ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SIMPLE AND GREEN STRATEGY FOR THE SYNTHESIS OF MIKTOARM STAR COPOLYMERS BY MULTI-MODE POLYMERIZATIONS

M.Sc. THESIS

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÇOKLU POLİMERİZASYON TEKNİKLERİ İLE FARKLI KOLLU YILDIZ KOPOLİMERLERİN BASİT VE ÇEVREYE DUYARLI SENTEZİ

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To my beloved family,

FOREWORD

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ABBREVIATIONS

ROP : Ring-Opening Polymerization
CRP : Controlled/Living Radical Polymerization
ATRP : Atom Transfer Radical Polymerization
RAFT : Reversible-Addition-Fragmentation Chain Transfer Polymerization
NMP : Nitroxide Mediated Polymerizaiton
PI : Photoinitiator
BP : Benzophenone
TX : Thioxanthone
CQ : Camphoroquinone
P_2-*t*-Bu : Phosphazene base
DMEA : *N*,*N*-Dimethylethanolamine
MDEA : *N*-Methyldiethanolamine
ε-CL : ε-Caprolactone
MMA : Methyl Methacrylate
PCL : Poly(ε-caprolactone)
PMMA : Poly(methyl methacrylate)
^{1}H-NMR : Nuclear Magnetic Resonance Spectroscopy
GPC : Gel Permeation Chromatography
FT-IR : Fourier Transform Infrared Spectroscopy
DSC : Differential Scanning Calorimetry
RI : Refractive Index
LS : Light Scattering
PS : Photosensitizer

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SIMPLE AND GREEN STRATEGY FOR THE SYNTHESIS OF MIKTOARM STAR COPOLYMERS BY MULTI-MODES POLYMERIZATIONS

SUMMARY

Many reactions are carried out with the help of solar energy by itself in ecosystem. Therefore, chemists are inspired from this energy and apply these photochemical strategies on different chemical synthesis. Photoinitiated polymerization is an important research area for polymer chemistry due to the necessity of low energy and temperature. To obtain polymers at lower temperatures than the traditional polymerization with rapid rates leads to the suppression of side reactions, so that polymerization reaction can be controlled easily. Photopolymerization is most importantly applied to heat sensitive monomers and biochemical systems.

Ring opening polymerization (ROP) is a technique used for the polymerization of cyclic compounds such as unsaturated cyclic ethers, cyclic esters (lactones), cyclic amides (lactams) and cyclic amines (imines). Poly(butylene oxide), poly(ethylene oxide), poly(ethylene imine) and poly(caprolactam) are some examples of polymers frequently used in industry synthesized by ROP. ROP possesses some similarities with addition polymerization including addition of monomers to the polymer chains by one by and reaction takes places only between active chains and monomers. In spite of the fact that the similarities, there are also some differences between ROP and addition polymerization. For instance, there must be double-bounded compounds in addition polymerization yet in ROP there is no obligation for this kind of monomers. Besides, in addition polymerization, high molecular weighted polymers are obtained at the beginning of polymerization process while in some of the ROPs they are obtained at the last stages of polymerization.

Free radical polymerization is an important field of polymer chemistry whose mechanism was discovered by Flory in 1937. He suggested that the free radical polymerization contains three steps namely initiation, propagation and termination. A great number of physical or chemical factors can initiate the polymerization. At propagation step, chain grows via radicals. Finally, the polymerization terminates either disproportionation or coupling.

In this thesis, a simple and green strategy for the synthesis of miktoarm star copolymers by the combination of ROP and free radical polymerization is described. Using a multifunctional initiator, bearing primary hydroxyl and tertiary amine functionalities, vinyl and lactone monomers were sequentially polymerized under mild conditions. In the first step, phosphazene base (P_2-*t*-Bu) catalyzed ROP of ε-caprolactone is employed. Secondly, thus obtained poly(ε-caprolactone) with amine end groups was used as co-initiator for the polymerization of methyl methacrylate by utilizing conventional *Type II* photoinitiators such as camphoroquione, benzophenone and thioxanthone. The structures, molecular weight characteristics and thermal properties of the polymers are analyzed by NMR, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) measurements, respectively.

ÇOKLU POLİMERİZASYON TEKNİKLERİ İLE FARKLI KOLLU YILDIZ KOPOLİMERLERİN BASİT VE ÇEVREYE DUYARLI SENTEZİ

ÖZET

Ekosistemde birçok reaksiyon güneş enerjisi yardımıyla kendiliğinden gerçekleşir. Bilim insanları, sıklıkla doğalı taklit ederek problemlere çözümler bulmaya çalışmışlardır. Böylelikle, güneş enerjisinden etkilenen kimyagerler, bu stratejiyi çeşitli kimyasal tepkimelere uygulamışlardır. Işıkla başlatılmış polimerizasyon, polimer kimyasının önemli bir çalışma alanıdır ve bazı monomerlerin, monomerin ışık hassasiyeti olmaması durumunda ise ışığa duyarlı maddelerin (photosensitizer), ışığı absorplaması ile yapılarında meydana gelen kimyasal değişimler sonucu polimerleşmesi temeline dayanır. Düşük enerji ve düşük sıcaklık gerektirmesi nedeniyle çokça tercih edilen bir yöntemdir. Geleneksel polimerizasyona göre çok daha düşük sıcaklıklarda yüksek hızlarla polimerler elde edilmesi, yan reaksiyonların bastırılmasını ve polimerizasyonun rahatça kontrol edilmesini sağlar. Ayrıca bu yöntem, biyokimyasal uygulamalarda kullanılabilecek ya da ısı duyarlılığı olan maddelerin polimerizasyonunda hayati öneme sahiptir. Genellikle görünür bölge veya UV ışınları kullanılır ve deneysel çalışma dalga boyları 250-500 nm aralığını kapsar. Ekonomik ve ekolojik beklentileri karşılamasından dolayı mikroelektronik, yapıştırıcı, mürekkep, üç boyutlu yazıcı, kaplama gibi birçok endüstriyel uygulamada kullanılmaktadır.

Polimerizasyon yöntemleri katılma ve kondenzasyon olmak üzere ikiye ayrılır. Katılma polimerizasyonu yapısında Π bağları içeren, doymamış bileşiklerin vermiş olduğu polimerizasyon çeşitidir. Katılma polimerizasyonunda monomerler aktif merkezlere, ki bu aktif merkezler radikalik ya da iyonik olabilir, ard arda ve hızla katılarak zinciri büyütürler ve polimerizasyonun ilk anlarında yüksek molekül kütleli polimerler oluşur. Polimerizasyon süresince ortamda yalnızca yüksek molekül kütleli polimerler ve reaksiyona girmemiş monomerler bulunur. Günlük hayatımızda sıkça kullandığımız maddelerin yapıldığı poli(sitiren), poli(vinil klorür), poli(akrilonitril) gibi maddeler katılma polimerlerine örnek verilebilir. Diğer yandan kondenzasyon polimerizasyonu ise üzerinde en az iki tane -OH, -NH_2, -COOH gibi fonksiyonel grup taşıyan moleküllerin birleşirken aralarından küçük bir molekülün reaksiyon ortamına salınmasıyla oluşan polimerizasyon tepkimeleridir. Örneğin bir diol olan etilen glikol ile bi diasit olan adipik asitin kondenzasyon polimerizasyonuyla yapıdan suyun ayrılması sonucu poliester oluşur. Poliesterin dışında poliamidler, poliüretanlar önde gelen kondenzasyon polimerlerindendir. Basamaklı polimerizasyonun katılma polimerizasyonundan en önemli farkı oluşan polimerin molekül ağırlığının yavaş yavaş artması sonucu reaksiyonun ilk anlarında değil, sonlara doğru yüksek kütleli polimerlerin elde edilmesidir. Yukarıda bahsedildiği gibi, katılma polimerizasyonu aktif merkezin yapısına göre üç farklı şekilde ilerleyebilir. Bunlar anyonik, katyonik ve radikalik mekanizmalardır. Serbest radikal polimerizasyonu polimer kimyasının önemli araştırma konularından biri olup mekanizması 1937'de Flory tarafından

aydınlatılmıştır. Serbest radikal polimerizasyonu tümü radikaller üzerinden yürüyen üç basamaktan oluşur; başlama, zincir uzaması ve sonlanma. Başlatıcılar bu polimerizasyon türünde büyük önem taşır. Sıcaklık, ısı gibi etkenler sonucu radikal oluşumu ve oluşan bu radikalin monomere hücum etmesi başlama aşaması olarak adlandırılır. Fotobaşlatıcılar *Tip I* ve *Tip II* olarak ikiye ayrılırlar. *Tip I* fotobaşlatıcılar α-yarılması ile radikaller oluştururan ve çeşitli gruplar içeren karbonil bileşikleridir. Asetofenon, açil fosfin oksit, amino alkil-fenon ve benzil ketal *Tip I* başlatıcıların önemli örnekleridir. *Tip II* fotobaşlatıcılar ise hidrojen koparma yoluyla radikal oluştururlar. Başlıca örnekleri benzofenon, tiyokzanton, kamforokinondur. Başlama aşaması tamamlanınca zincir uzaması meydana gelir. Monomerler zincire teker teker eklenirler ve ortamda yan ürün olarak küçük moleküller yer almazlar. Son basamak ise zincirin sonlanmasıdır ve iki yolla gerçekleşir. Bunlardan birisi uçlarında radikaller bulunan iki aktif zincirin kenetlenerek tek bir uzun polimer zinciri oluşturuduğu birleşerek sonlanma; diğeri ise bir zincirden diğer zincire hidrojen transferi ile aktif uçların yok olması sonucu iki ayrı polimer zincirinin oluştuğu orantısız sonlanmadır. Bu polimerizasyonda gözlenebilecek ve zinciri sonlandıran bir ara basamak daha vardır ve bu zincir transfer reaksiyonu olarak adlandırılır. Bu reaksiyon ortamda hidrojen verebilecek bir tür varlığında gerçekleşir. Molekül ağırlığının kontrolü bu basamağın en büyük avantajlarından birisidir.

Halka açılma polimerizasyonu, halkalı esterler (laktonlar), doymamış halkalı eterler, halkalı aminler (iminller), halkalı amidler (laktamlar) gibi bir çok halkalı bileşiğin polimerizasyonu için kullanılan bir tekniktir. Sanayide ve bilimsel araştırmalarda büyük bir öneme sahip olan Naylon-6 gibi polimerler halka açılma polimerizasyonuyla kolaylıkla üretiliebilirler. Katılma polimerizasyonunda olduğu gibi reaksiyon aktif zincirler ve aktif monomerler arasında gerçekleşir. Katılma reaksiyonlarına karşı avantajları ise yapıların çift bağ bulundurma zorunluluklarının olmamasıdır. Halka açılma polimerizasyonu anyonik ve katyonik mekanizmalar başta olmak üzere, metatez ve radikalik mekanizmaları da takip edebilir. Anyonik mekanizmada nükleofil uygun pozisyona atak ederek halkayı açarken, katyonik mekanizmada ise oluşacak olan katyon kararlılığına göre S_N1 ya da S_N2 mekanizmalarıyla yüreyen iki farklı yol vardır. Halka açılma polimerizasyonlarındaki önemli diğer bir etmen de kullanılan katalizörlerdir. Lewis asitleri, metal kompleksleri halka açılma polimerizasyonlarında sık kullanılan katalizörlerdir. Kullanılacak olan metal ve ligantın uygun şekilde seçilmesiyle istenilen polimerik yapıların net bir şekilde elde edilebilmesine karşın bu sistemlerde yüksek sıcaklık gereksinimi büyük bir dezavantaj olarak karşımıza çıkmaktadır. Metal katalizör içermeyen polimerizasyon sistemleri ise daha ılımlı şartlarda, yüksek verimlerle gerçekleştirilerek enerji tasarrufu sağlamasından ve çevreye duyarlı bir sistem olmasından dolayı araştırmacılar tarafından son yıllarda sıkça kullanılmaktadır. Fosfazen bazları, nükleofilik özelliğe sahip olmayan Brönsted bazlarıdır ve oda sıcaklığında kısa sürede yüksek verimlerle reaksiyonu katalizlediğinden dolayı metalsiz halka açılma polimerizasyonlarında tercih edilirler. Birçok solventte yüksek çözünürlüğü vardır. Kötü nükleofillerden proton kopartarak aktiflenmelerini sağlar. Bir diğer mekanizma türü ise katalizör kullanılmayan halka açılma polimerizasyonlarıdır. Bu reaksiyon iki farklı halkalı yapının zwitter iyonik ara yapısı üzerinden çok yüksek olmayan sıcaklıklarda gerçekleşir.

Tek bir monomerden oluşmuş polimere homopolimer denirken birden fazla monomerden oluşmuş polimerler (kopolimerler) bu monomerlerin diziliş sıralarına göre aşı, blok, rastgele, ardışık kopolimerler gibi çeşitli isimler alırlar. Bu türlerin yanında yıldız polimerler gibi daha kompleks yapıda olan polimerler de mevcuttur.

Yıldız polimerlerin kolları aynı monomerlerden oluşabileceği gibi farklı monomerlerden de oluşabilmektedir ve kollarına göre isimlendirilirler. En az iki kolu farklı olan yıldız kopolimerlere farklı kollu (miktoarm) yıldız kopolimerler denir. Farklı kollu yıldız kopolimerlerin birden fazla monomerin özelliklerini bir bünyede barındırmaları onların birçok alanda etkili bir şekilde kullanılmalarına olanak sağlar. Yıldız kopolimerler çekirdek öncelikli, kol öncelikli ve eşleşme yöntemleriyle sentezlenebilirler. Çekirdek öncelikli yıldız kopolimer sentezinde çok fonksiyonlu bir çekirdek kullanılarak kolların bu çekirdek üzerinde büyümesi sağlanırken diğer bir metod olan kol öncelikli sentez yönteminde ise kollar lineer bir şekilde büyütülüp tek bir noktadan çapraz bağlanarak yıldız kopolimerler elde edilir. Eşleşme yöntemiyle sentezde kollar ve çekirdek ayrı ayrı hazırlanır. Bu yöntemde yapının kontrolü zordur ve diğerlerine göre daha az tercih edilir. Dallanmış yapıların en basit örneği olan yıldız polimerler film oluşumu, kaplama, ilaç salınımı gibi alanlarda rahatlıkla kullanılabilmektedirler.

Polimerler oluştukları monomerlere göre belirli fiziksel ve kimyasal özellikler gösterirler. Birçok bilim insanı bu özellikleri geliştirmek ve iyileştirmek için çalışmalar yapmışlardır. Kopolimerizasyon yöntemiyle farklı polimerlerin özellikleri bir bünyede barındırılabilir. Fakat her zaman iki monomer aynı mekanizmayla polimerleştirilemez. Farklı polimerizasyon yöntemlerinin bir arada kullanılmaları, tek bir mekanizmayla sentezlenemeyen kopolimerlerin sentezlenmelerini sağlayan önemli bir tekniktir. Bu yönteme mekanik transformasyon da denir. Bu metod ilk polimer segmentinin izolasyon ve saflaştırılmasına ve son olarak fonksiyonel grupların ikinci monomerin polimerizasyonunu başlatabilecek başka bir türe dönüşümüne bağlıdır. Transformasyon kavramı, elde edilen polimerlerde boyut ve yapı kontrolü sağlar. Bunun yanı sıra uygulanan polimerizasyon tekniklerine göre ekonomik ve çevreye dost olması yönünden avantaja sahip olabilir. Eğer koşullar uygunsa farklı polimerizasyon teknikleri aynı anda kullanılarak ara saflaştırma işlemleri atlanabilir. Bu özellikle maliyeti düşürmesi ve zamandan tasarruf sağlaması nedenleriyle endüstride tercih edilebilecek bir yöntemdir.

Bu tezde, çoklu polimerizasyon teknikleri ile farklı kollu yıldız kopolimerlerin basit ve çevreye duyarlı sentezi açıklanmıştır. Birincil hidroksi ve üçüncül amin fonksiyonalitelerini taşıyan çok fonksiyonlu başlatıcılar kullanarak vinil ve lakton monomerleri ılımlı reaksiyon koşulları altında ardışık olarak polimerleştirilmiştir. İlk basamakta, ε-kaprolakton, fosfozen bazı (P_2-*t*-Bu) katalizörü eşliğinde halka açılma polimerizasyonu ile polimereştirilmiştir. Ardından, elde edilen amin uç gruplu poli(ε-kaprolakton), metil metakrilatın polimerizasyonunda yardımcı başlatıcı olarak kullanılmıştır. Bu reaksiyonda kamforokinon, benzofenon ve tiyokzanton gibi *Tip II* fotobaşlatıcılardan yararlanılmıştır. Ayrıca, bu iki polimerizasyon yöntemi aynı anda gerçkelşetirilerek tek basamakta da sentez yapılmıştır. Elde edilen yapılar nükleer manyetik rezonans spektroskopisi (NMR), jel geçirgenlik kromatografisi (GPC), fourier dönüşümlü infrared spektroskopisi (FT-IR) ve diferansiyel taramalı kalorimetre (DSC) analizleri ile kanıtlanmıştır.

1. INTRODUCTION

Star polymers have been of great interest since they possess unique rheological behavior and superior mechanical properties compared to their linear counterparts arising from their three dimensional architectures [1-7]. Different strategies toward the synthesis of star polymers exist which can be broadly divided into three modes: (i) core-first [8], (ii) arm-first [9, 10], and (iii) grafting-onto approaches [5]. The former approach involves design and synthesis of a “core” which is a multifunctional initiator [11]. The polymer chains are grown outwards from this core via combination of different polymerization methods, such as living anionic polymerization [12], ring-opening polymerization (ROP) [13], or a diversity of controlled/“living” radical polymerization (CRP) techniques [14-16] comprised of atom transfer radical polymerization (ATRP) [17-19], reversible addition–fragmentation chain transfer (RAFT) polymerization [20, 21] and nitroxide mediated polymerization (NMP) polymerization [22-25]. Based on the variety of polymerization methods and their accompanying choice of monomers, the “core-first” strategy has been a versatile and efficient approach for the synthesis of star polymers [26, 27].

Miktoarm star polymers are star-shaped architecture having different types of polymer arms emanate from a focal point. These polymeric arms with chemically dissimilar and/or different molecular weight were prepared by various synthetic strategies [28].

Photoinitiated free radical polymerization offers a number of advantages different from thermally initiated free radical polymerization due to low-temperature conditions, facilitation of temporal and spatial control, and especially for practical application solvent-free formulation wavelength flexibility and high curing speed.

Photoinitiators for free radical polymerization can be mainly classified into two categories; cleavage (*Type I*) and H-abstraction type (*Type II*) initiators [29, 30] Benzoin and derivatives, acylphosphine oxides [31, 32] and acyl germanes [33, 34] are commonly used as *Type I* photoinitiators for radical photopolymerization and are able to unimolecular bond cleavage on irradiation. Contrarily, in *Type II* systems, the initiation relies on a bimolecular reaction and photoinitiators require a co-initiator (H-donor) such as amines, thiols, alcohols and ethers to generate initiating radicals. Following the photoexcitation of sensitizer by irradiation, electron transfer reaction and subsequently hydrogen abstraction from co-initiator occurs and thus, two radicals are formed; a radical affording from the carbonyl compound (ketyl-type radical) and another radical produced from the hydrogen donor. Only the radicals formed from the co-initiator are capable of initiating free radical polymerization as ketyl radicals are not noticeably active in the initiation process.

Such reactivity difference gives particular advantage for block and graft copolymerization when hydrogen-donating sites are incorporated to the polymer chains. Benzophenone (BP), thioxanthone (TX), camphoroquinone (CQ) and their derivatives are widely used as *Type II* photoinitiators [35-42] (Figure 1.1).

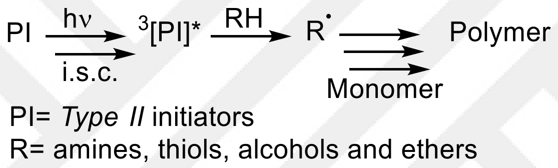


Figure 1.1: Photoinitiated free-radical polymerization by *Type II* photoinitiators.

In a previous study, we have described preparation of block copolymers of vinyl monomers by using well-established *Type II* free radical photoinitiation method in the presence of BP and triethylamine (NEt_3) which afforded poly(methyl methacrylate) (PMMA) with terminal *N,N*-dimethyl amino functionality. Subsequent BP sensitized photopolymerization of *tert*-butyl acrylate was conducted with PMMA-$N(Et)_2$ as hydrogen donor resulted in poly(methyl methacrylate)-*block*-poly(*tert*-butyl acrylate). Within a facile hydrolysis process, the *tert*-butyl ester moieties of the hydrophobic block copolymers were converted to acid functionalities to obtain amphiphilic block copolymer [43].

Recently, there have been great research attempts to realize various polymerization in the absence of inorganic catalysts particularly for green chemistry applications. Hadjichristidis and co-workers demonstrated the possibility of performing ROP without using stannous octoate under mild conditions to obtain monodisperse polylactones. A phosphazene base (P_2-*t*-Bu) catalyzed process was shown to successfully induce ε-caprolactone (ε-CL) polymerization [44, 45].

We have recently combined this strategy with a metal free photo ATRP approach to form block copolymers in a sequential and simultaneous manner. Such combinations of different polymerization processes provide possibility to construct a range of polymeric structures including block [46], graft [47], hyperbranched [48-52], star copolymers [53-57] and telechelic polymers [58, 59]. Herein, we report an operationally simple method for the synthesis of star copolymers through combination of two different polymerization methods; ROP and *Type II* photoinitiation. Depending on the initiator used, star copolymers with different arm combinations, PMMA and poly(ε-caprolactone) (PCL) were successfully prepared.

2. THEORETICAL PART

2.1 Photoinitiated Polymerization

Hermann Staudinger's concept of macromolecules, linking of small molecules via covalent bonds to obtain big molecules, has been a pioneer in this area as a source of inspiration for many scientists and has provided a new era for the design of new functional polymeric materials. Today, one of the most widely used methods in the design and handling of functional polymers is photoinitiated polymerization. Compared with traditional polymerization, this methodology has many advantages such as solvent-free applications, the necessity of lower energy and temperatures, sustainability. This technique provides polymerization of monomers with low ceiling temperatures. It is generally applied to addition polymerizations and the reaction takes place only between active monomer and the active side of the growing chain. This active center can be either a cation, anion or radical.

2.2 Photoinitiated Cationic Polymerization

This technique used widely in industry in UV curing applications, ink, adhesives [60]. Generally, unsaturated monomers as alkyl vinyl ethers and epoxy based cyclic monomers can be polymerized via cationic photopolymerization. Only an initiator having a counter ion, which exhibits low nucleophilicity, can initiate cationic polymerization. Photoinitiator decomposed after absorbing the light and composed radical cation reacts with solvent or monomer. Hereby, H^+ is released in the reaction medium and initiates polymerization. So, it is called direct initiation (Figure 2.1).

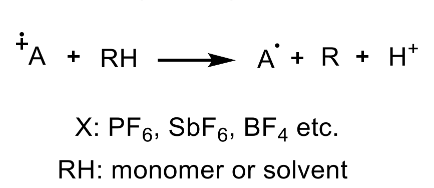
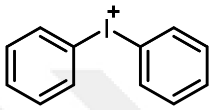
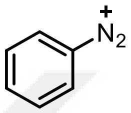
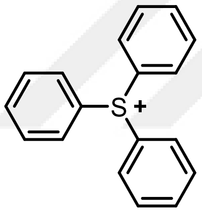
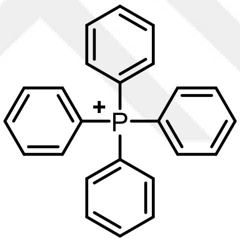
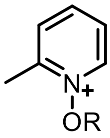
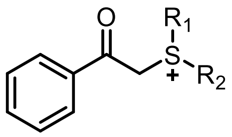


Figure 2.1: General route of direct cationic photoinitiation via onium salts.

Besides, initiation by photosensitization, initiation by free radical oxidization [61, 62] and initiation via charge transfer complexes [63, 64] can be performed and these all can be classified under indirect initiation. Onium-type photoinitiators like iodonium, sulfonium are the mostly used ones in cationic photoinitiation and they generally works under λ<300 nm (Table 2.1) . By preferring indirect initiation, wavelength flexibility can be provided.

Table 2.1: Examples of onium-type photoinitiators generally used in cationic photoinitiation.

 iodonium salt	 aryldiazonium salt
 sulfonium salt	 phosphonium salt
 *N*-alkoxy pyridinium salt	 phenacylsulfonium salt

As can be seen in figure 2.2, aromatic hydrocarbons can be used as photosensitizer (PS) and the energy of light needed to initiate the polymerization is lowered. PS absorbs the light and excited. Therefore, an electron is transferred from excited PS to salt by the formation of the intermediate complex. The rest proceeds like the direct initiation. Again, Brønsted acid released in the reaction media and initiates the polymerization.

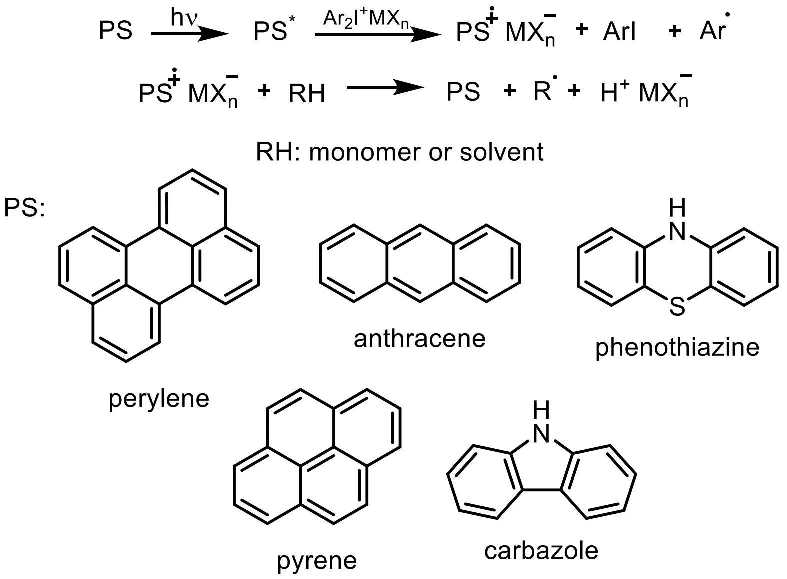


Figure 2.2: Initiation via photosensitization by electron transfer.

Initiation via charge transfer complexes, another type of indirect initiation, is crucial only for pyridinium salts; iodonium and sulfonium salts does not form such complexes. In this of initiation, pyridinium salt forms a charge transfer complex with an electron donor. By the excitation of this complex, the radical cations responsible from the initiation of polymerization are formed and the rest of the polymerization proceeds in the same way (Figure 2.3). Depending on the electron donor, charge transfer complexes of pyridinium salts can absorbs light range between 350-650 nm [65].

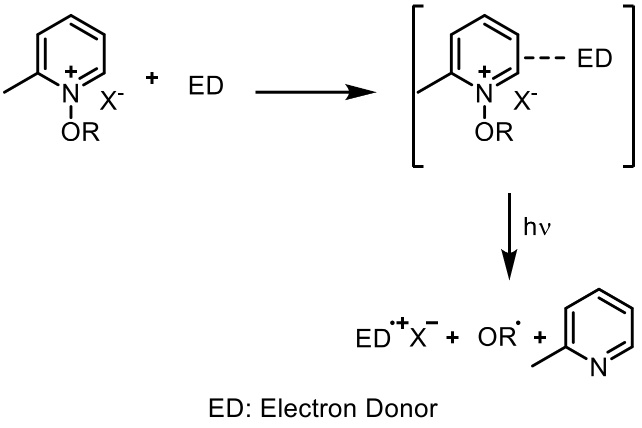


Figure 2.3: Initiation via charge transfer complexes.

The other type of indirect initiation is the initiation by free radical oxidation. Due to using free radical photoinitiators, this process is also called as free radical promoted cationic polymerization. This is the most flexible one among indirect initiation systems. Once photochemically generated radical is formed, it is oxidized by onium salts [66]. So, cation responsible from initiation of polymerization was produced (Figure 2.4).

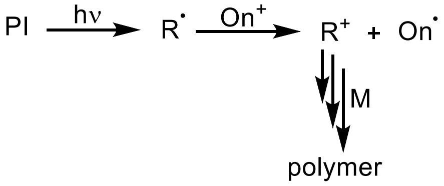


Figure 2.4: Initiation by free radical oxidation.

The most important disadvantage of this polymerization type is the sensitivity against moisture that terminates the polymerization.

2.2.1 Photoinitiated free radical polymerization

Photoinitiated free radical polymerization follows the same initiation, propagation, chain transfer and termination steps with other polymerizations in a radicalic manner. Photoinitiator absorbs the light via its chromophore groups like C=O, N=N, C=C and yields radicals (Figure 2.5). Either both or the proper one from that radicals attacts to one monomer unit and initiates the polymerization. Then, this radical continues to add monomers to the growing chain. That step is called propagation. Chain transfer also takes place if there is any hydrogen donor species in the reaction media. This step provides chemists to control the molecular weight of polymer due to terminating active chain. The last step of polymerization is called termination and it may takes place via coupling or disproportionation. In case of coupling, two active polymer chains are combined with each other to form one polymer. In contrast to the coupling process, with the transfer of a hydrogen to another active polymer chain leads to termination of both chains. Finally, two different polymers are formed.

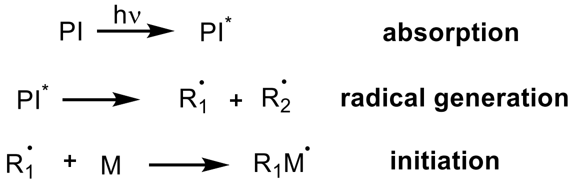


Figure 2.5: General route of photoinitiation of free radical polymerization.

Photoinitiators can be categorized into two groups namely *Type I* and *Type II* that forms radicals via α-cleavage and H abstraction, respectively.

2.2.1.1 *Type I* photoinitiators (unimolecular photoinitiation type)

This type of initiators involves one molecular species that yields radicalic active centers with the help of light. When photoinitiator absorbs the light homolytic bond cleavage occurs and radicals formed. Quantum yield of radical formation is an important parameter for photoinitiating systems. It is the number of initiating radicals formed via the absorption of one photon (Figure 2.6).

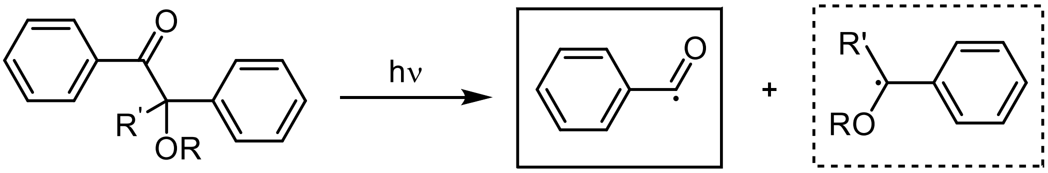
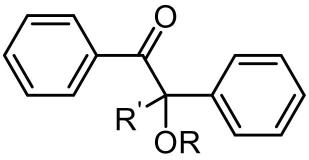
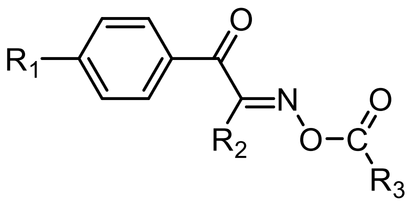
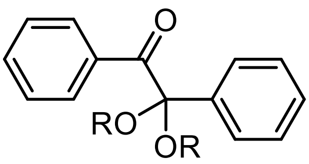
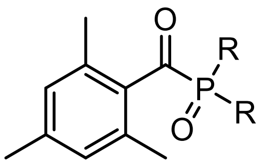
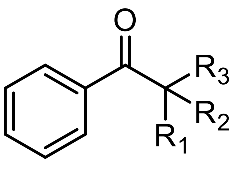
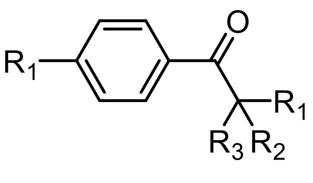


Figure 2.6: Radical generation via *Type I* photoinitiation.

Quantum yields of such systems should be two due to forming two radicals at the end. But it was not as expected; while one radical initiates the polymerization, the other one undergoes either combination or disproportionation. So, the efficiency of radicals changes and affects the quantum yield directly [67]. Benzoin ethers and its derivatives are used frequently (Table 2.2) [30, 68, 69].

Table 2.2: Examples of *Type I* photoinitiators.

 Benzoin ethers	 Benzyl oximes
 Benzil ketals	 Acylphosphines oxides
 Acetophenone	 Aminoalkyl phenones

2.2.1.2 *Type II* photoinitiators (bimolecular photoinitiatoion type)

In that type of initiation, two molecular species are needed to form radicals: a photoinitiator that can absorb the light and a hydrogen donor species that can coinitiate the radical formation.

First, photoinitiator absorbs the light and excited to triplet state by intersystem crossing. A hydrogen donor substance R-H (amine, thiol, alcohol or ether) donates one hydrogen to excited photoinitiator. Finally, radicals are formed (Figure 2.7).

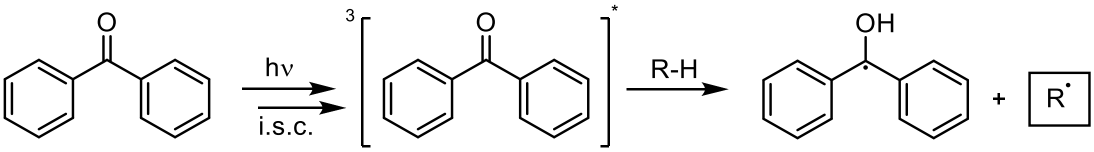
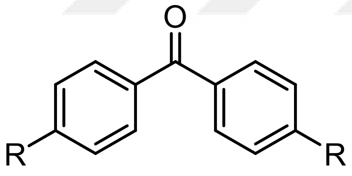
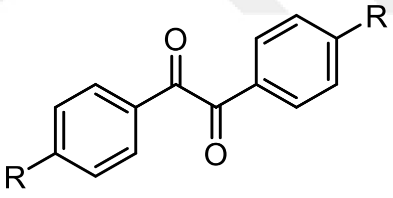
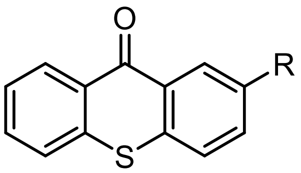
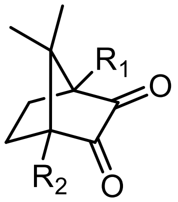
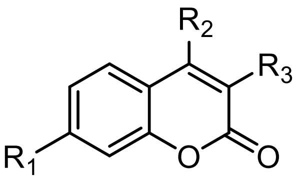


Figure 2.7: Initiation via *Type II* photoinitiation.

Benzophenone, camphoroquinone, thioxanthone are the examples used frequently in *Type II* photoinitiation systems (Table 2.3) [70-72].

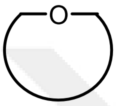
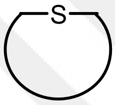
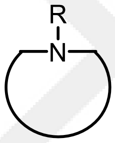
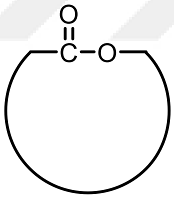
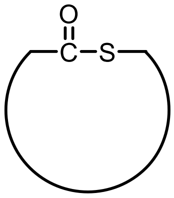
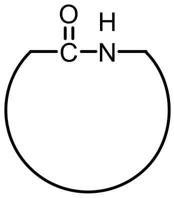
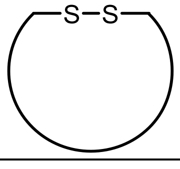
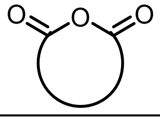
Table 2.3: Examples of *Type II* photoinitiators.

 Benzophenones	 Benzils
 Thioxanthones	 Camphoroquinones
 Coumarins	

2.3 Ring Opening Polymerization of Lactones

Ring opening polymerization is the term used for the polymerization of cyclic monomers like cyclic unsaturated ethers, cyclic esters (lactones), cyclic amines (imines), cyclic amides (lactams) (Table 2.4). ROP is used in industry frequently, especially for the production of Nylon-6. Poly(etylene oxide), polycaprolactam, pol(ybutylene oxide) are some examples of commercial polymers.

Table 2.4: Examples of cyclic monomers and their polymerization mechanism [73].

Structure	Name	Ring Number	Mechnasim
	Olefin	4, 5, 8	Methathesis
	Ether	3-5, 7	Cationic, anionic
	Thioether	3, 4	Cationic, anionic
	Amine	3, 4, 7	Cationic
	Lactone	4, 6-8	Anionic, cationic
	Thiolactone	4-8	Anionic, cationic
	Lactam	>3	Anionic, cationic
	Disulfide	>7	Radical
	Anyhride	5, >6	Anionic

Like addition polymerization, monomers are added one by one to the active chain in ROP. But, these monomers do not need to contain double bonds. Cylic compounds can be polymerized by methathesis, radicalic, anionic and cationic mechanisms but as shown in Table 2.4, lactones prefer anionic or cationic polymerizations.

In anionic mechanism, a nucleophile attacks to a monomer having a polarized bond and polymerization initiates (Figure 2.8). With the nucleophilic addition of monomer units to growing chain, propagation takes place. Finally, active chain terminates and generally, low-molecular weighted polymers obtained.

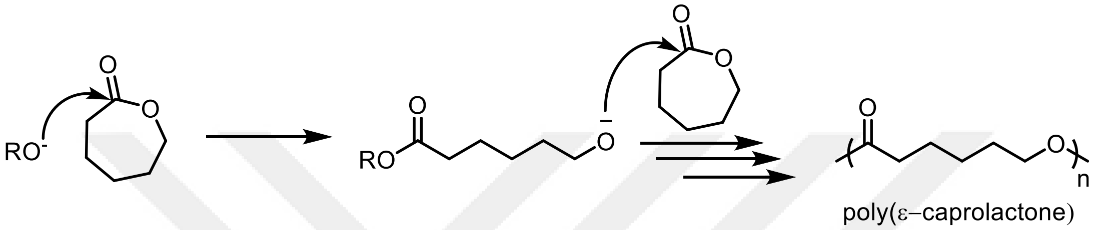


Figure 2.8: General procedure of anionic ring opening polymerization of caprolactone.

In cationic mechanism, polymerization is initiated via a cationic initiator. Depending on the stability of cation, propagation can follow either S_N1 or S_N2 mechanisms. If an electron donation group stabilizes the formed cation, S_N1 mechanism is carried out (Figure 2.9).

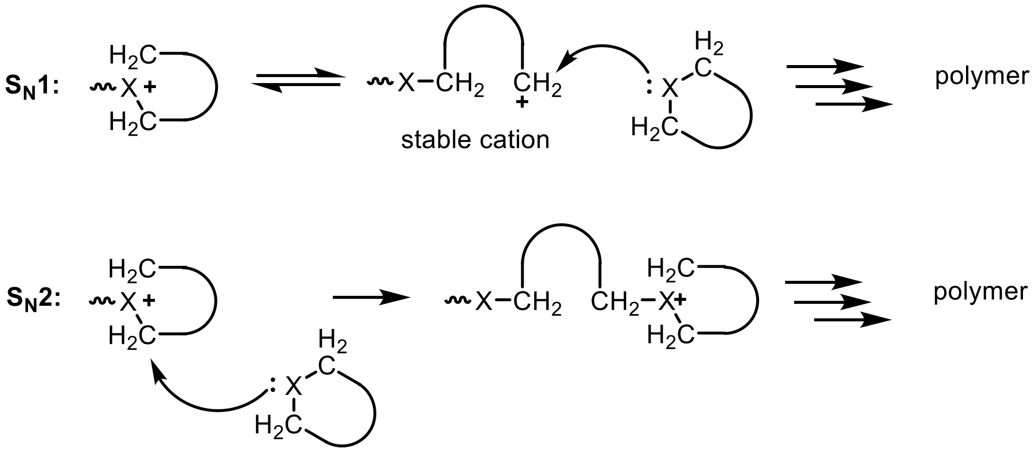
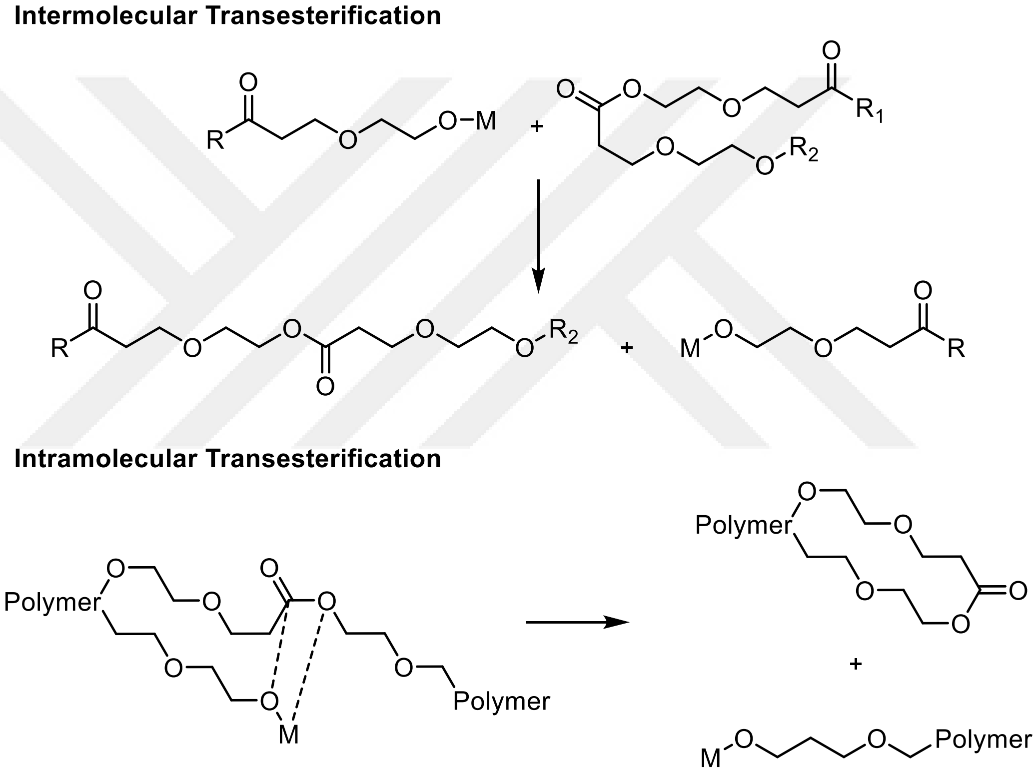


Figure 2.9: General mechanism of cationic ring opening polymerization.

Cationic ring opening polymerizations are usually take places slowly and microwave may be used to increase the reaction rate rather than simple heating.

2.3.1 Organometallic catalyst for the ROP of lactones

Stannous(II) 2-ethylhexanoate, aluminum tri-isopropoxide, tin-alkoxides like organometallic metal complexes catalyze ROP of lactones via their free p or d orbitals. They give side reactions like intermolecular or intramolecular transesterification reactions depending on the temperature and reaction time. As shown in Figure 2.10, intermolecular transesterification reaction inhibits the formation of block copolymers, intramolecular transesterification reactions (back-biting) cause degradation of chain [74]. Moreover, carboxylates have more catalytic properties than alkoxides due to having weaker nucleophilicity.


Intermolecular Transesterification

Intramolecular Transesterification

Figure 2.10: Transesterification reactions caused by catalysts used at ROP.

Stannous(II) 2-ethylhexanoate, also called as stannous octoate, is the most widely used ROP catalyst of lactones because of being economic and commercially available (Figure 2.11). It is also not hazardous, so it can be used as a food additive. Despite some proposals, the mechanism is still unclear.

In 1991, McLain and Drysdale used lanthanide alkoxides for the first time for polymerization of lactones [75]. It is used especially for ROP of lactide due to being more reactive. The best point of using lanthanide alkoxides is the repression of side reactions.

The other catalyst used in ROP of lactones is aluminum tri-isopropoxide that gives well-defined polymers via living polymerization (Figure 1.11). It follows the coordination-insertion mechanism by the formation of any side products. Recent researches on this catalyst focused on the heterogeneous systems by binding the catalyst on aluminum alkoxide which makes the recycling easier.

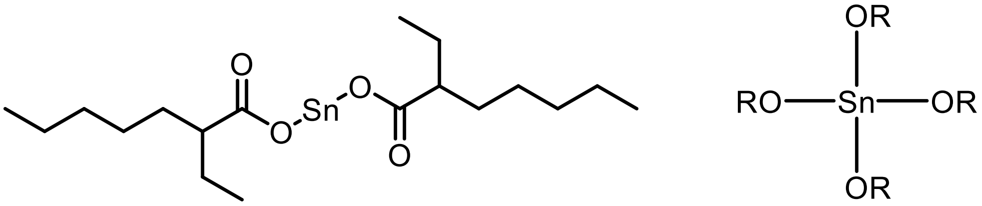


Figure 2.11: Chemical structure of stannous octoate and aluminum tri-isopropoxide.

2.3.2 Metal free ROP systems via phosphazene bases

Metal free polymerization techniques are the main concern of many researchers. Polymers synthesized via ATPR, ROP cannot purified from metal traces. PBs, strong Brønsted bases with non-nucleophilic property, are used as catalysts in ROP of different monomers like lactones, lactams, epoxides etc [76-78]. They are soluble in many organic solvents and makes easier to deprotonation of hydroxyl like protic moieties. When the basicity of PB increased, both polymerization rate and side products are increased. The other advantage of using PBs as catalyst is to obtain polymers at room temperatures. When PBs are used, ROP follows an anionic mechanism (Figure 2.12).

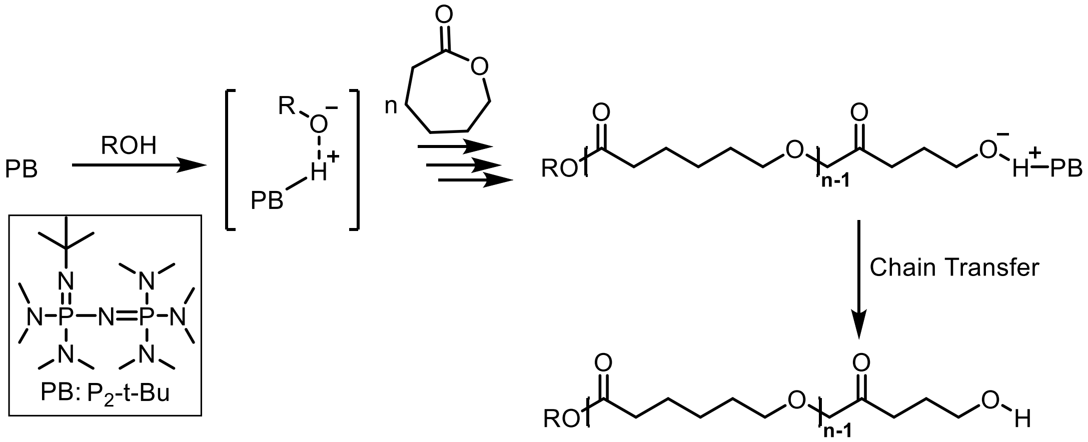


Figure 2.12: Phosphazene base catalyzed ROP of caprolactone.

2.4 Star Polymers

Each polymer chain has unique physical properties and characteristics of monomers that they are formed from. The easiest way to modify these properties is copolymerization. Copolymers can either be linear like block copolymers or branched. The advantage of branching is to obtain more compact polymers with higher densities, which affects the mechanical, crystalline and viscoelastic properties [79]. Star polymers are the examples of branched polymers that can easily be synthesized. Arms are linked from a core in that type of polymers. Furthermore, they can be either symmetric or asymmetric. In symmetric star polymers, branches have the same length and same chemical composition. They generally represented as A_n where A is the monomer polymerized and n is the number of arms recurred. Asymmetric ones, the other type of star polymers can be classified under two main categories; molecular weight asymmetry and chemical asymmetry (Figure 2.14) [80-82]. Chemically asymmetric star copolymers can also be called as heteroarm or miktoarm.

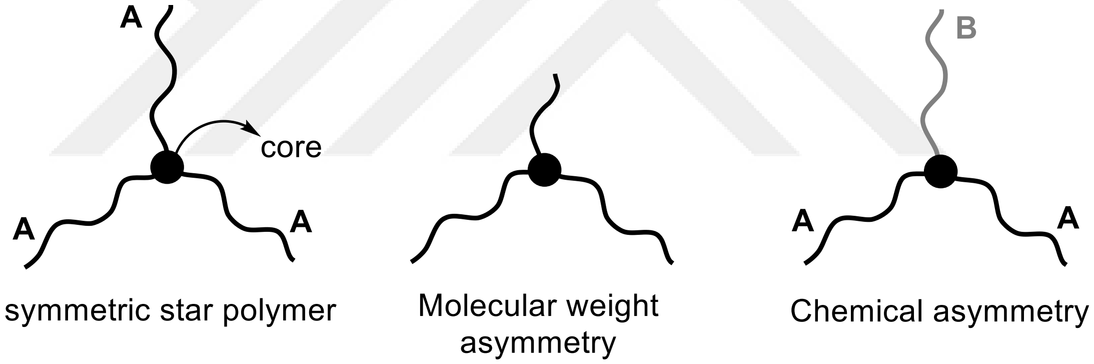


Figure 2.13: Structures of different type of star polymers.

Several methods can be applied in the synthesis of star polymers [5].

2.4.1 Arm-first method

Arm-first methodology can be applied in two ways:

a) Macromonomer approach

b) Macroinitiator approach

In first approach, reaction of higher molecular weighted monomer chains with small initiators are carried out (Figure 2.15). Generally, brush like molecules that have degree of polymerization around 10-25 are obtained.

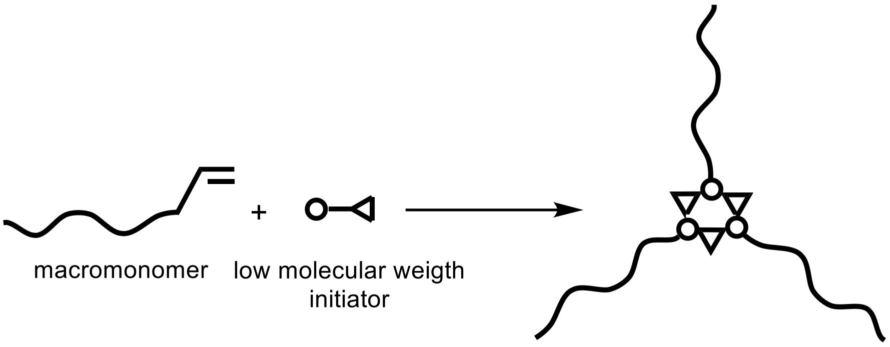


Figure 2.14: Formation of star polymer by macromonomer method.

Arm-first method can also be carried out by crosslinking of nonfunctional living polymers and difunctional monomers (Figure 2.16). But, it is very hard to obtain well-defined polymers at the end. Number of arms can only be predicted by molecular weight measurements.

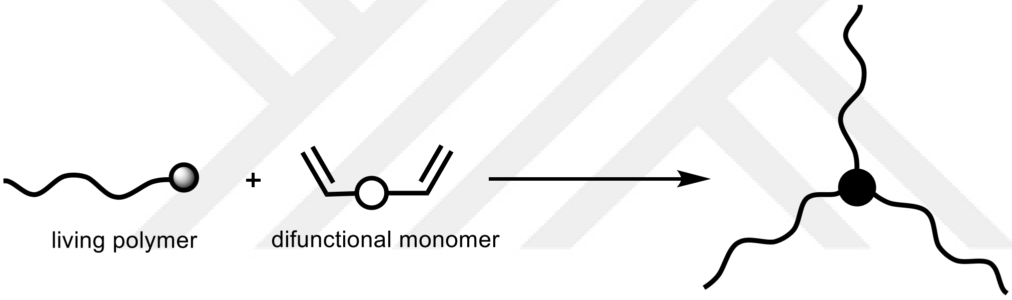


Figure 2.15: Formation of star polymer by using macroinitiator.

2.4.2 Core-first method

Core-first methodology is applied frequently because of being easier. Monomers and multifunctional core reacted directly and arms are grown on the core (Figure 2.17). Multifunctional core used in that polymerization type must have the same rate of initiation and be equally reactive. So, by using this method symmetric star polymers can be obtained easily and number of arms are definite [83].

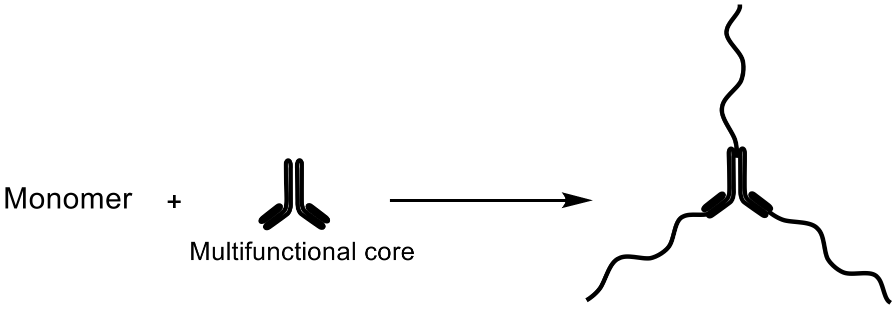


Figure 2.16: Synthesis of star polymers by core-first method.

2.4.3 Grafting onto

In grafting onto method, pre-synthesized reactive arm and multifunctional core are coupled together (Figure 2.18). Both structures can be analyzed independently. So, the control of the final structure is easier than other polymerization types. Generally, low arm numbered star polymers are obtained at the end because of having a small core. Purification steps must be applied in order to purify star polymer from unreacted arms.

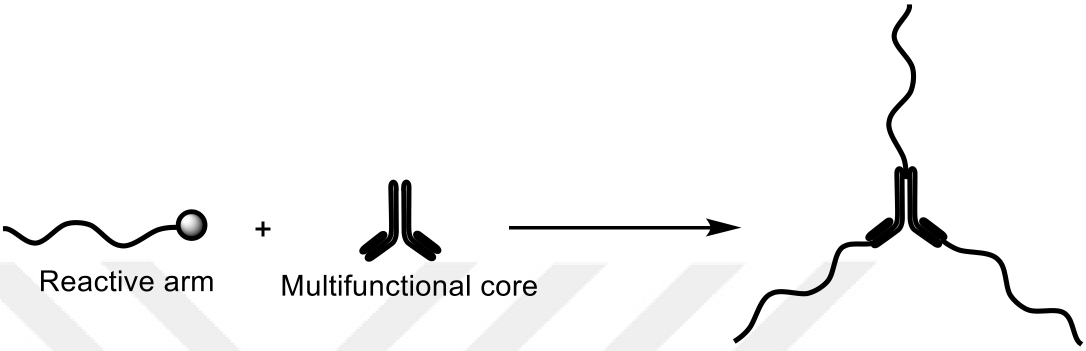


Figure 2.17: Synthesis of star polymers by grafting onto approach.

2.5 Miktoarm Star Polymers

The term mikto (comes from the Greek word miktos means mixed) is used for star polymers having at least two chemically different arms and proposed by Hadjichristidis in 1992 [12]. They are represented as A_nB_m where A and B symbolizes different monomers; n and m clarifies the number of repetition of arms (Figure 2.19). ABC, ABCD or AB_5 like less common structures is also available.

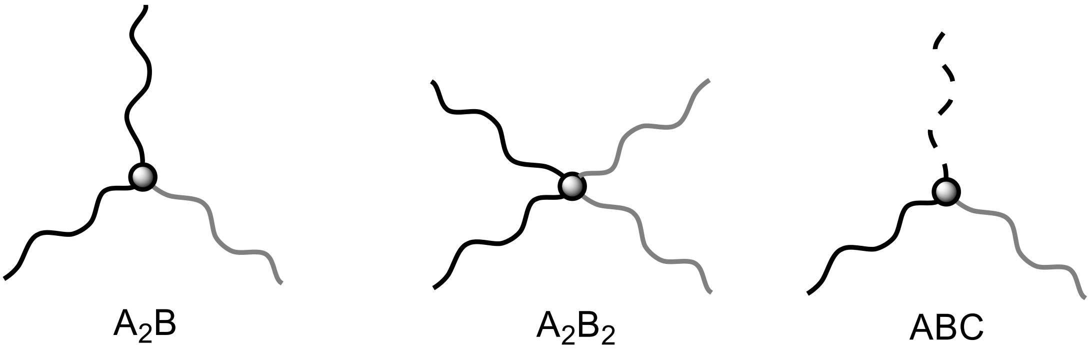


Figure 2.18: Representation of miktoarm star polymers.

2.6 Combination of Different Polymerization Modes

Copolymers have a wide area of usage especially in industry because of having advanced properties. But sometimes, they cannot be synthesized in one manner. Combination of different polymerization modes occupy an important position at this point [84, 85]. In conventional way, block copolymers are synthesized by the polymerization of first segment followed by isolation and purification of that homopolymer. Either initiaton or termination steps, that polymer was converted into another functionality that can initiate the polymerization of the other species. After, by using this polymer as a precursor, block or graft polymers can easily be synthesized. This manner is also called as mechanistic transformation reactions and it is a well-accepted route to formation of copolymers that cannot be synthesized by one mode. If it is needed, these monomers can be polymerized simultaneously [46]. By applying this methodology, intermediate isolation and purification steps are not applied. As seen in Figure 2.20, transformations involving cationic and controlled radical polymerizations, anionic and cationic polymerizations, activated monomer polymerization, metathesis polymerization are some examples studied and reviewed widely.

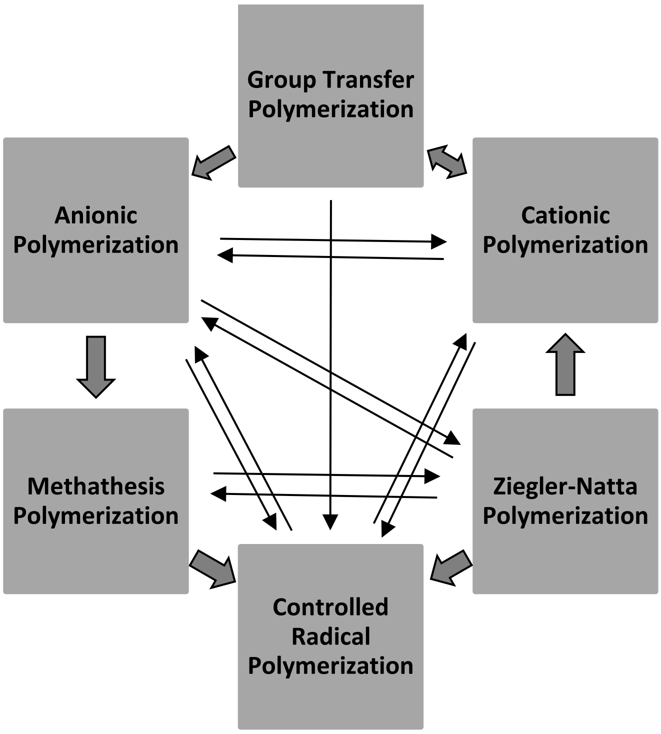


Figure 2.19: Combination of different polymerization modes.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Reagents

Methyl methacrylate (MMA, ≥99%, Sigma-Aldrich): Methyl methacrylate was purified by passing through basic alumina column and stored in nitrogen atmosphere in cold.

ε-Caprolactone (ε-CL, 97%, Aldrich): ε-Caprolactone was vacuum distilled over calcium hydride and stored over activated molecular sieves in nitrogen atmosphere in cold.

Benzophenone (BP, 98%, Sigma-Aldrich): Benzophenone was used as received.

Camphoroquinone (CQ, 97%, Sigma-Aldrich): Camphoroquinone was used as received.

Thioxanthone (TX, 98%, Sigma-Aldrich): Thioxanthone was crystallized from ethanol prior to use.

Phosphazene Base (P_2*-t-Bu, ~2.0 M THF solution, Sigma-Aldrich):* Phosphazene base was used as received.

N,N-dimethylethanolamine (DMEA, Fluka): N,N-dimethylethanolamine was dried with anhydrous KOH and vacuum distilled.

N-methyldiethanolamine (MDEA, 99%, Sigma-Aldrich): N-methyldiethanolamine was used as received.

3.1.2 Solvents

Toluene (≥99.5%, J.T. Barker): Toluene was dried heating over sodium wire and benzophenone as indicator. Dry toluene was collected in molecular sieves before use and stored in nitrogen atmosphere.

Methanol (Technical): Methanol was used for the precipitation of polymers without further purification.

3.2 Equipments

3.2.1 Light source

A Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18 W) emitting light nominally at 400-500 nm where only CQ absorbs the light. The light intensity was measured by Delta Ohm model HD-9021 radiometer and found as 45 mW.cm^{-2}. In case of using TX and BP as photoinitiator, a rayonet type equipped with 16 lamps (Philips 8W/O6) emitting light nominally at 350 nm with an intensity of 3.0 mW.cm^{-2}.

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

^{1}H-NMR spectra were recorded in deuterated chloroform ($CDCl_3$ with $Si(CH_3)_4$ as an internal standart) at 500 MHz on an Agilent VNMRS 500 spectometer at room temperature.

3.2.3 Gel permeation chromatography (GPC)

Apparent and absolute molecular weights were measured from a Viscotek GPCmax Autosampler sys-tem consisting of a pump module (GPCmax, Viscotek Corp., Houston, TX, USA), a combined lightscat-tering (Model 270 Dual Detector, Viscotek Corp.), and a refractive index (RI) detector (VE 3580, Vis-cotek Corp.). The light scattering detector (λ_0 = 670 nm) included two scattering angles: 7° and 90°. The RI detector was calibrated with polystyrene standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers are expressed in terms of polystyrene equivalents. Two columns 7 × 300 mm, 8 × 300 mm (LT5000L, Mixed, Medium Org and LT3000L, Mixed, Ultra-Low Org) with a guard column 4.6 × 10 mm (Viscotek, T Guard) were used for the chloroform eluent at 35°C (flow rate: 1 mL min^{-1}). Data were analyzed using Viscotek OmniSEC Omni-01 software.

3.2.4 Differential scanning calorimetry (DSC)

DSC measurements were performed on Perkin-Elmer Diamond DSC with a heating rate of 10°C min^{-1} under nitrogen flow.

3.2.5 Fourier transform infrored spectroscopy (FT-IR)

FT-IR spectra were recorded on Perkin−Elmer FTIR Spectrum One spectrometer with an ATR accessory (ZnSe, PikeMiracle Accessory) and mercury cadmium telluride (MCT) detector.

3.3 Preparation Methods

3.3.1 Synthesis of PCL by ROP

A dried Schlenk tube was charged with ε-CL (200 eq), P_2-*t*-Bu (5 eq), DMEA or MDEA (1 eq), and dry toluene (1 mL) under nitrogen atmosphere. The solution was simply mixed at room temperature for 2 h. Resulting solution was precipitated in excess methanol. Obtained polymers were filtered and dried under vacuum.

3.3.2 General procedure for sequential polymerization

In a typical reaction, precursor polymer (2.5 eq), MMA (100 eq), photoinitiator (BP, 1 eq), and dry toluene (V_{MMA}=$V_{Toluene}$= 0.5 mL) were put into a dried Schlenk tube. After degassed with nitrogen gase, tube was covered tightly and irradiated at proper wavelength for photoinitiators for 4 hours. Resulted polymers were precipitated in excess methanol, filtered and dried under vacuum.

3.3.3 General procedure for concurrent free radical and ROP

Following chemicals were taken in a dried Schlenk tube under nitrogen atmosphere: [MMA]/[PI]/[DMEA or MDEA]:100/1/0.5, [ε-CL]/[P2-t-Bu]/[DMEA or MDEA]: 200/1/5, $V_{Toluene}$= 0.5 mL. After irradiation with a suitable light source at room temperature for 4 h, resulted polymers were precipitated in excess methanol, filtered and dried under reduced pressure.

4. RESULTS AND DISCUSSION

Star copolymers were successfully synthesized by combining ROP and photoinitiated free radical polymerization using DMEA and/or MDEA possessing hydroxyl and amine initiating functionalities for the respective polymerization processes. The concept is based on a core-first strategy which allows the polymerization of different monomers through different polymerization mechanisms. The hydroxyl groups of the cores were used as initiating sites for ROP of ε-CL, whereas the amine functionalities serve as hydrogen donating sites for the photoinduced radical polymerization of MMA using *Type II* initiators. Thus, two successive polymerizations were combined sequentially to yield triblock copolymers under mild reaction conditions. In the first step, ε-CL was polymerized via P_2-*t*-Bu catalyzed process at room temperature in the presence of DMEA or MDEA. Subsequently, thus formed precursor polymer was used as macro hydrogen donor for the excited states of *Type II* photoinitiators to give the desired block copolymers (Figure 4.1).

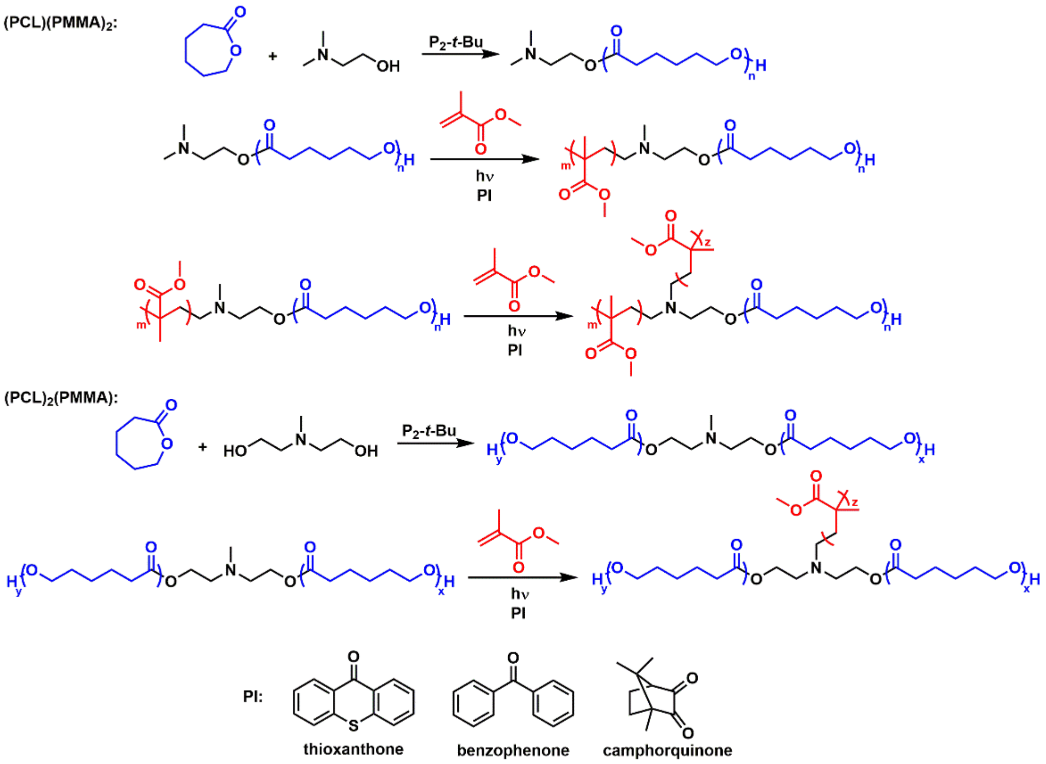


Figure 4.1: Synthesis of $(PCL)(PMMA)_2$ and $(PCL)_2(PMMA)$ star copolymers.

It should be noted that BP and TX absorb light at the near-UV region, whereas CQ is photosensitive to visible light signifying a broad wavelength flexibility.

The structures of the obtained the precursor polymers and final block polymers were investigated by ^{1}H-NMR spectroscopy. As seen in Figure 4.2, all the expected the characteristic signals belonging to PCL and PMMA segments were clearly observed.

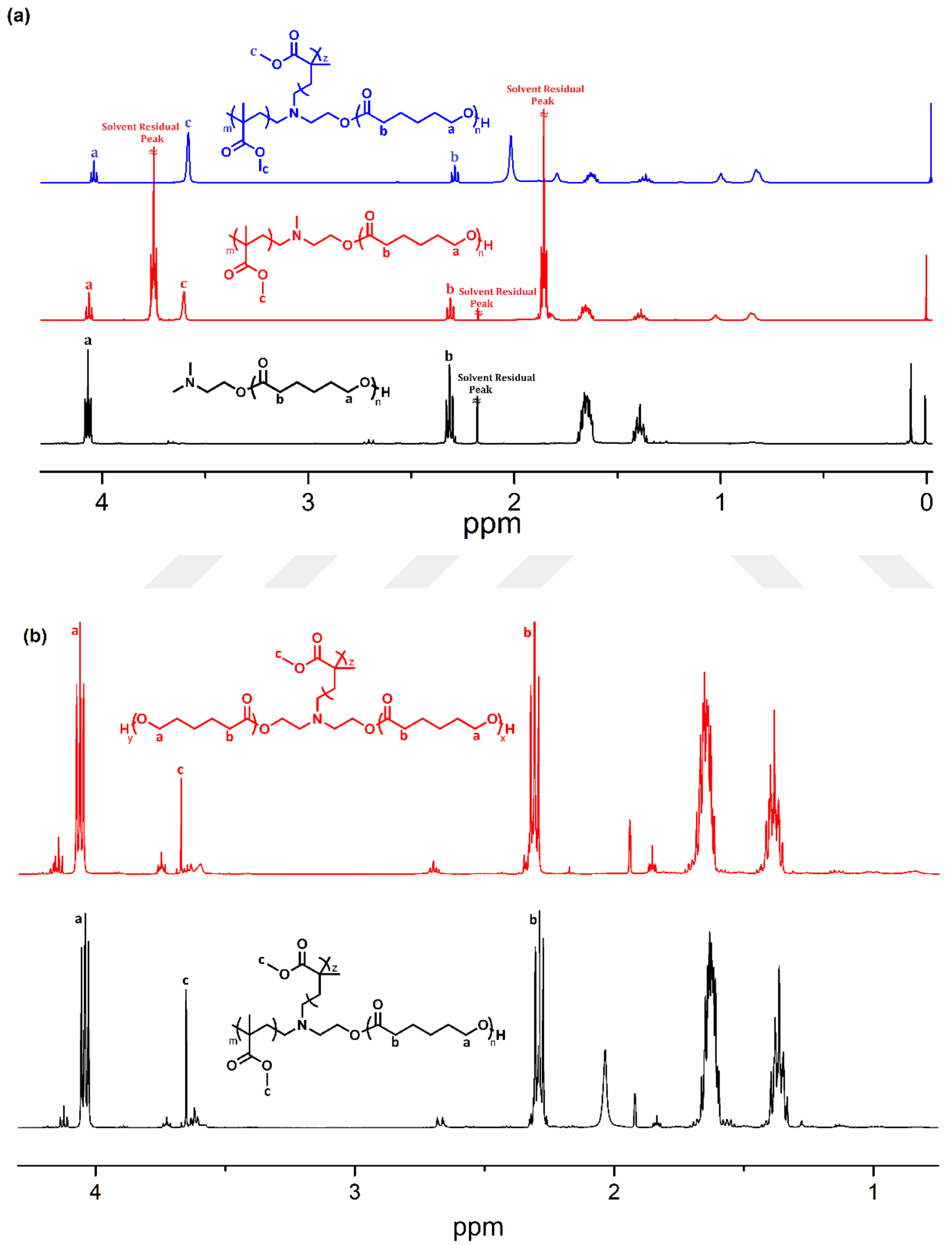


Figure 4.2: ^{1}H-NMR spectra of the polymers by sequential (a) and concurrent polymerization (b).

Table 4.1 shows the type of star polymers and their molecular weight characteristics. Notably, the observed differences in the molecular weights determined by two methods give indication of star structure.

Table 4.1: Molecular weight characteristics of the polymers at various stages.

Run	Polymer	H-donor	PI	$M_{n,GPC\text{-}RI}$[e,g] (g mol^{-1})	$M_{n,GPC\text{-}LS}$[f,g] (g mol^{-1})	M_w/M_n[g]
1	(PCL)[a]	-	-	7100	7400	1.3
2	(PCL)(PMMA)[b]	DMEA	BP[c]	12200	16000	1.9
3	(PCL)(PMMA)$_2$[b]	DMEA	BP[c]	17000	31500	2.6
4	(PCL)(PMMA)[b]	DMEA	CQ[d]	9000	9450	1.6
5	(PCL)(PMMA)$_2$[b]	DMEA	CQ[d]	14200	23500	2.2
6	(PCL)(PMMA)[b]	DMEA	TX[c]	9300	11150	1.4
7	(PCL)(PMMA)$_2$[b]	DMEA	TX[c]	10900	13000	3.1
8	(PCL)$_2$[a]	-	-	3900	nd	1.6
9	(PCL)$_2$(PMMA)[b]	MDEA	BP[c]	10900	15000	2.7
10	(PCL)$_2$(PMMA)[b]	MDEA	CQ[d]	12950	22850	3.1
11	(PCL)$_2$(PMMA)[b]	MDEA	TX[c]	6550	7600	3.5

[a] Polymerization at room temperature for 2 h, [ε-CL]/[P2-t-Bu]/[DMEA or MDEA]: 200/1/5, $V_{Toluene}$= 1 mL.
[b] [MMA]/[PI]/[DMEA or MDEA]: 100/1/2.5, $V_{Toluene}$=VMMA= 0.5 mL.
[c] Irradiated at 350 nm.
[d] Irradiated at 400-500 nm.
[e] With refractive index detector.
[f] With light scattering detector.
[g] Determined by GPC using polystyrene standards.

Typical conversion range is 60-80% and 15-50% for ROP and *Type II* photoinitiation, respectively.

The process was also conducted in one-pot fashion under identical experimental conditions. However, both polymerization modes were affected from the other mode and star copolymers with relatively lower molecular weight were obtained (Table 4.2).

Table 4.2: Concurrent *Type II* photoinitiated polymerization and ROP[a].

H-donor	PI	$M_{n,GPC\text{-}RI}$[d] (g mol^{-1})	M_w/M_n[d]
DMEA	BP[b]	2700	1.5
DMEA	CQ[c]	3200	1.4
DMEA	TX[b]	2700	1.5
MDEA	BP[b]	3000	1.8
MDEA	CQ[c]	2500	1.6
MDEA	TX[b]	2600	1.5

[a][MMA]/[PI]/[DMEA or MDEA]: 100/1/0.5, [ε-CL]/[P2-t-Bu]/[DMEA or MDEA]: 200/1/5, $V_{Toluene}$= 0.5 mL. [b]Irradiated at 350 nm. [c]Irradiated at 400-500 nm. [d]Determined by GPC using polystyrene standards.

The success of the total process was further demonstrated by examining the GPC traces of the polymers at different stages. Clear shifts to lower retention volumes after sequential polymerizations in comparison to the precursor polymers demonstrates the success of the total process. The unimodal regime of the chromatograms endorses that no side reactions such as degradation or transfer reactions were operative during the photochemical step (Figure 4.3).

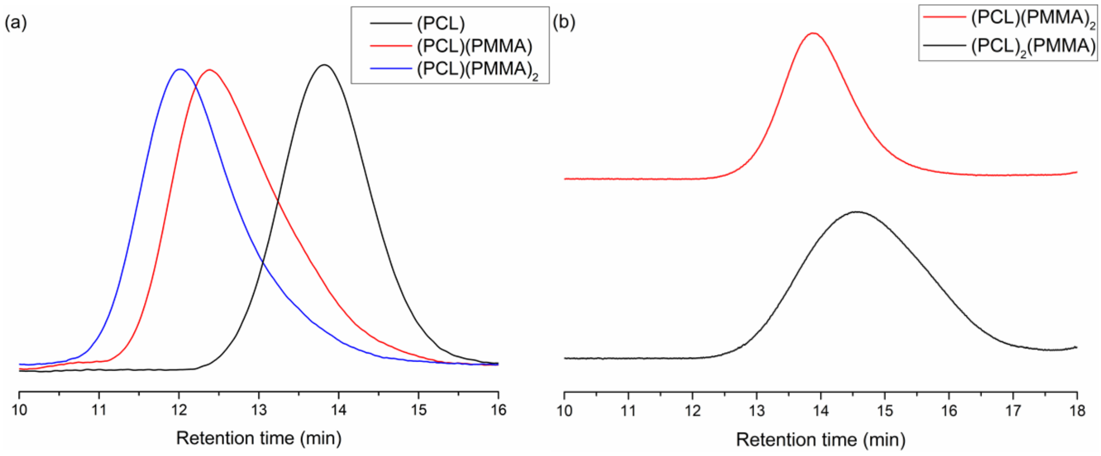


Figure 4.3: (a) GPC traces of PCL and star copolymers obtained by sequential polymerization, (b) (PCL)(PMMA)$_2$ and (PCL)$_2$(PMMA) star copolymers obtained from concurrent polymerization.

As seen from Figure 4.4, main bands of both segments were observed. For example, carbonyl stretching bands around 1727 cm^{-1}, asymmetric and symmetric CH_2 stretching bands around 2946 and 2865 cm^{-1} can be detected in FT-IR spectroscopy.

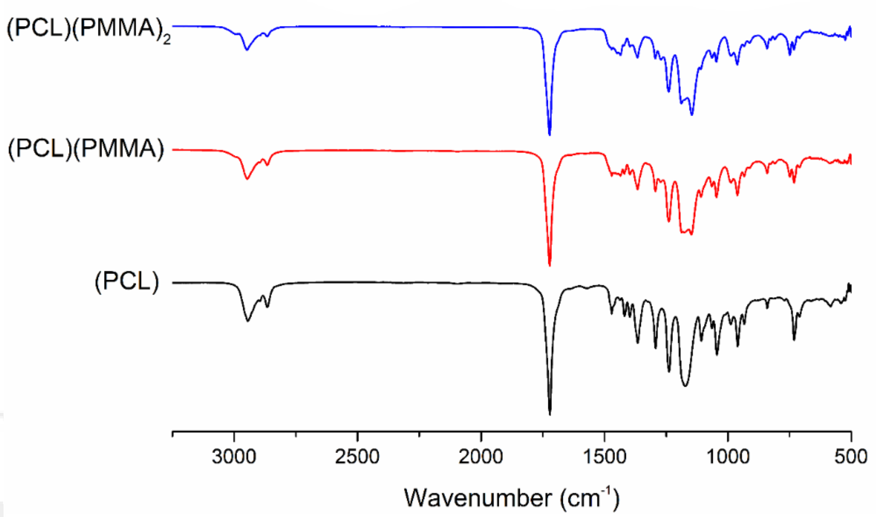


Figure 4.4: FT-IR spectra of PCL and polymers obtained by sequential *Type II* photoinitiation.

Thermal properties of the star copolymers were also studied by DSC analysis (Figure 4.5). Apparently, all polymers show a strong peak at around 55 °C corresponding to the PCL segment's T_m value. Additionally, small transitions around 100 °C was observed, which corresponds to the PMMA segments of the block copolymers.

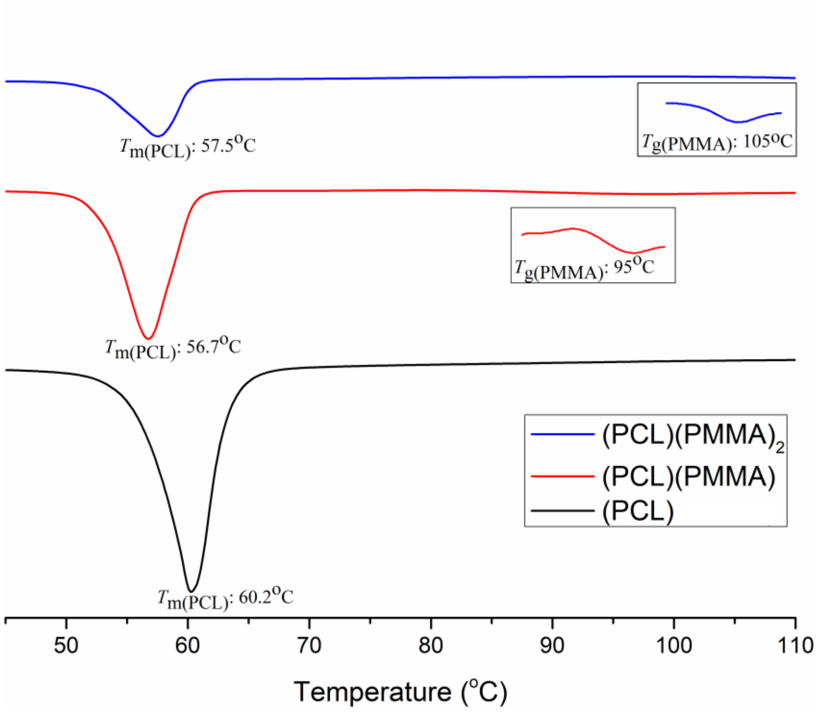


Figure 4.5: DSC thermograms of PCL and star copolymers.

5. CONCLUSIONS

In conclusion, a novel approach for the synthesis of (PCL)(PMMA)$_2$ and (PCL)$_2$(PMMA) star copolymers by combination of sequential ROP and photoinitiated free radical polymerization was described. The number and structure of the arms of the star copolymers can readily be adjusted by selecting the type of the hydrogen donor employed and recurrence of the individual polymerization sequences. It is shown that, instead of complex and expensive method, fabrication of star copolymers can be achieved from commercially available, cheap materials in a simple and environmentally friendly way. Considering the metal free conditions and biocompatibility of the PCL segments, the approach offers a molecular design flexibility for various bio applications. Further studies in this line are now in progress.

REFERENCES

[1] **N. Hadjichristidis, H. Iatrou, M. Pitsikalis, and J. Mays**. (2006). Macromolecular architectures by living and controlled/living polymerizations, *Progress in Polymer Science*, ***31***(12), 1068-1132.

[2] **H. Gao and K. Matyjaszewski**. (2009). Synthesis of functional polymers with controlled architecture by CRP of monomers in the presence of cross-linkers: From stars to gels, *Progress in Polymer Science*, ***34***(4), 317-350.

[3] **T. Higashihara, M. Hayashi, and A. Hirao**. (2011). Synthesis of well-defined star-branched polymers by stepwise iterative methodology using living anionic polymerization, *Progress in Polymer Science*, ***36***(3), 323-375.

[4] **W. Wu, W. Wang, and J. Li**. (2015). Star polymers: Advances in biomedical applications, *Progress in Polymer Science*, ***46***, 55-85.

[5] **J. M. Ren, T. G. McKenzie, Q. Fu, E. H. Wong, et al.** (2016). Star polymers, *Chemical reviews*, ***116***(12), 6743-6836.

[6] **Z. Shi, F. Guo, R. Tan, H. Niu, et al.** (2017). “Arm-first” approach for the synthesis of star-shaped stereoregular polymers through living coordination polymerization, *Polymer Chemistry*, ***8***(9), 1449-1453.

[7] **C. J. Hawker**. (1995). Architectural control in “living” free radical polymerizations: preparation of star and graft polymers, *Angewandte Chemie International Edition in English*, ***34***(13-14), 1456-1459.

[8] **H. Gao and K. Matyjaszewski**. (2008). Synthesis of star polymers by a new “core-first” method: sequential polymerization of cross-linker and monomer, *Macromolecules*, ***41***(4), 1118-1125.

[9] **C. Barner-Kowollik, T. P. Davis, J. Heuts, M. H. Stenzel, et al.** (2003). RAFTing down under: Tales of missing radicals, fancy architectures, and mysterious holes, *Journal of Polymer Science Part A: Polymer Chemistry*, ***41***(3), 365-375.

[10] **C. Barner-Kowollik, T. P. Davis, and M. H. Stenzel**. (2006). Synthesis of star polymers using RAFT polymerization: what is possible?, *Australian journal of chemistry*, ***59***(10), 719-727.

[11] **A. Heise, M. Trollsås, T. Magbitang, J. L. Hedrick, et al.** (2001). Star polymers with alternating arms from miktofunctional μ-initiators using consecutive atom transfer radical polymerization and ring-opening polymerization, *Macromolecules*, ***34***(9), 2798-2804.

[12] **H. Iatrou and N. Hadjichristidis**. (1992). Synthesis of a model 3-miktoarm star terpolymer, *Macromolecules*, ***25***(18), 4649-4651.

[13] **H. R. Kricheldorf, I. Kreiser-Saunders, and A. Stricker**. (2000). Polylactones 48. SnOct2-initiated polymerizations of lactide: a mechanistic study, *Macromolecules*, ***33***(3), 702-709.

[14] **W. A. Braunecker and K. Matyjaszewski**. (2007). Controlled/living radical polymerization: Features, developments, and perspectives, *Progress in Polymer Science*, ***32***(1), 93-146.

[15] **C. J. Hawker, A. W. Bosman, and E. Harth**. (2001). New polymer synthesis by nitroxide mediated living radical polymerizations, *Chemical reviews*, ***101***(12), 3661-3688.

[16] **J. Ueda, M. Matsuyama, M. Kamigaito, and M. Sawamoto**. (1998). Multifunctional initiators for the ruthenium-mediated living radical polymerization of methyl methacrylate: di-and trifunctional dichloroacetates for synthesis of multiarmed polymers, *Macromolecules*, ***31***(3), 557-562.

[17] **K. Matyjaszewski, P. J. Miller, J. Pyun, G. Kickelbick, et al.** (1999). Synthesis and characterization of star polymers with varying arm number, length, and composition from organic and hybrid inorganic/organic multifunctional initiators, *Macromolecules*, ***32***(20), 6526-6535.

[18] **T. Ando, M. Kamigaito, and M. Sawamoto**. (1998). Silyl enol ethers: end-capping agents for living radical polymerization of methyl methacrylate with ruthenium complex, *Macromolecules*, ***31***(19), 6708-6711.

[19] **A. P. Narrainen, S. Pascual, and D. M. Haddleton**. (2002). Amphiphilic diblock, triblock, and star block copolymers by living radical polymerization: Synthesis and aggregation behavior, *Journal of Polymer Science Part A: Polymer Chemistry*, ***40***(4), 439-450.

[20] **R. T. Mayadunne, J. Jeffery, G. Moad, and E. Rizzardo**. (2003). Living free radical polymerization with reversible addition− fragmentation chain transfer (RAFT Polymerization): Approaches to star polymers, *Macromolecules*, ***36***(5), 1505-1513.

[21] **M. Stenzel-Rosenbaum, T. P. Davis, V. Chen, and A. G. Fane**. (2001). Star-polymer synthesis via radical reversible addition–fragmentation chain-transfer polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, ***39***(16), 2777-2783.

[22] **T. Kakuchi, A. Narumi, T. Matsuda, Y. Miura, et al.** (2003). Glycoconjugated polymer. 5. Synthesis and characterization of a seven-arm star polystyrene with a β-cyclodextrin core based on TEMPO-mediated living radical polymerization, *Macromolecules*, ***36***(11), 3914-3920.

[23] **I. Li, B. Howell, R. Koster, and D. Priddy**. (1996). Mono-and dinitroxide styrene polymerization initiators, *Macromolecules*, ***29***(26), 8554-8555.

[24] **R. D. Puts and D. Y. Sogah**. (1996). Control of living free-radical polymerization by a new chiral nitroxide and implications for the polymerization mechanism, *Macromolecules*, ***29***(9), 3323-3325.

[25] **T. Emrick, W. Hayes, and J. M. Fréchet**. (1999). A TEMPO-mediated "living" free-radical approach to ABA triblock dendritic linear hybrid copolymers, *Journal of Polymer Science Part A: Polymer Chemistry*, ***37***(20), 3748-3755.

[26] **W. Zhang, W. Zhang, J. Zhu, Z. Zhang, et al.** (2009). Controlled synthesis of pH-responsive amphiphilic A2B2 miktoarm star block copolymer by combination of SET-LRP and RAFT polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, ***47***(24), 6908-6918.

[27] **Y. Yamazaki, N. Ajioka, A. Yokoyama, and T. Yokozawa**. (2009). Synthesis of well-defined miktoarm star copolymers of aromatic polyether and polystyrene by chain-growth condensation polymerization and atom transfer radical polymerization, *Macromolecules*, ***42***(3), 606-611.

[28] **K. Khanna, S. Varshney, and A. Kakkar**. (2010). Miktoarm star polymers: advances in synthesis, self-assembly, and applications, *Polymer Chemistry*, ***1***(8), 1171-1185.

[29] **H. Gruber**. (1992). Photoinitiators for free radical polymerization, *Progress in polymer Science*, ***17***(6), 953-1044.

[30] **H. Hageman**. (1985). Photoinitiators for free radical polymerization, *Progress in organic coatings*, ***13***(2), 123-150.

[31] **C. Dursun, M. Degirmenci, Y. Yagci, S. Jockusch, et al.** (2003). Free radical promoted cationic polymerization by using bisacylphosphine oxide photoinitiators: substituent effect on the reactivity of phosphinoyl radicals, *Polymer*, ***44***(24), 7389-7396.

[32] **L. Cokbaglan, N. Arsu, Y. Yagci, S. Jockusch, et al.** (2003). 2-Mercaptothioxanthone as a novel photoinitiator for free radical polymerization, *Macromolecules*, ***36***(8), 2649-2653.

[33] **B. Ganster, U. K. Fischer, N. Moszner, and R. Liska**. (2008). New photocleavable structures, 4, *Macromolecular Rapid Communications*, ***29***(1), 57-62.

[34] **B. Ganster, U. K. Fischer, N. Moszner, and R. Liska**. (2008). New photocleavable structures. Diacylgermane-based photoinitiators for visible light curing, *Macromolecules*, ***41***(7), 2394-2400.

[35] **G. Yilmaz, A. Tuzun, and Y. Yagci**. (2010). Thioxanthone–carbazole as a visible light photoinitiator for free radical polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, ***48***(22), 5120-5125.

[36] **D. K. Balta, N. Arsu, Y. Yagci, A. K. Sundaresan, et al.** (2011). Mechanism of photoinitiated free radical polymerization by thioxanthone− anthracene in the presence of air, *Macromolecules*, ***44***(8), 2531-2535.

[37] **E. Murtezi, M. Ciftci, and Y. Yagci**. (2015). Synthesis of clickable hydrogels and linear polymers by type II photoinitiation, *Polymer International*, ***64***(5), 588-594.

[38] **L. F. J. Schneider, C. S. Pfeifer, S. Consani, S. A. Prahl, et al.** (2008). Influence of photoinitiator type on the rate of polymerization, degree of conversion, hardness and yellowing of dental resin composites, *Dental Materials*, ***24***(9), 1169-1177.

[39] **N. Moszner, U. Salz, and J. Zimmermann**. (2005). Chemical aspects of self-etching enamel–dentin adhesives: a systematic review, *Dental Materials*, ***21***(10), 895-910.

[40] **N. Moszner and U. Salz**. (2007). Recent developments of new components for dental adhesives and composites, *Macromolecular Materials and Engineering*, ***292***(3), 245-271.

[41] **N. Moszner and U. Salz**. (2001). New developments of polymeric dental composites, *Progress in polymer science*, ***26***(4), 535-576.

[42] **Y. Yagci, S. Jockusch, and N. J. Turro**. (2010). Photoinitiated polymerization: advances, challenges, and opportunities, *Macromolecules*, ***43***(15), 6245-6260.

[43] **F. S. Aykac and Y. Yagci**. (2018). Simple Photochemical Route to Block Copolymers via Two-Step Sequential Type II Photoinitiation, *Macromolecular Chemistry and Physics*, 1700589.

[44] **J. Zhao, D. Pahovnik, Y. Gnanou, and N. Hadjichristidis**. (2014). A "catalyst switch" strategy for the sequential metal-free polymerization of

epoxides and cyclic esters/carbonate, *Macromolecules*, ***47***(12), 3814-3822.

[45] **J. Zhao, D. Pahovnik, Y. Gnanou, and N. Hadjichristidis**. (2014). Sequential polymerization of ethylene oxide, ε-caprolactone and l-lactide: a one-pot metal-free route to tri-and pentablock terpolymers, *Polymer Chemistry*, ***5***(12), 3750-3753.

[46] **C. Aydogan, C. Kutahya, A. Allushi, G. Yilmaz, et al.** (2017). Block copolymer synthesis in one shot: concurrent metal-free ATRP and ROP processes under sunlight, *Polymer Chemistry*, ***8***(19), 2899-2903.

[47] **Y. Yağci and W. Schnabel**. (1990). Light-induced synthesis of block and graft copolymers, *Progress in Polymer Science*, ***15***(4), 551-601.

[48] **C. Aydogan, G. Yilmaz, and Y. Yagci**. (2017). Synthesis of Hyperbranched Polymers by Photoinduced Metal-Free ATRP, *Macromolecules*, ***50***(23), 9115-9120.

[49] **C. Aydogan, M. Ciftci, V. Kumbaraci, N. Talinli, et al.** (2017). Hyperbranced Polymers by Photoinduced Self-Condensing Vinyl Polymerization Using Bisbenzodioxinone, *Macromolecular Chemistry and Physics*, ***218***(10).

[50] **C. Aydogan, M. Ciftci, and Y. Yagci**. (2016). Hyperbranched Polymers by Type II Photoinitiated Self-Condensing Vinyl Polymerization, *Macromolecular rapid communications*, ***37***(7), 650-654.

[51] **S. Bektas, M. Ciftci, and Y. Yagci**. (2013). Hyperbranched polymers by visible light induced self-condensing vinyl polymerization and their modifications, *Macromolecules*, ***46***(17), 6751-6757.

[52] **T. Isık, M. M. Demir, C. Aydogan, M. Ciftci, et al.** (2017). Hydrophobic coatings from photochemically prepared hydrophilic polymethacrylates via electrospraying, *Journal of Polymer Science Part A: Polymer Chemistry*, ***55***(8), 1338-1344.

[53] **C. Geyik, M. Ciftci, B. Demir, B. Guler, et al.** (2015). Controlled release of anticancer drug Paclitaxel using nano-structured amphiphilic star-hyperbranched block copolymers, *Polymer Chemistry*, ***6***(30), 5470-5477.

[54] **M. Aydin, M. Atilla Tasdelen, T. Uyar, and Y. Yagci**. (2013). In situ synthesis of A3-type star polymer/clay nanocomposites by atom transfer radical polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, ***51***(24), 5257-5262.

[55] **S. Ozlem, B. Iskin, G. Yilmaz, M. Kukut, et al.** (2012). Synthesis and pyrolysis of ABC type miktoarm star copolymers with polystyrene, poly (lactic acid) and poly (ethylene glycol) arms, *European Polymer Journal*, ***48***(10), 1755-1767.

[56] **B. Iskin, G. Yilmaz, and Y. Yagci**. (2011). Synthesis of ABC type miktoarm star copolymers by triple click chemistry, *Polymer Chemistry*, ***2***(12), 2865-2871.

[57] **B. Iskin, G. Yilmaz, and Y. Yagci**. (2011). ABC type miktoarm star copolymers through combination of controlled polymerization techniques with thiol-ene and azide-alkyne click reactions, *Journal of Polymer Science Part A: Polymer Chemistry*, ***49***(11), 2417-2422.

[58] **S. S. Okcu, Y. Y. Durmaz, and Y. Yagci**. (2010). Synthesis and characterization of telechelic block co-polymers by combination of atom transfer radical

polymerization and click chemistry processes, *Designed Monomers and Polymers*, ***13***(5), 459-472.

[59] **B. Iskin, G. Yilmaz, and Y. Yagci**. (2013). Telechelic Polymers by Visible-Light-Induced Radical Coupling, *Macromolecular Chemistry and Physics*, ***214***(1), 94-98.

[60] **S. P. Pappas**. (1978). *UV curing: science and technology*. ed., ed. Vol. 2. Technology Marketing Corporation, Pub. Division.

[61] **Y. Yağci, I. Lukáč, and W. Schnabel**. (1993). Photosensitized cationic polymerization using N-ethoxy-2-methylpyridinium hexafluorophosphate, *Polymer*, ***34***(6), 1130-1133.

[62] **D. Dossow, Q. Q. Zhu, G. Hizal, Y. Yag, et al.** (1996). Photosensitized cationic polymerization of cyclohexene oxide: a mechanistic study concerning the use of pyridinium-type salts, *Polymer*, ***37***(13), 2821-2826.

[63] **G. Hizal, Y. Yaḡci, and W. Schnabel**. (1994). Charge-transfer complexes of pyridinium ions and methyl-and methoxy-substituted benzenes as photoinitiators for the cationic polymerization of cyclohexene oxide and related compounds, *Polymer*, ***35***(11), 2428-2431.

[64] Y. Yagci. *Photoinitiated cationic polymerization of unconventional monomers*. in *Macromolecular symposia*. 2006. Wiley Online Library.

[65] Y. Yagci. *Wavelength flexibility in photoinitiated cationic polymerization*. in *Macromolecular Symposia*. 2004. Wiley Online Library.

[66] **Y. Yaḡci, J. Borbely, and W. Schnabel**. (1989). On the mechanism of acylphosphine oxide promoted cationic polymerization, *European polymer journal*, ***25***(2), 129-131.

[67] **M. A. TAŞDELEN**. (2008). İSTANBUL TECHNICAL UNIVERSITY★ INSTITUTE OF SCIENCE AND TECHNOLOGY.

[68] **B. M. Monroe and G. C. Weed**. (1993). Photoinitiators for free-radical-initiated photoimaging systems, *Chemical Reviews*, ***93***(1), 435-448.

[69] **R. S. Davidson**. (1993). The chemistry of photoinitiators—some recent developments, *Journal of Photochemistry and Photobiology A: Chemistry*, ***73***(2), 81-96.

[70] **N. Allen, F. Catalina, P. Green, and W. Green**. (1986). Photochemistry of carbonyl photoinitiators. Photopolymerisation, flash photolysis and spectroscopic study, *European polymer journal*, ***22***(1), 49-56.

[71] **F. Catalina, J. Tercero, C. Peinado, R. Sastre, et al.** (1989). Photochemistry and photopolymerization study on 2-acetoxy and methyl-2-acetoxy derivatives of thioxanthone as photoinitiators, *Journal of Photochemistry and Photobiology A: Chemistry*, ***50***(2), 249-258.

[72] **D. P. Specht, P. A. Martic, and S. Farid**. (1982). Ketocoumarins: A new class of triplet sensitizers, *Tetrahedron*, ***38***(9), 1203-1211.

[73] **O. Nuyken and S. D. Pask**. (2013). Ring-opening polymerization—an introductory review, *Polymers*, ***5***(2), 361-403.

[74] **A.-C. Albertsson and I. K. Varma**. (2003). Recent developments in ring opening polymerization of lactones for biomedical applications, *Biomacromolecules*, ***4***(6), 1466-1486.

[75] S. J. McLain and N. E. Drysdale, *Yttrium and rare earth compounds catalyzed lactone polymerization*, in, Editor^Editors. 1991, Google Patents. p.

[76] **J. Zhao, N. Hadjichristidis, and H. Schlaad**, (2015). Polymerization Using Phosphazene Bases, in *Anionic Polymerization*, Editor^Editors., *Springer*. p. 429-449.

[77] **J. Zhao, N. Hadjichristidis, and Y. Gnanou**. (2014). Phosphazene-promoted anionic polymerization, *Polimery*, ***59***(1), 49--59.

[78] **L. Zhang, F. Nederberg, J. M. Messman, R. C. Pratt, et al.** (2007). Organocatalytic stereoselective ring-opening polymerization of lactide with dimeric phosphazene bases, *Journal of the American Chemical Society*, ***129***(42), 12610-12611.

[79] E. Bedri, *Synthesis of miktoarm star polymers VIA combination of controlled polymerization systems*, in, Editor^Editors. 2007. p.

[80] **N. Hadjichristidis, M. Pitsikalis, S. Pispas, and H. Iatrou**. (2001). Polymers with complex architecture by living anionic polymerization, *Chemical reviews*, ***101***(12), 3747-3792.

[81] **N. Hadjichristidis, S. Pispas, M. Pitsikalis, H. Iatrou, et al.**, (1999). Asymmetric star polymers: synthesis and properties, in *Branched polymers I*, Editor^Editors., *Springer*. p. 71-127.

[82] **N. Hadjichristidis**. (1999). Synthesis of miktoarm star (μ-star) polymers, *Journal of Polymer Science Part A: Polymer Chemistry*, ***37***(7), 857-871.

[83] **E. Gungor, C. Bilir, H. Durmaz, G. Hizal, et al.** (2009). Star polymers with POSS via azide–alkyne click reaction, *Journal of Polymer Science Part A: Polymer Chemistry*, ***47***(22), 5947-5953.

[84] **A. Puglisi, E. Murtezi, G. Yilmaz, and Y. Yagci**. (2017). Synthesis of block copolymers by mechanistic transformation from photoinitiated cationic polymerization to a RAFT process, *Polymer Chemistry*, ***8***(47), 7307-7310.

[85] **Y. Yagci and M. A. Tasdelen**. (2006). Mechanistic transformations involving living and controlled/living polymerization methods, *Progress in Polymer Science*, ***31***(12), 1133-1170.

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- **Aykac F. S., Aydogan C., and Yagci Y.** (2018) Simple and Green Strategy for the Synthesis of Miktoarm Star Copolymers by Combination of ROP and Photoinitiated Free Radical Polymerization (to be submitted).

OTHER PUBLICATIONS, PRESENTATIONS AND PATENTS:

- **Aykac F. S., and Yagci Y.** (2018) Simple Photochemical Route to Block Copolymers via Two-Step Sequential Type II Photoinitiation, *Macromolecular Chemistry and Physics*, ***219***(7), 1700589.
- **Yilmaz G., Kutahya C., Allushi A., Aydogan C., Aykac S., and Yagci Y. (**2017) Photoinduced Metal Free Strategies for Atom Transfer Radical Polymerization. 254th ACS National Meeting, August 20-24, 2017 Washington DC, USA.
- **Kutahya C., Aykac F. S., Yilmaz G., and Yagci Y.** (2016) LED and Visible Light Induced Metal Free ATRP Using Reducible Dyes in the Presence of Amines, *Polymer Chemistry*, ***7***(39), 6094-6098.
- **Kutahya C., Aykac F. S., Yilmaz G., and Yagci Y. (**2016) LED and Visible Light Induced Metal Free ATRP Using Electron Acceptor Dyes in Conjunction With Amines. IUPAC World Polymer Congress (MACRO 2016), July 17-21, 2016 Istanbul, Turkey.