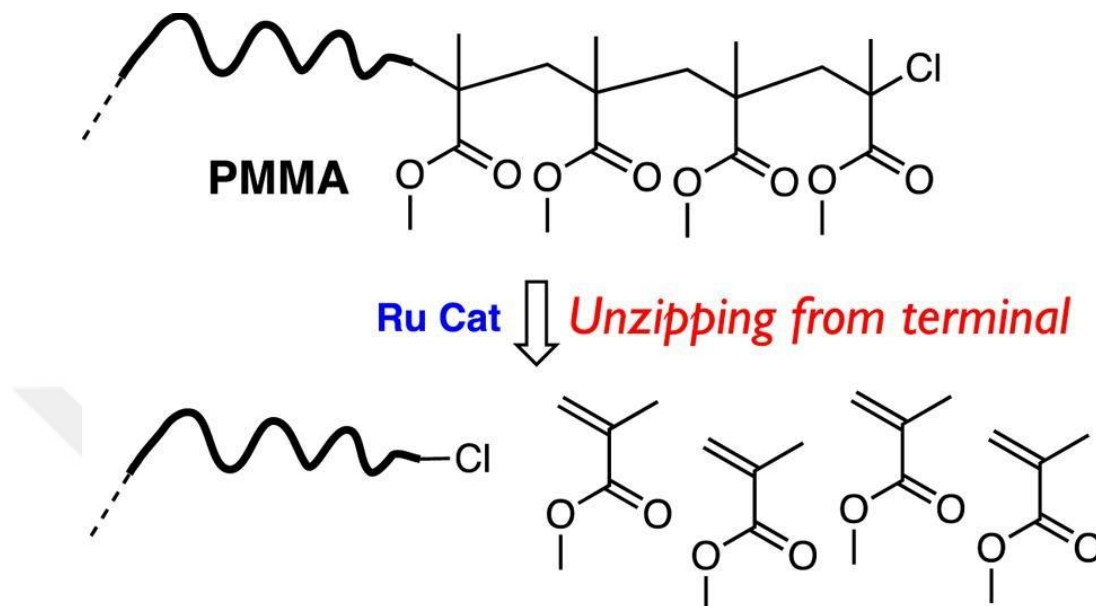
## 2.5 Depolymerization / Degradation

Plastic recycling solutions to fight rapidly rising trash buildup are critical for the environment [81]. Since, mechanical recycling has inherent limits, chemical recycling to monomer has evolved as a potent alternative that offers recyclability by depolymerization [82]. Moreover degradation, itself, might be described as a process that is often undesirable [83,84]. Controlled polymer degradation, however, can be helpful in some circumstances. For instance, it can make the polymer more processable or it can be utilized to recycle or decompose waste polymer naturally.

In conventional depolymerization/degradation process, cleavage of covalent bonds in the main chain that includes hetero atoms like ester, acetate and carbonate is often required. The carbon-carbon bond in some polymers made from acrylic monomers is not hydrolazable, thus depolymerization or degradation of such polymers can be more challenging [35]. Regarding the thermal depolymerization and degradation of PMMA, there are numerous examples in the literature, but comparatively few research that used light-induced techniques. Several known research groups have published extensive studies in this topic and in this section these prominent studies which were based on degradation and depolymerization of PMMA are chronologically listed.

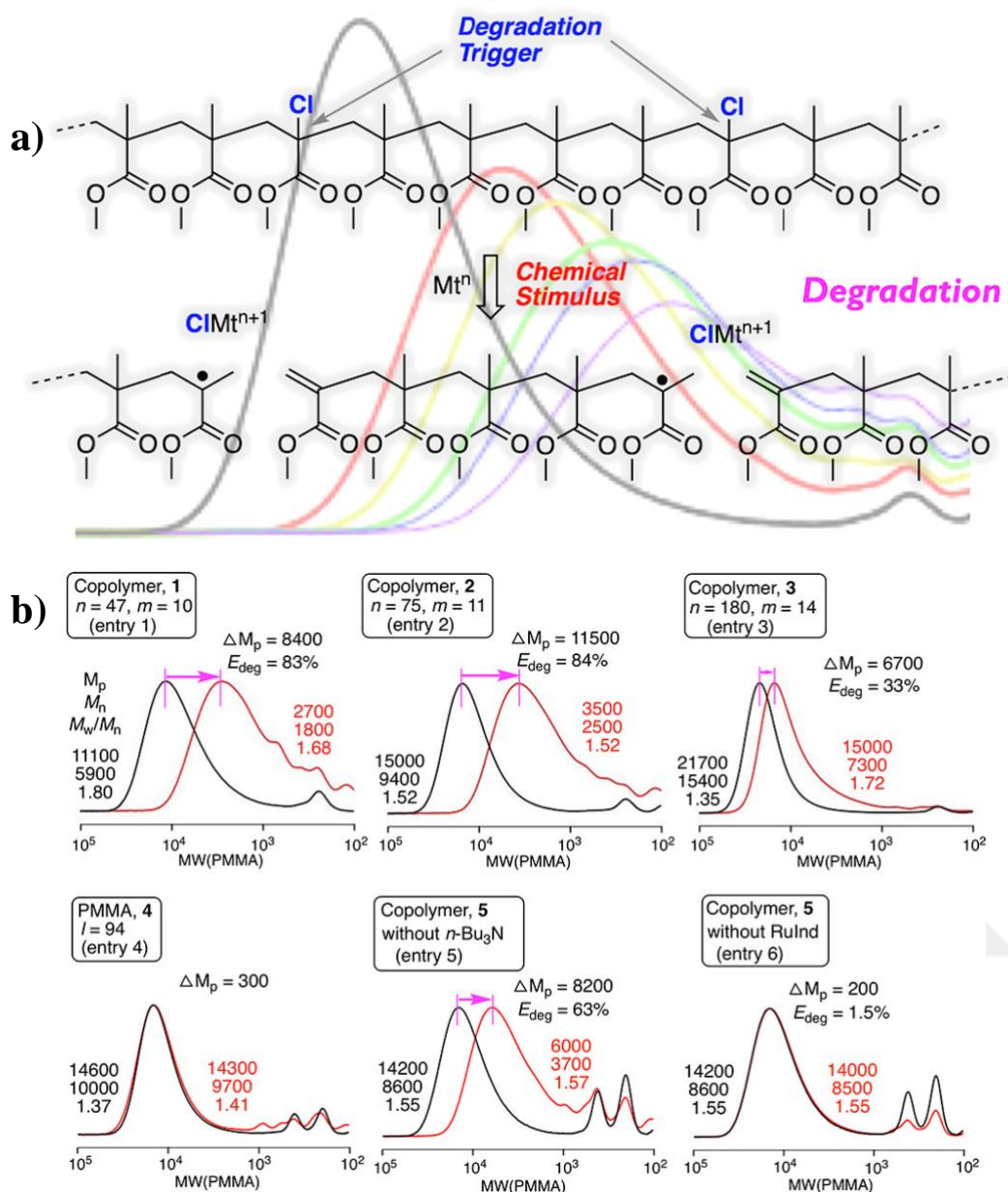
Ouchi and his coworkers aimed to depolymerize and degrade modified PMMA derivatives via using metal catalyst. Primarily, his research group used ruthenium as a catalyst in normal ATRP technique of chlorine-terminated poly(methyl methacrylate) (PMMA-Cl), to show how carbon-halogen bond triggers the depolymerization reaction under reduced pressure system at 100C [33]. At the end of the reaction,

methylmethacrylate (MMA) monomer was observed from the olefinic protons peaks in the  $^1\text{H}$  NMR spectrum, which enhances our comprehension of the depolymerization processes of modified PMMA derivatives. Depolymerization illustration of PMMA-Cl is shown in Figure 2.5.



**Figure 2.5** : Depolymerization illustration of PMMA-Cl [33].

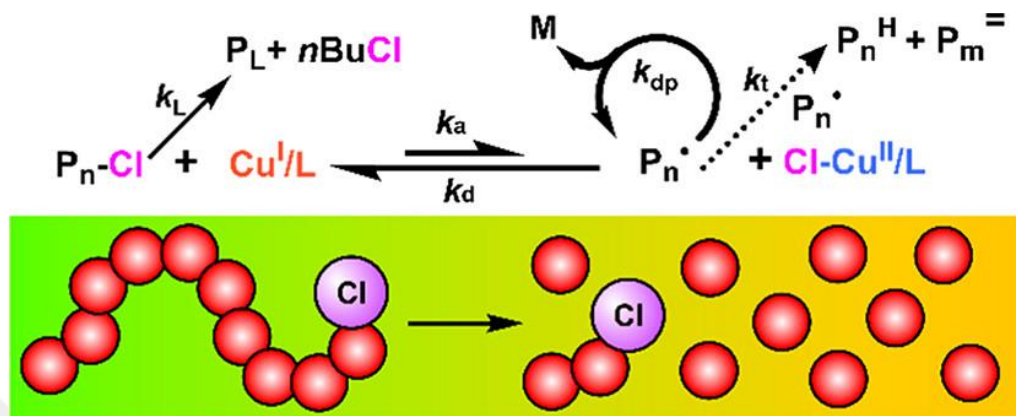
The another work of the same group, was focused on the degradation mechanism. For this study, firstly, RAFT technique was used to synthesize MMA/MCA copolymer, involving the partial substitution of chlorine for the alpha group in the PMMA backbone [85]. To initiate degradation reaction, polymers were treated with a ruthenium complex and amine compound ( $n\text{-Bu}_3\text{N}$ ) at  $100^\circ\text{C}$  for a duration of 4 hours. In order to determine the degradation ratio and efficiency of copolymers with varying molecular weights, monomer, and comonomer ratios, samples were taken for gel permeation chromatography analysis and notable shifts were detected towards lower molecular weights. Degradation illustration and GPC chromatograms of copolymers (MMA-MCA) are in Figure 2.6.



**Figure 2.6 :** (a) Degradation illustration of copolymers, (b) GPC chromatograms of copolymers (MMA-MCA) (1–3,5) and PMMA (4) before (black line) and after degradation (red line) in the presence or absence of catalyst (RuInd) or cocatalyst ( $n$ -Bu<sub>3</sub>N) [85].

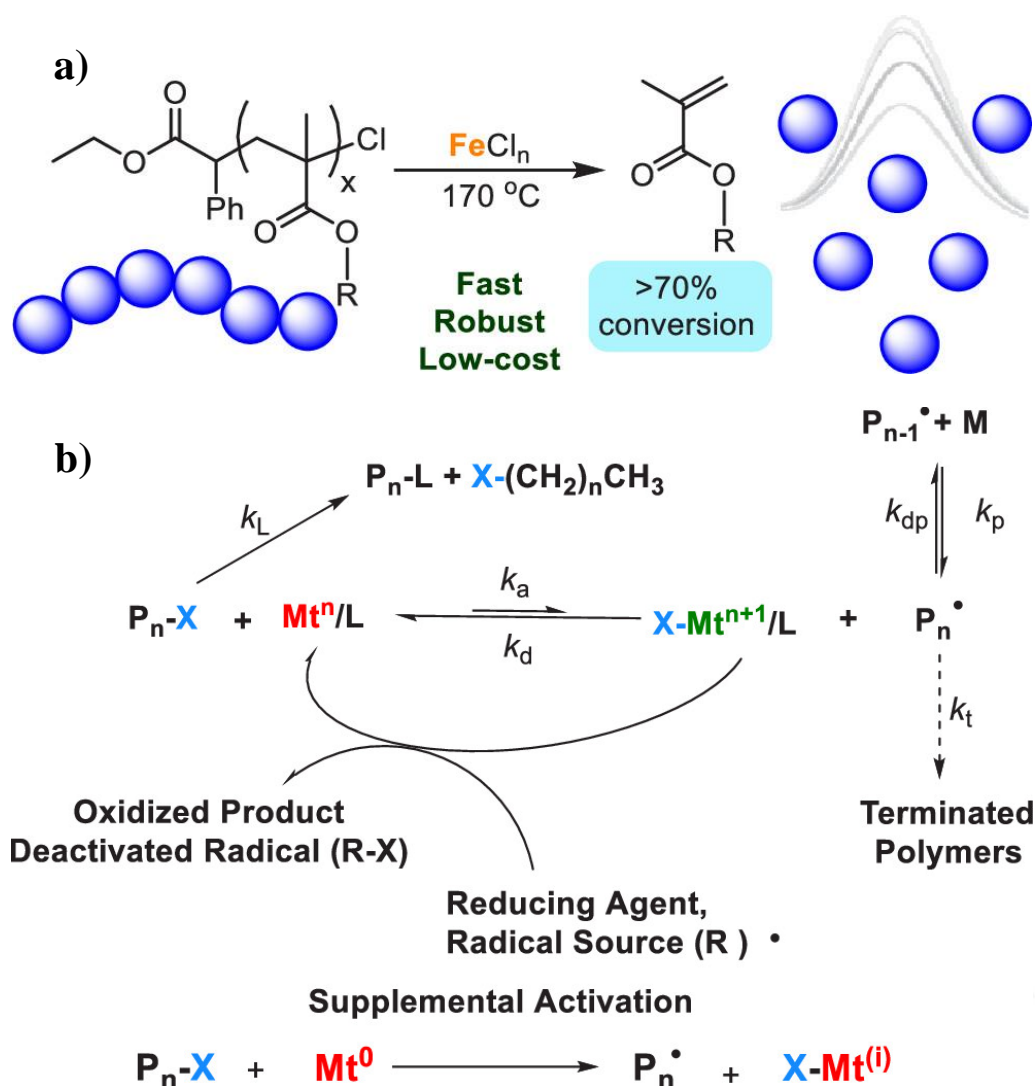
Matyjaszewski and his coworkers published a study which represents the catalyzed depolymerization of poly( $n$ -butyl methacrylate) (PBMA) macroinitiator with terminal chlorine chain-end functionality via copper(II) chloride/tris(2-pyridylmethyl)amine ( $CuCl_2/TPMA$ ) as a catalyst at 170 °C [34]. Poly( $n$ -butyl methacrylate) (PBMA) was selected for the experiment, since it has diverse usage areas such as industrial resins, coatings and adhesives. Depolymerization reactions were conducted with solid loadings between 8% to 21% by weight, leading to the recovery of more than 40% of the monomer within 10 minutes, with the potential to achieve up to 67% monomer

recovery at an 8% solid loading. The aim of the experimental set up was to be selective toward the n-butyl methacrylate monomer, thus it designed as it simultaneously carrying out depolymerization and distillation on a rotary evaporator. Graphical abstract is presented in Figure 2.7.



**Figure 2.7 :** Illustration of catalyzed depolymerization of poly(n-butyl methacrylate) (PBMA) macroinitiator with terminal chlorine chain-end functionality via  $\text{CuCl}_2/\text{TPMA}$  [34].

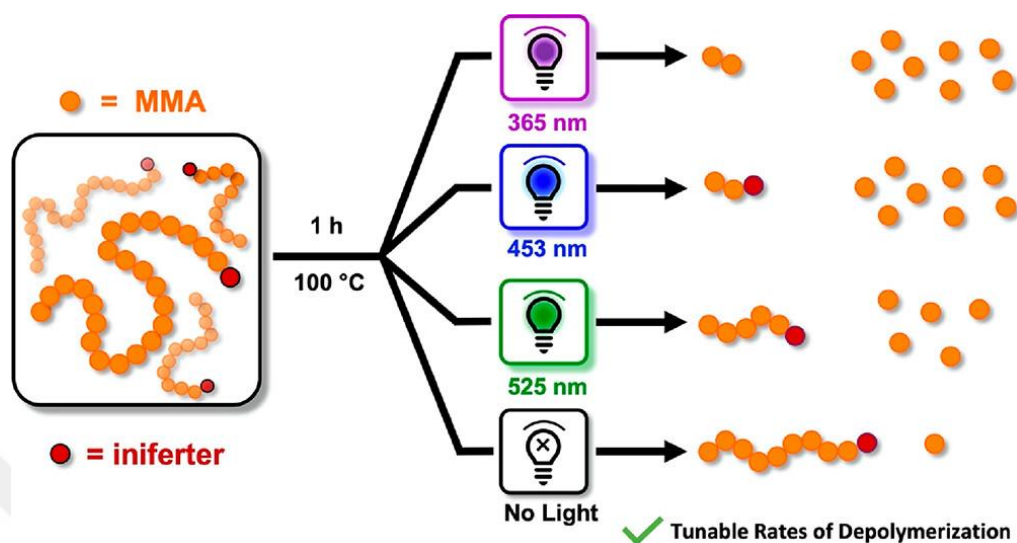
Matyjaszewski's research group reported another study about the depolymerization of poly(methyl methacrylate) (PMMA) and poly(n-butyl methacrylate) (PBMA) by employing iron complexes as catalyst at  $170^\circ\text{C}$  [86]. Compared to the metal catalysts utilized in the previous published studies, iron salts and iron powder are more cost-effective, simpler, and environmentally friendly. The iron catalysts are composed of a mixture of  $\text{FeCl}_2$  and tetra(ethylene glycol) dimethyl ether, which serves as both a solvent and ligand. They displayed significant activity and effectively reducing the alkyl chlorine chain-end functionality under the elevated temperature. As a result, the depolymerization of chlorine-capped poly(n-butyl methacrylate) (PBMA-Cl) and poly(methyl methacrylate) (PMMA-Cl) macroinitiators, achieving a conversion rate of over 70% in under 15 minutes. After that, the monomers obtained from the depolymerization reaction were recovered via distillation process. Graphical abstract and proposed mechanism of depolymerization is presented in Figure 2.8.



**Figure 2.8 :** (a) Illustration of depolymerization via iron catalysts, (b) Proposed mechanism of ATRP with Reversible Propagation, Activator Regeneration, Supplemental Activation of the Alkyl Halide, and Lactonization of the Chain-End [86,87].

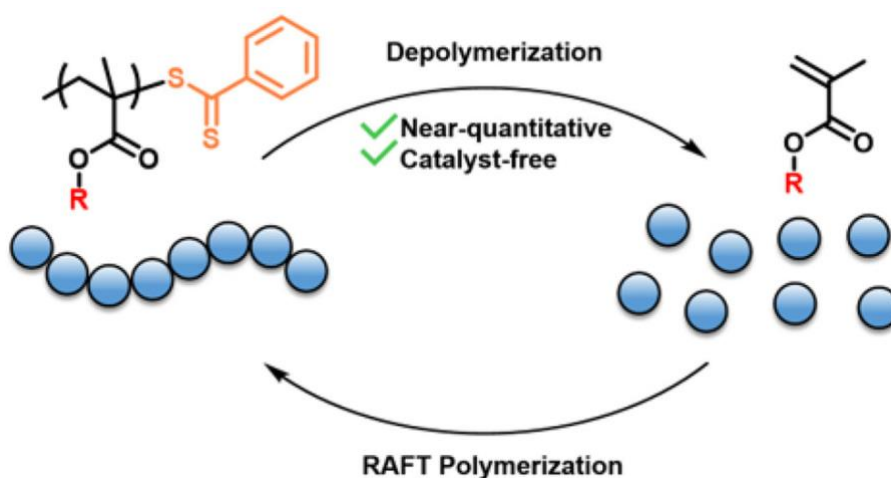
Sumerlin and his team conducted a study investigating the role of light as a trigger for the thermal depolymerization of polymers [87]. These polymers were initially synthesized using the reversible-addition-fragmentation chain-transfer (RAFT) technique, which is one of the controlled radical polymerization methods. They mostly primarily focused on the depolymerization of trithiocarbonate, dithiocarbamate, and p-substituted dithiobenzoate end groups polymers at low temperatures to see the effect of how depolymerization efficiency effects with the presence of light. The results showed that, the photoassisted depolymerization method achieved a promising depolymerization efficiency of up to 87% within just one hour. Additionally, the results indicate that as the wavelength shifts from the visible range to the UV range, there is

a substantial and dramatic increase in the rate of depolymerization. The visual representation of photoassisted thermal depolymerization system is shown in Figure 2.9.



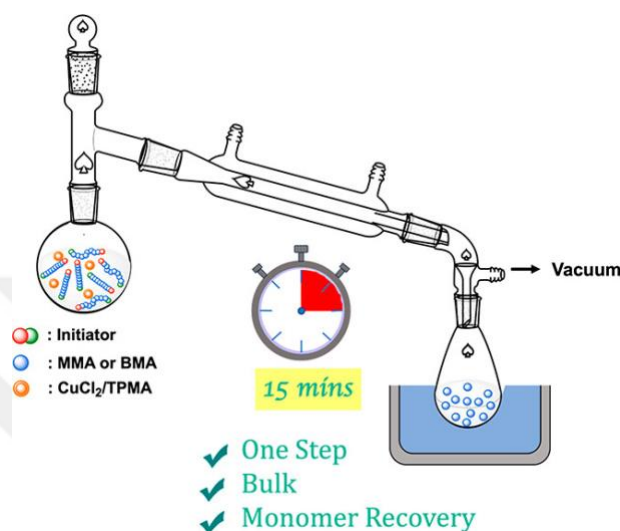
**Figure 2.9 :** Illustration of light assisted thermal depolymerization system [87].

Anastasaki and her group members investigated catalyst-free depolymerization systems of various linear, bulky, cross-linked, and functional polymethacrylic materials synthesized by reversible-addition-fragmentation chain-transfer (RAFT) technique [88]. This process yields remarkably high depolymerization conversions, reaching up to 92%. The strategy essentially entails heating polymethacrylate solutions to 120°C, which generates chain-end radicals and subsequently initiating a rapid depolymerization reaction. In Figure 2.10, catalyst-free depolymerization system is presented.



**Figure 2.10 :** Illustration of catalyst-free depolymerization of various materials by reversible-addition-fragmentation chain-transfer (RAFT) technique [88].

Matyjaszewski and his group, reported a study of fast bulk ATRP depolymerization systems which was catalyzed via  $\text{CuCl}_2/\text{TPMA}$  complexes of Cl-terminated PBMA and PMMA [89]. The depolymerization achieved high yields, up to 84%, and recovered nearly all the available monomer within just 15 minutes when the temperature range between 180 to 230°C. As can be seen from the graphical abstract presented in Figure 2.11, a short-path distillation set up was utilized in experiment.



**Figure 2.11** : Visual representation of depolymerization system through short-path distillation setup [89].

### 2.5.1 Photodepolymerization

Photodepolymerization is a chemical process in which a polymer is broken down into its constituent monomers or smaller polymer fragments when exposed to light, typically ultraviolet (UV) or visible light. Simply, this process is the opposite of photopolymerization, in which monomers are joined to form polymers when exposed to light. Compared to UV light, visible light based systems offers several advantages such as it has a broad wavelength selectivity, it enables precise spatial temporal control, it is readily available, cost-effective and eco-friendly [90]. Most notably, visible light can penetrate deeper into polymer film layers or living organisms than UV light. Thus, it enhances its potential application fields in tissue engineering and light curing and making it a valuable tool in polymer chemistry.

In recent years, there has been an increasing demand and a growing interest in depolymerization systems which are initiated by visible light. This trend is driven by the safety of visible light, making it a promising tool for advance recycling and

degradation process which has a great benefit for environment and sustainability. Overall, it could be said that photo-induced depolymerization systems would offer great advancements in both materials science and biomedical engineering. As technology and science improves, the challenges of the photodepolymerization systems could be handle and make a promising solutions, both from engineering and polymer chemistry perspective.





### 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.
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.
$\alpha$ -chloroethylbutyrate	: used as received and stored in the fridge.
CuCl (Aldrich, 98%)	: used as received and stored in dark.
CuBr (Aldrich, 98%)	: used as received and stored in dark.
Benzyl chloride (Aldrich, 99%),	: used as received and stored in dark.

#### 3.2 Equipments

##### 3.2.1 GPC

Gel permeation chromatography (GPC) analysis were carried out 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 a TSK gel superhZ2000 4.6mm ID  $\times$  15cm  $\times$  2cm column. 1.0 mL.min<sup>-1</sup> of tetrahydrofuran was utilized as the eluent at a temperature of 40°C. Calibrations were done by polystyrene standards with a limited molecularweight distribution and the obtained data were analyzed by the Eco-SEC Analysis software.

### 3.2.2 NMR

$^1\text{H}$  NMR spectra of the PMMA-Cl and its depolymerized products were recorded on an Agilent VNMRs 500 NMR spectrometer system at room temperature in  $\text{CDCl}_3$  with  $\text{Si}(\text{CH}_3)_4$  as an internal standard.

### 3.2.3 Light-source

The photoreactor is used as the light source and it has been developed to enable visible-light-driven reactions in polymerization and depolymerization reactions for photochemical routes.

## 3.3 Preparation Methods

### 3.3.1 Using ATRP to synthesize PMMA-Cl<sup>1</sup>

To obtain PMMA-Cl, toluene (5.35 mL), MMA (5.25 mL), PMDETA (72.5  $\mu\text{L}$ ), CuCl (50 mg) to define the end group and benzyl chloride (38.5  $\mu\text{L}$ ) to depend the halogen of the copper salt were placed into a dried Schlenk tube in this order at ambient temperature under the nitrogen atmosphere. The reaction mixture was degassed by repeated freeze-pump thaw cycles consecutively to remove unwanted oxygen from the reaction media, sealed off, and placed in an oil bath. Polymerization was held at 90°C for 22 minutes in an oil bath. Then, the obtained mixture was precipitated in hexane and left under low pressure to dry.

### 3.3.2 Using ATRP to synthesize PMMA-Cl<sup>2</sup>

To obtain PMMA-Cl, toluene (5.35 mL), MMA (5.25 mL), PMDETA (72.5  $\mu\text{L}$ ), CuCl (50 mg) to define the end group and benzyl chloride (38.5  $\mu\text{L}$ ) to depend the halogen of the copper salt were placed into a dried Schlenk tube in this order at ambient temperature under the nitrogen atmosphere. The reaction mixture was degassed by repeated freeze-pump thaw cycles consecutively to remove unwanted oxygen from the reaction media, sealed off, and placed in an oil bath. Polymerization was held at 90°C for 16 minutes in an oil bath. Then, the obtained mixture was precipitated in hexane and left under low pressure to dry.

### 3.3.3 Using ATRP to synthesize PMMA-Br

To obtain PMMA-Br, toluene (5.35 mL), MMA (5.25 mL), PMDETA (72.5  $\mu$ L), CuBr (70 mg) to define the end group and benzyl bromide (55  $\mu$ L) to depend the halogen of the copper salt were placed into a dried Schlenk tube in this order at ambient temperature under the nitrogen atmosphere. The reaction mixture was degassed by repeated freeze-pump thaw cycles consecutively to remove unwanted oxygen from the reaction media, sealed off, and placed in an oil bath. Polymerization was held at 90°C for 16 minutes in an oil bath. Then, the obtained mixture was precipitated in hexane and left under low pressure to dry.

### 3.3.4 Using ATRP to synthesize PMMA-co-PGMA-Cl

To obtain PMMA-co-PGMA-Cl, toluene (10,7 mL), MMA (10 mL), GMA (0,66 mL) PMDETA (145  $\mu$ L), CuCl (100 mg) and  $\alpha$ -chloroethylbutyrate (125  $\mu$ L) were placed into a dried Schlenk tube in this order at ambient temperature under the nitrogen atmosphere. The reaction mixture was degassed by repeated freeze-pump thaw cycles consecutively to remove unwanted oxygen from the reaction media, sealed off, and placed in an oil bath. Polymerization was held at 90°C for 9 minutes in an oil bath. Then, the obtained mixture was precipitated in hexane and left under low pressure to dry.

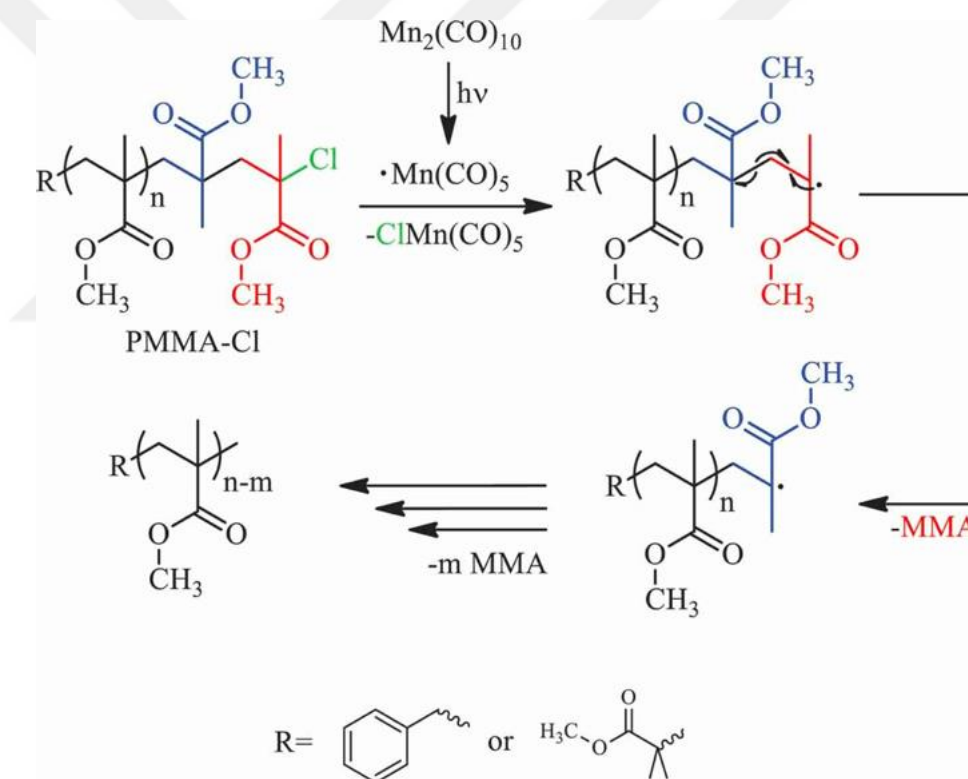
## 3.4 Photodepolymerization

Different PMMA derivatives were irradiated to depolymerize under 400 nm light. In this process PMMA derivative (0,065 M), 12,4 mg  $\text{Mn}_2(\text{CO})_{10}$  and 6,7 mL toluene (or p-dichlorobenzene for 170°C) were added and combined in a Schlenk tube and filled with  $\text{N}_2$  to make an inert reaction environment. Later on, the tube was put in a photoreactor and irradiated for up to 6 hours under various temperatures or ambient temperature. For tracking the depolymerization reaction kinetics, GPC samples were taken to calculate the depolymerization efficiency.



#### 4. RESULT AND DISCUSSION

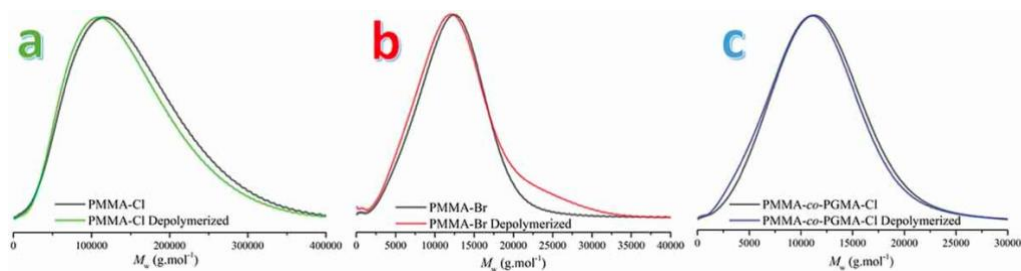
The proposed visible light induced depolymerization mechanism is initiated via homolytic halogen abstraction at the chain end of the molecule. The presence of a diluted reaction medium enhances depropagation, which leads to the formation of polymers with shorter chains. This depropagation process is termed "unzipping type" as it commences at the chain end and progresses along through the polymer main chain. The mechanism of visible light initiated unzipping type depropagation of PMMA-Cl with  $\text{Mn}_2(\text{CO})_{10}$  at ambient temperature was depicted in Figure 4.1.



**Figure 4.1** : Photoinitiated unzipping type depropagation of PMMA-Cl with  $\text{Mn}_2(\text{CO})_{10}$  at 400 nm.

Various PMMA derivatives with halogen chain ends were synthesized via traditional ATRP process for photodepolymerization. Initially, the effects of different halogens at the chain end was considered, resulting in the synthesis of two types of PMMA derivatives, namely PMMA-Cl<sup>1</sup> and PMMA-Br. In order to control the decrease of molecular weight, referred to as depolymerization yield, benzyl chloride and benzyl bromide were selected as ATRP initiators, and their effects were monitored through <sup>1</sup>H-NMR spectroscopy.

The primary factors which affects the depolymerization processes are the nucleophilic characteristics of the halogen and the abstraction yield. Bromine positioned at the chain end of PMMA is expected to be abstracted easily, potentially elevating the radical concentration in the medium. This, in turn, lead to undesired coupling reactions between polymer chains, ultimately forming polymers without halide functionality. Although, there is some observed depolymerization of PMMA-Br in the GPC chromatogram, the abstraction of bromine leads to the formation of longer polymer chains due to subsequent coupling. Consequently, this results in broadened peaks and an increase in polydispersity index(Đ) as depicted in Figure 4.2 and Table 4.1. Conversely, PMMA-Cl<sup>1</sup> experiences a more regulated generation of radicals, catalyzing depolymerization rather than coupling reactions, leading to a depolymerization yield of 20%. Also, another structurally diverse polymer, chlorine end-functional poly(methyl methacrylate-co-glycidyl methacrylate) (PMMA-co-PGMA-Cl) was synthesized to investigate the method's applicability. This polymer contains epoxide rings in the side chain and they remain unaffected during the visible light induced depolymerization. The obtained results were comparable within the same interval, as shown in Figure 4.2 and Table 4.1. Additionally, an experiment set up was conducted under dark conditions, and as expected, no depolymerization results was detected.



**Figure 4.2 :** GPC analysis of a) PMMA-Cl and depolymerized PMMA-Cl b) PMMA-Br and depolymerized PMMA-Br c) PMMA-co-PGMA-Cl and depolymerized PMMA-co-PGMA-Cl.

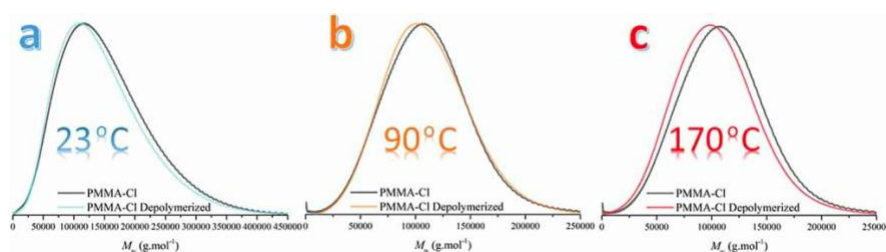
**Table 4.1 :** Molecular weight characteristics of PMMA-Cl<sup>1</sup>, PMMA-Br and PMMA-co-PGMA-Cl before and after visible light irradiation (a).

Polymer	$M_n^b$ (g.mol <sup>-1</sup> )		$\mathcal{D}^b$	
	Before	After	Before	After
PMMA-Cl <sup>1</sup>	67,000	53,000	1,4	1,4
PMMA-Br	5400	5400	1,2	1,3
PMMA-co-PGMA-Cl	5100	4600	1,2	1,3

<sup>a-</sup>  $[Mn_2(CO)_{10}]:[Polymer]:[Toluene] = 1:2:2300$  irradiated at 400 nm for 6 h.

<sup>b-</sup> Determined by GPC using polystyrene standards

Moreover, it is well-established in scientific understanding that temperature plays a pivotal role in the depolymerization process. In light of this, the primary objective of our research is to mitigate the need for elevated temperatures by introducing visible light as an alternative. As part of this investigation, the depolymerization process was monitored at various temperature spectrum, 23°C, 90°C, and 170°C respectively and presented in Table 4.2 and Figure 4.3. To achieve the higher temperatures, p-dichlorobenzene (p-DCB) was employed in the experimental setup. This analysis aims to assess the viability of employing visible light in depolymerization as an eco-friendly alternative to temperature-dependent depolymerization systems.



**Figure 4.3 :** GPC analysis of PMMA-Cl and depolymerized PMMA-Cl under 400 nm visible light and a) 23°C b) 90°C c) 170°C.

**Table 4.2 :** Molecular weight characteristics of PMMA-Cl before and after visible light irradiation (a).

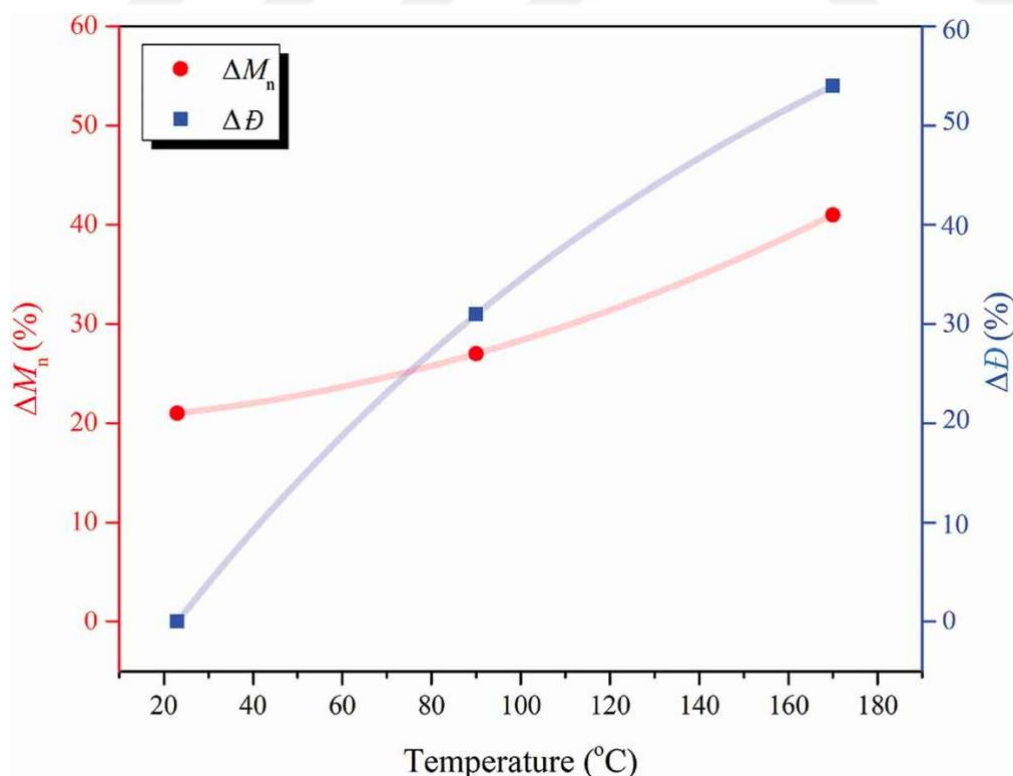
Polymer	Temp. (°C)	$M_n^c$ (g.mol <sup>-1</sup> )		$\bar{D}^c$	
		Before	After	Before	After
PMMA-Cl <sup>1</sup> a	23	67,000	53,000	1.4	1.4
PMMA-Cl <sup>2</sup> a	90	56,000	41,000	1.3	1.7
PMMA-Cl <sup>2</sup> b	170	56,000	33,000	1.3	2.0

<sup>a-</sup> [Mn<sub>2</sub>(CO)<sub>10</sub>]: [Polymer]: [Tol.] = 1:2:2300 irradiated at 400 nm for 6 h.

<sup>b-</sup> [Mn<sub>2</sub>(CO)<sub>10</sub>]: [Polymer]: [p-DCB] = 1:2:2300 irradiated at 400 nm for 6 h.

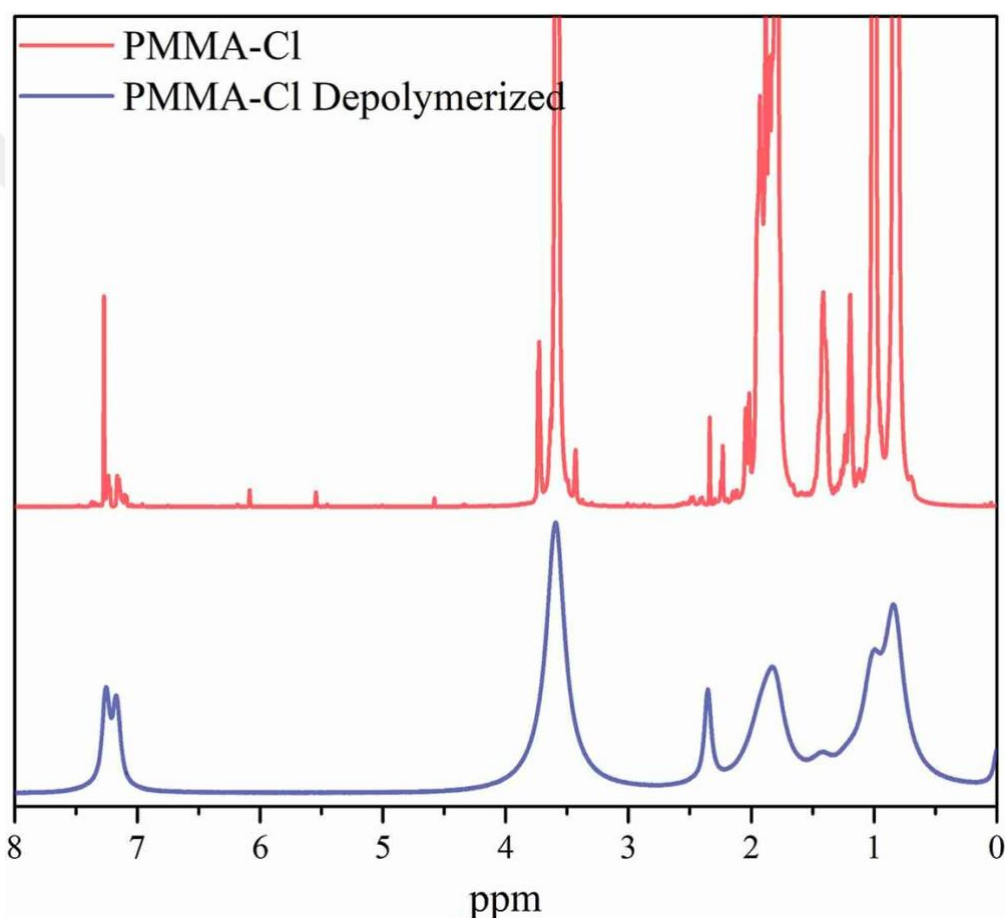
<sup>c-</sup> Determined by GPC using polystyrene standards.

Similar  $M_n$  values were achieved through depolymerization at both 23°C and 90°C, as outlined in Table 4.2. Notably, there was a substantial dispersity gap observed, reaching up to 34%. Elevating the temperature to 170°C led to a significant decrease in  $M_n$  and an increase in polydispersity index, pointing to more favorable depolymerization conditions facilitated by increasing heat. Figure 4.4 indicates how heat affects the depolymerization process, offering a complete understanding of the gradually increasing temperature trends. It's essential to highlight that despite the catalyzing effect of temperature, the depolymerization results at ambient temperature remain competitive.



**Figure 4.4 :** The effect of temperature on the  $M_n$  and  $\bar{D}$  values obtained through gel permeation chromatography.

To control the depolymerization yield using  $^1\text{H-NMR}$  spectroscopy, benzyl chloride and benzyl bromide were selected as ATRP initiators. In Figure 4.5,  $^1\text{H-NMR}$  spectra of Bz-PMMA-Cl before and depolymerization is presented. It is clear that the increasing integration ratio of aromatic peaks from the benzylic chain end and the peaks corresponding to the methoxy groups of PMMA, which is a proof for depolymerization reaction. While  $^1\text{H-NMR}$  spectral analysis suggests approximately 40% depolymerization yield, it should be pointed out that integration values do not give extremely reliable results due to the paramagnetic broadening effect of  $\text{Mn}_2(\text{CO})_{10}$ .



**Figure 4.5 :**  $^1\text{H-NMR}$  spectra of Bz-PMMA-Cl before (red) and after depolymerized (blue).



## 5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion, a novel approach for visible light induced photodepolymerization of PMMA under ambient conditions has been established. This concept makes use of  $\text{Mn}_2\text{CO}_{10}$  as a catalyst in order to overcome the requirement of heat or energy for depolymerization process. In this system polymers which have different halogens at the chain end were investigated. As a result, PMMA-Br was found to be result in undesirable chain extension due to radical coupling reactions, although PMMA-Cl is capable of achieving up to twenty percent depolymerization efficiency. In order to understand the reaction kinetics, an investigation was conducted on the photodepolymerization system by altering the temperature while keeping the irradiation conditions constant. To examine the polymer characteristics  $^1\text{H-NMR}$  and GPC analyses were done. This new concept, as presented, has several benefits compared to conventional procedures, including reduced energy requirements, lower toxicity, precise control over the reaction media, and environmentally friendly circumstances. Further studies in this line are now in progress.



## REFERENCES

- [1] **Bongiovanni, R., Dalle Vacche, S. and Vitale, A.** (2021) Photoinduced processes as a way to sustainable polymers and innovation in polymeric materials. *Polymers*, MDPI AG. **13**.  
<https://doi.org/10.3390/POLYM13142293>
- [2] **Chen, M., Zhong, M. and Johnson, J.A.** (2016) Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. *Chemical Reviews*, American Chemical Society. **116**, 10167–211.  
[https://doi.org/10.1021/ACS.CHEMREV.5B00671/ASSET/IMAGES/MEDIUM/CR-2015-006712\\_0045.GIF](https://doi.org/10.1021/ACS.CHEMREV.5B00671/ASSET/IMAGES/MEDIUM/CR-2015-006712_0045.GIF)
- [3] **Yagci, Y., Jockusch, S. and Turro, N.J.** (2010) Photoinitiated polymerization: Advances, challenges, and opportunities. *Macromolecules*, **43**, 6245–60. <https://doi.org/10.1021/MA1007545>
- [4] **Adili, A., Korpusik, A.B., Seidel, D. and Sumerlin, B.S.** (2022) Photocatalytic Direct Decarboxylation of Carboxylic Acids to Derivatize or Degrade Polymers. *Angewandte Chemie - International Edition*, John Wiley and Sons Inc. **61**. <https://doi.org/10.1002/ANIE.202209085>
- [5] **Brieke, C., Rohrbach, F., Gottschalk, A., Mayer, G. and Heckel, A.** (2012) Light-controlled tools. *Angewandte Chemie - International Edition*, **51**, 8446–76. <https://doi.org/10.1002/ANIE.201202134>
- [6] **Moreno, S., Sharan, P., Engelke, J., Gumz, H., Boye, S., Oertel, U. et al.** (2020) Light-Driven Proton Transfer for Cyclic and Temporal Switching of Enzymatic Nanoreactors. *Small*, Wiley-VCH Verlag. **16**.  
<https://doi.org/10.1002/SMLL.202002135>
- [7] **Albini, A. and Fagnoni, M.** (2004) Green chemistry and photochemistry were born at the same time. *Green Chemistry*, **6**, 1–6.  
<https://doi.org/10.1039/B309592D>
- [8] **Tasdelen, M.A., Lalevée, J. and Yagci, Y.** (2020) Photoinduced free radical promoted cationic polymerization 40 years after its discovery. *Polymer Chemistry*, The Royal Society of Chemistry. **11**, 1111–21.  
<https://doi.org/10.1039/C9PY01903K>
- [9] **Lee, K., Corrigan, N. and Boyer, C.** (2021) Rapid High-Resolution 3D Printing and Surface Functionalization via Type I Photoinitiated RAFT Polymerization. *Angewandte Chemie International Edition*, John Wiley & Sons, Ltd. **60**, 8839–50.  
<https://doi.org/10.1002/ANIE.202016523>
- [10] **Zhang, Z., Corrigan, N. and Boyer, C.** (2022) A Photoinduced Dual-Wavelength Approach for 3D Printing and Self-Healing of Thermosetting Materials. *Angewandte Chemie International Edition*, John Wiley & Sons, Ltd. **61**, e202114111.  
<https://doi.org/10.1002/ANIE.202114111>
- [11] **Xu, Y., Noirbent, G., Brunel, D., Liu, F., Gignes, D., Sun, K. et al.** (2020) Ketone derivatives as photoinitiators for both radical and cationic photopolymerizations under visible LED and application in 3D

- printing. *European Polymer Journal*, Pergamon. **132**, 109737.  
<https://doi.org/10.1016/J.EURPOLYMJ.2020.109737>
- [12] **Dietlin, C., Schweizer, S., Xiao, P., Zhang, J., Morlet-Savary, F., Graff, B. et al.** (2015) Photopolymerization upon LEDs: new photoinitiating systems and strategies. *Polymer Chemistry*, The Royal Society of Chemistry. **6**, 3895–912. <https://doi.org/10.1039/C5PY00258C>
- [13] **Nasir, K.M., Halim, N.A., Tajuddin, H.A., Arof, A.K. and Abidin, Z.H.Z.** (2013) The effect of PMMA on physical properties of dammar for coating paint application. *Pigment and Resin Technology*, **42**, 137–45. <https://doi.org/10.1108/03699421311301133>
- [14] **Bennet, F., Hart-Smith, G., Gruending, T., Davis, T.P., Barker, P.J. and Barner-Kowollik, C.** (2010) Degradation of poly(methyl methacrylate) model compounds under extreme environmental conditions. *Macromolecular Chemistry and Physics*, Wiley-VCH Verlag. **211**, 1083–97. <https://doi.org/10.1002/MACP.200900625>
- [15] **Zafar, M.S.** (2020) Prosthodontic applications of polymethyl methacrylate (PMMA): An update. *Polymers*, MDPI AG. **12**, 1–35. <https://doi.org/10.3390/POLYM12102299>
- [16] **Wheeler, J.S.R., Reynolds, S.W., Lancaster, S., Romanguera, V.S. and Yeates, S.G.** (2014) Polymer degradation during continuous ink-jet printing. *Polymer Degradation and Stability*, Elsevier Ltd. **105**, 116–21. <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2014.04.007>
- [17] **Carbaugh, D.J., Wright, J.T., Parthiban, R. and Rahman, F.** (2015) Photolithography with polymethyl methacrylate (PMMA). *Semiconductor Science and Technology*, Institute of Physics Publishing. **31**. <https://doi.org/10.1088/0268-1242/31/2/025010>
- [18] **Corrigan, N., Yeow, J., Judzewitsch, P., Xu, J. and Boyer, C.** (2019) Seeing the Light: Advancing Materials Chemistry through Photopolymerization. *Angewandte Chemie - International Edition*, Wiley-VCH Verlag. **58**, 5170–89. <https://doi.org/10.1002/ANIE.201805473>
- [19] **Tasdelen, M.A., Kahveci, M.U. and Yagci, Y.** (2011) Telechelic polymers by living and controlled/living polymerization methods. *Progress in Polymer Science (Oxford)*, Elsevier Ltd. **36**, 455–567. <https://doi.org/10.1016/J.PROGPOLYMSCI.2010.10.002>
- [20] **Aydogan, C., Ciftci, M. and Yagci, Y.** (2018) Hyperbranched Polymers by Light-Induced Self-Condensing Vinyl Polymerization. *Macromolecular Rapid Communications*, Wiley-VCH Verlag. **39**. <https://doi.org/10.1002/MARC.201800276>
- [21] **Ciftci, M., Batat, P., Demirel, A.L., Xu, G., Buchmeiser, M. and Yagci, Y.** (2013) Visible light-induced grafting from polyolefins. *Macromolecules*, **46**, 6395–401. <https://doi.org/10.1021/MA401431H>
- [22] **Kahveci, M.U., Yagci, Y., Avgeropoulos, A. and Tsitsilianis, C.** (2012) 6.13 - Well-Defined Block Copolymers. *Polymer Science: A Comprehensive Reference: Volume 1-10*, Elsevier. **1–10**, 455–509. <https://doi.org/10.1016/B978-0-444-53349-4.00171-0>
- [23] **Yagci, Y. and Schnabel, W.** (1990) Light-induced synthesis of block and graft copolymers. *Progress in Polymer Science*, **15**, 551–601. [https://doi.org/10.1016/0079-6700\(90\)90006-M](https://doi.org/10.1016/0079-6700(90)90006-M)

- [24] **Kiliclar, H.C., Gencosman, E. and Yagci, Y.** (2022) Visible Light Induced Conventional Step-Growth and Chain-Growth Condensation Polymerizations by Electrophilic Aromatic Substitution. *Macromolecular Rapid Communications*, John Wiley and Sons Inc. **43**. <https://doi.org/10.1002/MARC.202100584>
- [25] **Nakipoglu, B., Yilmaz, G. and Yagci, Y.** (2019) Visible light induced radical coupling reactions for the synthesis of conventional polycondensates. *Polymer Chemistry*, Royal Society of Chemistry. **10**, 5652–8. <https://doi.org/10.1039/C9PY01140D>
- [26] **Xiao, P., Zhang, J., Dumur, F., Tehfe, M.A., Morlet-Savary, F., Graff, B. et al.** (2015) Visible light sensitive photoinitiating systems: Recent progress in cationic and radical photopolymerization reactions under soft conditions. *Progress in Polymer Science*, Pergamon. **41**, 32–66. <https://doi.org/10.1016/J.PROGPOLYMSCI.2014.09.001>
- [27] **Sari, E., Mitterbauer, M., Liska, R. and Yagci, Y.** (2019) Visible light induced free radical promoted cationic polymerization using acylsilanes. *Progress in Organic Coatings*, Elsevier. **132**, 139–43. <https://doi.org/10.1016/J.PORGCOAT.2019.02.045>
- [28] **Sari, E., Yilmaz, G., Koyuncu, S. and Yagci, Y.** (2018) Photoinduced Step-Growth Polymerization of N-Ethylcarbazole. *Journal of the American Chemical Society*, American Chemical Society. **140**, 12728–31. [https://doi.org/10.1021/JACS.8B08668/SUPPL\\_FILE/JA8B08668\\_SI\\_001.PDF](https://doi.org/10.1021/JACS.8B08668/SUPPL_FILE/JA8B08668_SI_001.PDF)
- [29] **Yilmaz, G. and Yagci, Y.** (2016) New Photochemical Processes for Macromolecular Syntheses. *Journal of Photopolymer Science and Technology*, The Society of Photopolymer Science and Technology(SPST). **29**, 91–8. <https://doi.org/10.2494/PHOTOPOLYMER.29.91>
- [30] **Yilmaz, G. and Yagci, Y.** (2018) Photoinduced metal-free atom transfer radical polymerizations: state-of-the-art, mechanistic aspects and applications. *Polymer Chemistry*, The Royal Society of Chemistry. **9**, 1757–62. <https://doi.org/10.1039/C8PY00207J>
- [31] **Kiliclar, H.C., Yilmaz, G. and Yagci, Y.** (2021) Visible Light Induced Step-Growth Polymerization by Substitution Reactions. *Macromolecular Rapid Communications*, John Wiley & Sons, Ltd. **42**, 2000686. <https://doi.org/10.1002/MARC.202000686>
- [32] **Kiliclar, H.C., Altinkok, C., Yilmaz, G. and Yagci, Y.** (2021) Visible light induced step-growth polymerization by electrophilic aromatic substitution reactions. *Chemical Communications*, The Royal Society of Chemistry. **57**, 5398–401. <https://doi.org/10.1039/D1CC01444G>
- [33] **Sano, Y., Konishi, T., Sawamoto, M. and Ouchi, M.** (2019) Controlled radical depolymerization of chlorine-capped PMMA via reversible activation of the terminal group by ruthenium catalyst. *European Polymer Journal*, Pergamon. **120**, 109181. <https://doi.org/10.1016/J.EURPOLYMJ.2019.08.008>
- [34] **Martinez, M.R., De Luca Bossa, F., Olszewski, M. and Matyjaszewski, K.** (2022) Copper(II) Chloride/Tris(2-pyridylmethyl)amine-Catalyzed Depolymerization of Poly(n-butyl methacrylate). *Macromolecules*, American Chemical Society. **55**, 78–87. <https://doi.org/10.1021/ACS.MACROMOL.1C02246>

- [35] **Arslan, Z., Kiliçlar, H.C. and Yagci, Y.** (2022) Dimanganese decacarbonyl catalyzed visible light induced ambient temperature depolymerization of poly(methyl methacrylate). *Designed Monomers and Polymers*, Taylor & Francis. **25**, 271–6. <https://doi.org/10.1080/15685551.2022.2135730>
- [36] **Ciftci, M., Tasdelen, M.A. and Yagci, Y.** (2016) Macromolecular design and application using Mn<sub>2</sub>(CO)<sub>10</sub>-based visible light photoinitiating systems. *Polymer International*, John Wiley and Sons Ltd. **65**, 1001–14. <https://doi.org/10.1002/PI.5111>
- [37] **Schwarz, A.E., Ligthart, T.N., Boukris, E. and Van Harmelen, T.** (2019) Sources, transport, and accumulation of different types of plastic litter in aquatic environments: A review study ☆. <https://doi.org/10.1016/j.marpolbul.2019.04.029>
- [38] **Moshood, T.D., Nawanir, G., Mahmud, F., Mohamad, F., Ahmad, H. and Abdulghani, A.** (2022) Sustainability of biodegradable plastics: New problem or solution to solve the global plastic pollution? <https://doi.org/10.1016/j.crgsc.2022.100273>
- [39] **Awoyera, P.O. and Adesina, A.** (2020) Plastic wastes to construction products: Status, limitations and future perspective. *Case Studies in Construction Materials*, Elsevier. **12**, e00330. <https://doi.org/10.1016/J.CSCM.2020.E00330>
- [40] **Mamun, A. Al, Prasetya, T.A.E., Dewi, I.R. and Ahmad, M.** (2023) Microplastics in human food chains: Food becoming a threat to health safety. *The Science of the Total Environment*, Sci Total Environ. **858**. <https://doi.org/10.1016/J.SCITOTENV.2022.159834>
- [41] **Uekert, T., Singh, A., DesVeaux, J.S., Ghosh, T., Bhatt, A., Yadav, G. et al.** (2023) Technical, Economic, and Environmental Comparison of Closed-Loop Recycling Technologies for Common Plastics. *ACS Sustainable Chemistry and Engineering*, American Chemical Society. **11**, 965–78. [https://doi.org/10.1021/ACSSUSCHEMENG.2C05497/ASSET/IMAGES/LARGE/SC2C05497\\_0006.JPEG](https://doi.org/10.1021/ACSSUSCHEMENG.2C05497/ASSET/IMAGES/LARGE/SC2C05497_0006.JPEG)
- [42] **Ncube, L.K., Ude, A.U., Ogunmuyiwa, E.N., Zulkifli, R. and Beas, I.N.** (2021) An Overview of Plastic Waste Generation and Management in Food Packaging Industries. *Recycling 2021, Vol 6, Page 12*, Multidisciplinary Digital Publishing Institute. **6**, 12. <https://doi.org/10.3390/RECYCLING6010012>
- [43] **Hopewell, J., Dvorak, R. and Kosior, E.** Plastics recycling: challenges and opportunities. <https://doi.org/10.1098/rstb.2008.0311>
- [44] **Bhandari, K.K., Joshi, J.R. and Patel, J. V.** (2023) Recycling of polyethylene terephthalate (PET Or PETE) plastics-An alternative to obtain value added products: A review. *Journal of the Indian Chemical Society*, **100**, 100843. <https://doi.org/10.1016/j.jics.2022.100843>
- [45] **Nisticò, R.** (2020) Polyethylene terephthalate (PET) in the packaging industry. *Polymer Testing*, Elsevier. **90**, 106707. <https://doi.org/10.1016/J.POLYMERTESTING.2020.106707>
- [46] **Khopade, K. V., Chikkali, S.H. and Barsu, N.** (2023) Metal-catalyzed plastic depolymerization. *Cell Reports Physical Science*, Cell Press. **4**, 101341. <https://doi.org/10.1016/J.XCRP.2023.101341>

- [47] **Nyika, J. and Dinka, M.** (2022) Recycling plastic waste materials for building and construction Materials: A minireview. *Materials Today: Proceedings*, Elsevier. **62**, 3257–62.  
<https://doi.org/10.1016/J.MATPR.2022.04.226>
- [48] **Singh, M.K., Mohanty, A.K. and Misra, M.** (2023) Upcycling of waste polyolefins in natural fiber and sustainable filler-based biocomposites: A study on recent developments and future perspectives. *Composites Part B: Engineering*, Elsevier. **263**, 110852.  
<https://doi.org/10.1016/J.COMPOSITESB.2023.110852>
- [49] **Tola, F., Mosconi, E.M., Marconi, M. and Gianvincenzi, M.** (2023) Perspectives for the Development of a Circular Economy Model to Promote Ship Recycling Practices in the European Context: A Systemic Literature Review. *Sustainability (Switzerland)*, MDPI. **15**, 5919. <https://doi.org/10.3390/SU15075919/S1>
- [50] **Alim, M., Negi, K.S., Abhyankar, S., Tiwari, N., Harshey, A. and Srivastava, A.** (2020) Towards the investigation of shooting incidents: evaluation of fracture pattern on polymethylmethacrylate sheet made by .22" and .177" caliber air rifle. *Heliyon*, Elsevier. **6**, e04088. <https://doi.org/10.1016/J.HELIYON.2020.E04088>
- [51] **Yuan, M., Huang, D. and Zhao, Y.** (2022) Development of Synthesis and Application of High Molecular Weight Poly(Methyl Methacrylate). *Polymers 2022, Vol 14, Page 2632*, Multidisciplinary Digital Publishing Institute. **14**, 2632.  
<https://doi.org/10.3390/POLYM14132632>
- [52] **Yilmaz, E.** (2022) Compatibilization of polyvinyl chloride - polymethyl methacrylate polymer blends with maleic anhydride-styrene-methyl methacrylate terpolymer. *Journal of Applied Polymer Science*, John Wiley & Sons, Ltd. **139**, 51745. <https://doi.org/10.1002/APP.51745>
- [53] **Ali, U., Karim, K.J.B.A. and Buang, N.A.** (2015) A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). *Polymer Reviews*, Taylor & Francis. **55**, 678–705.  
<https://doi.org/10.1080/15583724.2015.1031377>
- [54] **Demir, M.M., Memesa, M., Castignolles, P. and Wegner, G.** (2006) PMMA/zinc oxide nanocomposites prepared by in-situ bulk polymerization. *Macromolecular Rapid Communications*, **27**, 763–70.  
<https://doi.org/10.1002/marc.200500870>
- [55] **Gunes, D., Karagoz, B. and Bicak, N.** (2009) Synthesis of methacrylate-based functional monomers via boron ester acidolysis and their polymerization. *Designed Monomers and Polymers*, **12**, 445–54.  
<https://doi.org/10.1163/138577209X12486896623571>
- [56] **Matyjaszewski, K. and Xia, J.** (2001) Atom transfer radical polymerization. *Chemical Reviews*, **101**, 2921–90. <https://doi.org/10.1021/cr940534g>
- [57] **Handbook of Vinyl Polymers: Radical Polymerization, Process, and Technology, Second Edition.** (2016) *Handbook of Vinyl Polymers*, CRC Press. <https://doi.org/10.1201/9781420015133>
- [58] **Qi, G., Tan, X., Tu, Y., Yang, X., Qiao, Y., Wang, Y. et al.** (2022) Ordered-Porous-Array Polymethyl Methacrylate Films for Radiative Cooling. *ACS Applied Materials and Interfaces*, American Chemical Society. **14**, 31277–84.

[https://doi.org/10.1021/ACSAMI.2C06809/SUPPL\\_FILE/AM2C06809\\_SI\\_001.PDF](https://doi.org/10.1021/ACSAMI.2C06809/SUPPL_FILE/AM2C06809_SI_001.PDF)

- [59] **Manuel, P., Almeida, M., Martins, M. and Oliveira, M.** (2022) Effects of nanoplastics on zebrafish embryo-larval stages: A case study with polystyrene (PS) and polymethylmethacrylate (PMMA) particles. *Environmental Research*, Academic Press. **213**, 113584. <https://doi.org/10.1016/J.ENVRES.2022.113584>
- [60] **Liu, Z. and Nowack, B.** (2022) Probabilistic material flow analysis and emissions modeling for five commodity plastics (PUR, ABS, PA, PC, and PMMA) as macroplastics and microplastics☆. *Resources, Conservation and Recycling*, Elsevier. **179**, 106071. <https://doi.org/10.1016/J.RESCONREC.2021.106071>
- [61] **De Tommaso, J. and Dubois, J.L.** (2021) Risk Analysis on PMMA Recycling Economics. *Polymers 2021, Vol 13, Page 2724*, Multidisciplinary Digital Publishing Institute. **13**, 2724. <https://doi.org/10.3390/POLYM13162724>
- [62] **Naziff, M., Said, A., Hasbullah, A., Ridhwan, M., Rosdi, H., Musa, S. et al.** (2023) Polymerization and Applications of Poly(methyl methacrylate)–Graphene Oxide Nanocomposites: A Review. *UTC*. **7**, 43. <https://doi.org/10.1021/acsomega.2c04483>
- [63] **Young, J.B., Hughes, R.W., Tamura, A.M., Bailey, L.S., Stewart, K.A. and Sumerlin, B.S.** (2023) Bulk depolymerization of poly(methyl methacrylate) via chain-end initiation for catalyst-free reversion to monomer. *Chem*, Cell Press. **9**, 2669–82. <https://doi.org/10.1016/J.CHEMPR.2023.07.004>
- [64] **Park, S. Il, Lee, S.I., Hong, S.J. and Cho, K.Y.** (2007) Suspension polymerization and characterization of transparent poly(methyl methacrylate-co-isobornyl methacrylate). *Macromolecular Research*, Polymer Society of Korea. **15**, 418–23. <https://doi.org/10.1007/BF03218808>
- [65] **Zhang, Y., He, Y. and Zhao, J.** (2014) Poly(methyl methacrylate) nanolatexes with high solid contents prepared by semi-continuous emulsion polymerization in the presence of oil-soluble initiators. *European Polymer Journal*, Pergamon. **61**, 316–25. <https://doi.org/10.1016/J.EURPOLYMJ.2014.11.004>
- [66] **Lease, J., Sahin, Z.-M. and Andou, Y.** (2023) Emulsion Polymerization of PMMA onto Natural Rubber. *ACS Applied Engineering Materials*, American Chemical Society (ACS). **1**, 2247–54. <https://doi.org/10.1021/ACSAENM.3C00303>
- [67] **Ghosh, P., Gupta, S.K. and Saraf, D.N.** (1998) An experimental study on bulk and solution polymerization of methyl methacrylate with responses to step changes in temperature. *Chemical Engineering Journal*, Elsevier. **70**, 25–35. [https://doi.org/10.1016/S1385-8947\(98\)00064-3](https://doi.org/10.1016/S1385-8947(98)00064-3)
- [68] **Matyjaszewski, K. and Spanswick, J.** (2005) Controlled/living radical polymerization. *Materials Today*, Elsevier. **8**, 26–33. [https://doi.org/10.1016/S1369-7021\(05\)00745-5](https://doi.org/10.1016/S1369-7021(05)00745-5)
- [69] **Matyjaszewski, K.** (2012) Atom Transfer Radical Polymerization (ATRP): Current status and future perspectives. *Macromolecules*, American Chemical Society. **45**, 4015–39.

[https://doi.org/10.1021/MA3001719/ASSET/IMAGES/MEDIUM/MA-2012-001719\\_0030.GIF](https://doi.org/10.1021/MA3001719/ASSET/IMAGES/MEDIUM/MA-2012-001719_0030.GIF)

- [70] **Matyjaszewski, K.** (2018) Advanced Materials by Atom Transfer Radical Polymerization. *Advanced Materials*, John Wiley & Sons, Ltd. **30**, 1706441. <https://doi.org/10.1002/ADMA.201706441>
- [71] **Nicolas, J., Guillaneuf, Y., Lefay, C., Bertin, D., Gimes, D. and Charleux, B.** (2013) Nitroxide-mediated polymerization. *Progress in Polymer Science*, Pergamon. **38**, 63–235. <https://doi.org/10.1016/J.PROGPOLYMSCI.2012.06.002>
- [72] **Petton, L., Ciolino, A.E., Dervaux, B. and Du Prez, F.E.** (2012) From one-pot stabilisation to in situ functionalisation in nitroxide mediated polymerisation: an efficient extension towards atom transfer radical polymerisation. *Polymer Chemistry*, The Royal Society of Chemistry. **3**, 1867–78. <https://doi.org/10.1039/C2PY00444E>
- [73] **Semsarilar, M. and Abetz, V.** (2021) Polymerizations by RAFT: Developments of the Technique and Its Application in the Synthesis of Tailored (Co)polymers. *Macromolecular Chemistry and Physics*, Wiley-VCH Verlag. **222**. <https://doi.org/10.1002/MACP.202000311>
- [74] **Perrier, S.S.** (2017) 50th Anniversary Perspective: RAFT Polymerization □ A User Guide. *Macromolecules*, UTC. **50**, 18. <https://doi.org/10.1021/acs.macromol.7b00767>
- [75] **Semsarilar, M. and Abetz, V.** (2021) Polymerizations by RAFT: Developments of the Technique and Its Application in the Synthesis of Tailored (Co)polymers. *Macromolecular Chemistry and Physics*, Wiley-VCH Verlag. **222**. <https://doi.org/10.1002/MACP.202000311>
- [76] **Aydogan, C., Yilmaz, G., Shegwal, A., Haddleton, D.M. and Yagci, Y.** (2022) Photoinduced Controlled/Living Polymerizations. *Angewandte Chemie International Edition*, John Wiley & Sons, Ltd. **61**, e202117377. <https://doi.org/10.1002/ANIE.202117377>
- [77] **Koumura, K., Satoh, K. and Kamigaito, M.** (2009) Mn<sub>2</sub>(CO)<sub>10</sub>-induced RAFT polymerization of vinyl acetate, methyl acrylate, and styrene. *Polymer Journal*, **41**, 595–603. <https://doi.org/10.1295/polymj.PJ2009070>
- [78] **Kahveci, M.U., Acik, G. and Yagci, Y.** (2012) Synthesis of Block Copolymers by Combination of Atom Transfer Radical Polymerization and Visible Light-Induced Free Radical Promoted Cationic Polymerization. *Macromolecular Rapid Communications*, John Wiley & Sons, Ltd. **33**, 309–13. <https://doi.org/10.1002/MARC.201100641>
- [79] **Ciftci, M., Norsic, S., Boisson, C., D'Agosto, F. and Yagci, Y.** (2015) Synthesis of Block Copolymers Based on Polyethylene by Thermally Induced Controlled Radical Polymerization Using Mn<sub>2</sub>(CO)<sub>10</sub>. *Macromolecular Chemistry and Physics*, John Wiley & Sons, Ltd. **216**, 958–63. <https://doi.org/10.1002/MACP.201500016>
- [80] **Ciftci, M., Tasdelen, M.A. and Yagci, Y.** (2016) Macromolecular design and application using Mn<sub>2</sub>(CO)<sub>10</sub>-based visible light photoinitiating systems. *Polymer International*, John Wiley & Sons, Ltd. **65**, 1001–14. <https://doi.org/10.1002/PI.5111>
- [81] **Thiounn, T., Smith, R.C. and Rhett Smith, C.C.** (2020) Advances and approaches for chemical recycling of plastic waste. <https://doi.org/10.1002/pol.20190261>

- [82] **Kugelmass, L.H. and Stache, E.E.** Photothermal catalysis: Recycling polymer to monomer with carbon quantum dots.
- [83] **Vohlidal, J.** (2021) Polymer degradation: A short review. *Chemistry Teacher International*, Walter de Gruyter GmbH. p. 213–20.  
<https://doi.org/10.1515/cti-2020-0015>
- [84] **Vohlidal, J.** (2021) Polymer degradation: A short review. *Chemistry Teacher International*, Walter de Gruyter GmbH. **3**, 213–20.  
<https://doi.org/10.1515/CTI-2020-0015/MACHINEREADABLECITATION/RIS>
- [85] **Kimura, T., Kuroda, K., Kubota, H. and Ouchi, M.** (2021) Metal-Catalyzed Switching Degradation of Vinyl Polymers via Introduction of an “in-Chain” Carbon-Halogen Bond as the Trigger. *ACS Macro Letters*, American Chemical Society. **10**, 1535–9.  
[https://doi.org/10.1021/ACSMACROLETT.1C00601/SUPPL\\_FILE/MZ1C00601\\_SI\\_001.PDF](https://doi.org/10.1021/ACSMACROLETT.1C00601/SUPPL_FILE/MZ1C00601_SI_001.PDF)
- [86] **Martinez, M.R., Schild, D., De Luca Bossa, F. and Matyjaszewski, K.** (2022) Depolymerization of Polymethacrylates by Iron ATRP. *Macromolecules*, American Chemical Society. **55**, 10590–9.  
[https://doi.org/10.1021/ACS.MACROMOL.2C01712/SUPPL\\_FILE/MA2C01712\\_SI\\_001.PDF](https://doi.org/10.1021/ACS.MACROMOL.2C01712/SUPPL_FILE/MA2C01712_SI_001.PDF)
- [87] **Young, J.B., Bowman, J.I., Eades, C.B., Wong, A.J. and Sumerlin, B.S.** (2022) Photoassisted Radical Depolymerization. *ACS Macro Letters*, American Chemical Society. **11**, 1390–5.  
[https://doi.org/10.1021/ACSMACROLETT.2C00603/SUPPL\\_FILE/MZ2C00603\\_SI\\_001.PDF](https://doi.org/10.1021/ACSMACROLETT.2C00603/SUPPL_FILE/MZ2C00603_SI_001.PDF)
- [88] **Wang, H.S., Truong, N.P., Pei, Z., Coote, M.L. and Anastasaki, A.** (2022) Reversing RAFT Polymerization: Near-Quantitative Monomer Generation Via a Catalyst-Free Depolymerization Approach. *Journal of the American Chemical Society*, American Chemical Society. **144**, 4678–84.  
[https://doi.org/10.1021/JACS.2C00963/ASSET/IMAGES/LARGE/JA2C00963\\_0004.JPEG](https://doi.org/10.1021/JACS.2C00963/ASSET/IMAGES/LARGE/JA2C00963_0004.JPEG)
- [89] **De Luca Bossa, F., Yilmaz, G. and Matyjaszewski, K.** (2023) Fast Bulk Depolymerization of Polymethacrylates by ATRP. *ACS Macro Letters*, American Chemical Society. **12**, 1173–8.  
<https://doi.org/10.1021/acsmacrolett.3c00389>
- [90] **Ahn, D., Stevens, L.M., Zhou, K. and Page, Z.A.** (2020) Rapid High-Resolution Visible Light 3D Printing. *ACS Central Science*, American Chemical Society. **6**, 1555–63.  
[https://doi.org/10.1021/ACSCENTSCI.0C00929/ASSET/IMAGES/LARGE/OC0C00929\\_0006.JPEG](https://doi.org/10.1021/ACSCENTSCI.0C00929/ASSET/IMAGES/LARGE/OC0C00929_0006.JPEG)

## **APPENDICES**

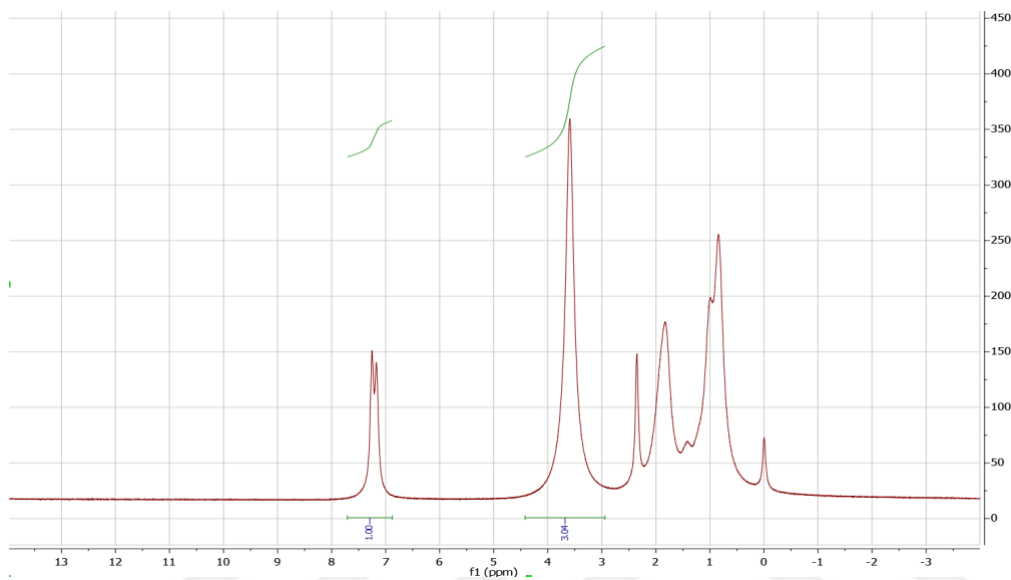
### **APPENDIX A: $^1\text{H}$ NMR and GPC spectra**



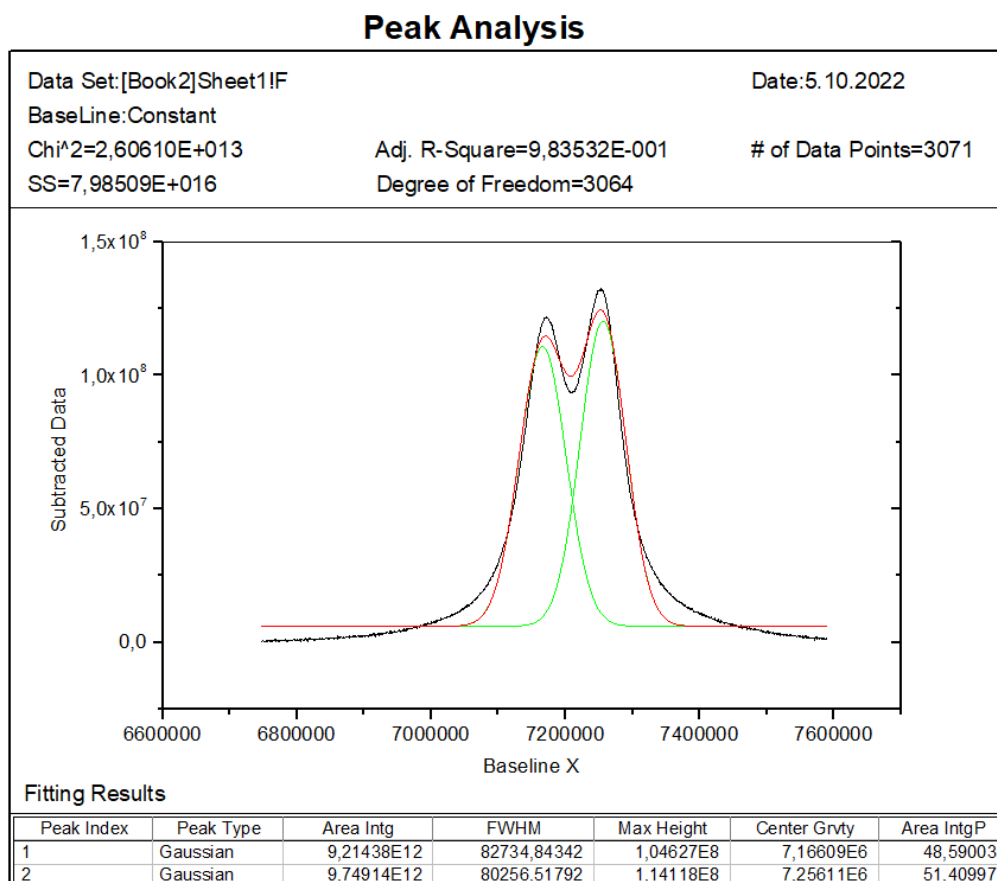
## APPENDIX A

### Calculation of depolymerization using $^1\text{H-NMR}$ .

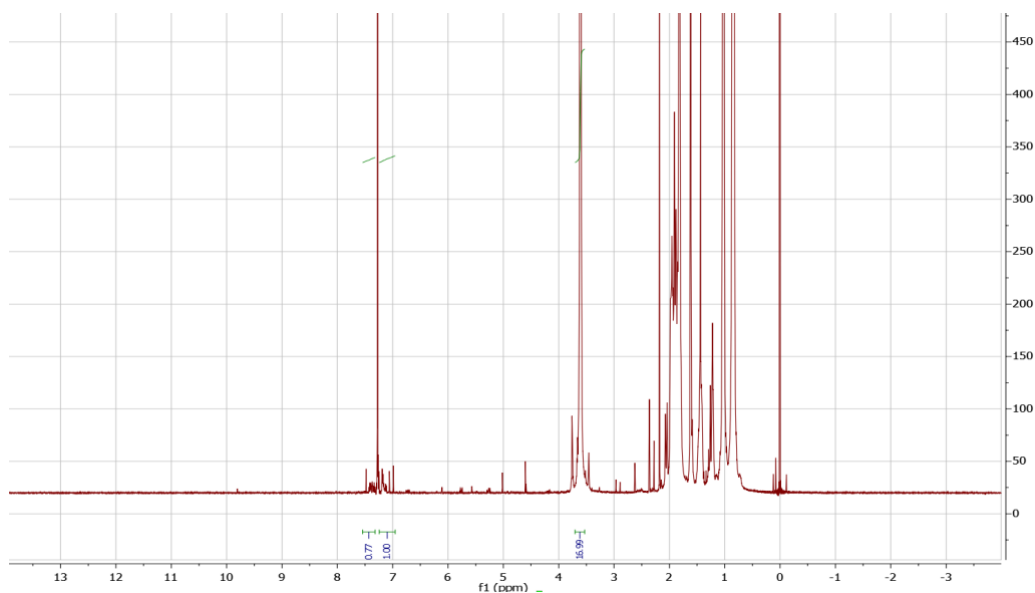
As indicated by integration ratio of the intensities of benzylic hydrogens present at the chain end of the initial polymer and depolymerized sample, esteric methoxide hydrogen abundance is decreased 40% which can be attributed to depolymerization. Molecular weights were calculated using  $^1\text{H-NMR}$  spectra, depicted in Figure A.1, Figure A.2 and Figure A.3.



**Figure A.1 :**  $^1\text{H-NMR}$  spectrum of depolymerized Bz-PMMA- Cl



**Figure A.2 :** Peak analysis of <sup>1</sup>H-NMR spectra of depolymerized Bz-PMMA- Cl to separate the integration values of CHCl<sub>3</sub> and aromatic hydrogen peaks.



**Figure A.3 :** <sup>1</sup>H-NMR spectrum of initial Bz-PMMA- Cl

**Table A.1** : Molecular weight decrease caused by depolymerization.

Polymer	Molecular Weight Before <sup>a</sup> (g mol <sup>-1</sup> )	Molecular Weight After <sup>a</sup> (g mol <sup>-1</sup> )
Bz-PMMA-Cl	1800	1100

<sup>a</sup> Calculated by <sup>1</sup>H-NMR spectrum

In Table A.1 by calculation with <sup>1</sup>H-NMR, it is observed that the initial polymer consists of 17 repeating units, 1 benzyl group and 1 chlorine at the chain end yielding approximately a molecular weight of 1800 g mol<sup>-1</sup>. After depolymerization, the composition of the polymer contains 10 repeating units and 1 benzyl group observable at the chain end yielding approximately a molecular weight of 1100 g mol<sup>-1</sup>.

### Determining the reaction time for depolymerization

Reaction time was determined by aliquot sample gathering and measuring  $M_n$  decrease in predetermined time interval, which depicted in Table A.2. 6 h was determined to be appropriate and therefore applied to all experiments.

**Table A.2** : Visible light induced depolymerization of different polymers.

Sample	Illumination Time (h)	$M_n$ (g.mol <sup>-1</sup> ) Before	$M_n$ (g.mol <sup>-1</sup> ) After	$D$ Before	$D$ After
PMMA- <i>co</i> -PGMA-Cl	3	5400	5200	1.2	1.2
PMMA- <i>co</i> -PGMA-Cl	6	5400	4700	1.2	1.3
PMMA- <i>co</i> -PGMA-Cl	12	5050	4600	1.2	1.3
PMMA-Br	12	5400	5400	1.2	1.3
PMMA-Br	18	5400	5400	1.2	1.3
PMMA-Cl	6	70000	62000	1.4	1.4
PMMA-Cl	8	70000	62000	1.4	1.4

## CURRICULUM VITAE

**Name Surname** : Zeynep Arslan Tangüler

**EDUCATION** :

- **B.Sc.** : 2021, Izmir Institute of Technology, Science Faculty, Chemistry

### PROFESSIONAL EXPERIENCE AND REWARDS:

- 2022 European Symposium of Photopolymer Sciences (ESPS) Congress – Best poster award
- 2022 Research and Development Assistant Specialist at Pulver Powder Coatings

### PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- **Arslan Z.**, Kiliçlar H.C., Yagci Y. 2022: A Novel Visible Light Induced Approach for Depolymerization of Poly (Methyl Methacrylate). The International Graduate Research Symposium (IGRS'22) - Istanbul, Turkey. (Oral Presentation)
- **Arslan Z.**, Kiliçlar H.C., Yagci Y. 2022. Dimanganese decacarbonyl catalyzed visible light induced ambient temperature depolymerization of poly(methyl methacrylate), *Designed Monomers and Polymers*, 271-276, <https://doi.org/10.1080/15685551.2022.2135730>

### OTHER PUBLICATIONS, PRESENTATIONS AND PATENTS:

- **Arslan Z.**, Kiliçlar H.C., Yagci Y. 2023. Visible Light Induced Degradation of Poly(methyl methacrylate- co -methyl  $\alpha$  -chloro acrylate) Copolymer at Ambient Temperature), *Macromolecular Rapid Communications*, 44:9, <https://doi.org/10.1002/marc.202300066>
- Kiliçlar 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)