ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

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Ph.D. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

VİNİL ETERLERİN KATYONİK POLİMERİZASYONU İÇİN YENİ BAŞLATICI SİSTEMLER

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To my family and my fiance,

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ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
RAFT	: Addition-Fragmentation Chain Transfer Polymerization
NMRP	: Nitroxide Mediated Radical Polymerization
SFRP	: Stable Free Radical Mediated Polymerization
ITP	: Iodine Transfer Polymerization
CMRP	: Cobalt Mediated Radical Polymerization
ROMP	: Ring Opening Metathesis Polymerization
ROP	: Ring Opening Polymerization
CTC	: Charge transfer complexes
MWD	: Molecular weight distribution
PDI	: Polydispersity index
PS	: Photosensitizer
PI	: Photoinitiator
TEMPO	: 2,2,6,6-tetramethylpiperidinyloxy
CTA	: Chain Transfer Agent
IB	: Isobutylene
AN	: Anthrecene
PER	: Perylene
DMPA	: 2, 2-dimethoxy-2-phenyl acetophenone
BP	: Benzophenone
TX	: Thioxanthone
VH	: Substituted vinyl halide
FT-IR	: Fourier Transform-Infrared Spectrophotometer
UV	: Ultra violet
UV-Vis	: Ultra violet and visible
GPC	: Gel permeation chromatography
TGA	: Thermal gravimetric analysis
$\mathbf{CH_2Cl_2}$	: Dichloromethane
$\mathbf{CDCl_3}$	: Deuterated chloroform
DMSO-d6	: Deuterated dimethyl sulfoxide
THF	: Tetrahydrofuran
$\mathbf{t_{gel}}$	: Gelation time
LI	: Light intensity
IBVE	: Isobutyl vinyl ether
DEGDVE	: Di(ethylene glycol) divinyl ether
TEGDVE	: Tri(ethylene glycol) divinyl ether
BDVE	: 1,4-Butanediol divinyl ether
HDVE	: 1,6-Hexanediol divinyl ether
NVC	: *N*-vinyl carbazole
VE-PEO-MA	: α-Vinyloxy-ω-methacryloyl-PEO
CHO	: Cyclohexene oxide
MMA	: Methyl methacrylate

***p*MOS**	: *p*-Methoxystyrene
EO	: Ethylene oxide
Ph_2I^+	: Diphenyliodonium
AAAVB	: 1-Bromo-1,2,2-tris(p-methoxyphenyl)ethene
PPAVB	: 1-Bromo-1-(p-methoxyphenyl)-2,2-phenylethene
PPPVB	: 1-Bromo-1,2,2-triphenylethene
PMDETA	: *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine
DSC	: Differential scanning Calorimetry
Photo-DSC	: Photo-differential scanning calorimetry
On^+	: Onium salt
Ar	: Aryl group
$Mn_2(CO)_{10}$	: Dimanganese decacarbonyl
BE	: *n*-Butyl vinyl ether
NVC	: *N*-Vinylcarbazole
BA	: Butyl acrylate
St	: Styrene
PSt	: Polystyrene
PIBVE	: Poly(isobutyl vinyl ether)
PIB	: Poly(isobutylene)
PEO	: Poly(ethylene oxide)
PVEC	: Poly(β-(vinyl oxy)ethyl cinnamate)
PMMA	: Poly(methyl methacrylate)
PCHO	: Poly(cyclohexene oxide)
PEO-*g*-PIBVE	: Poly(ethylene oxide)-*g*-poly(isobutyl vinyl ether)

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NEW PHOTOINITIATING SYSTEMS FOR CATIONIC POLYMERIZATION OF VINYL ETHERS

SUMMARY

Photo-initiated polymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated from photo-sensitive compounds, namely photoinitiators and/or photosensitizers, by ultra violet-visible (UV-Vis) light irradiation. In recent decades, it has become powerful industrial process widely used in various applications including coatings, inks, adhesives, varnishes, electronics, photolithography, and dyes due to its excellent advantages. It offers high rate of polymerization at ambient temperatures, lower energy cost, and solvent-free formulation, thus elimination of air and water pollution. It also devotes temporal and spatial control of the polymeriztion when high initiation rate is reached.

Much effort has been devoted to free radical systems mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers. Although the most popular industrial applications are based on the photo-initiated free radical polymerization there are some drawbacks associated with this type of polymerization, such as the inhibition effect of oxygen and post-cure limitations, which may affect the properties of the final product. Several advantages of the photo-initiated cationic polymerization over the photo-initiated free radical polymerization have also been reported. Cationic photopolymerization overcomes volatile emissions, limitations due to molecular oxygen inhibition, toxicity, and problems associated to high viscosity. Furthermore, once initiated, cationically polymerizable monomers such as vinyl ethers and epoxides undergo dark-polymerization in which they slowly polymerize without radiation.

Since discovery of the first living polymerization technique by Szwarc in 1950s, well-defined polymers with attractive properties have been readily prepared. In recent decades, development of other new methods such as ATRP, RAFT, NMRP, ROP and ROMP has opened new horizons in this line of the polymer science. Because of the enormous desire of tailor-made materials for specific purposes in many fields including bioengineering, medicine, biochemistry, material science, etc., syntheses of such engineered macromolecular structures have become the main subject of the polymer science. However, these common polymerization techniques have still some drawbacks that need attention of polymer community. As an alternative method, various approaches of living cationic polymerization have been reported for the synthesis of polymers of industrially important monomers to overcome the disadvantages related to free radical polymerization. In fact, among the ionic polymerization methods, living cationic polymerization has become one of the most attractive technique in recent years.

In the current thesis, we described new photoinitiating systems for living cationic polymerization of vinyl ethers relying on Lewis acid-catalyzed method. Additionally,

efficiencies of the recently developed systems were evaluated in UV curing and crosslinking applications of difunctional vinyl ether monomers.

The common drawbacks associated with cationic photopolymerizations are solubility problems of salt type components such as Lewis acids and photoinitiators, poor spectral properties of usual photoinitiators, and stability issue of Lewis acids. Therefore, the work mainly focused on introducing new photoinitiating and polymerization systems by replacing the components with proper ones or using different combinations of the present components for a specific purpose and overcome the shortcomings. In this respect, there are six outcomes of the thesis:

i. Diphenyliodonium halides as cationic photoinitiator were successfully employed in crosslinking of divinyl ethers in the presence of zinc halides.

ii. Photo-induced cationic polymerization of vinyl ethers was achieved in aqueous media.

iii. A novel non-salt type photoinitiator with high solubility and enhanced spectral properties (vinyl halides) was applied to living cationic polymerization of vinyl ethers.

iv. *In situ* generation of metal halide based Lewis acid (i.e. $ZnBr_2$) was accomplished and this Lewis acid was used in a subsequent living cationic photopolymerization and photo-crosslinking.

v. Poly(ethylene oxide)-*graft*-poly(isobutyl vinyl ether) (PEO-*g*-PIBVE) with methacryloyl pendant group was successfully prepared and utilized in free radical photo-crosslinking reactions.

vi. Block copolymers were synthesized by a mechanistic transformation involving combination of ATRP and visible-light induced free radical promoted cationic polymerization.

We firstly described the use of diphenyliodonium salts with highly nucleophilic counter anion photoinitiated cationic cross-linking of divinyl ethers. Both direct and indirect initiating modes were used. In the direct acting system, only a diphenyliodonium salt with highly nucleophilic counter anion and a zinc halide were employed as initiator and activator, respectively. In the indirect systems, in addition to direct system components, photosensitive additives such as anthrecene, perylene, 2, 2-dimethoxy-2-phenyl acetophenone, benzophenone and thioxanthone which absorb energy of the incident light and activate the iodonium salt, were used to initiate polymerization. All systems employed in this study initiated quite vigorous polymerizations.

In the second study, photoinitiated cationic polymerization of vinyl ethers in aqueous medium by using diphenyliodonium iodide (DPII) in the presence of a water-tolerant Lewis acid, ytterbium triflate ($Yb(OTf)_3$), was described. The polymerizations were performed in heterogeneous systems consisting of an aqueous phase containing $Yb(OTf)_3$ and photoinitiator and an organic phase of acetonitrile containing monomer. The polymerization consists of two-steps; (i) photoinduced adduct formation and (ii) subsequent propagation with the aid of $Yb(OTf)_3$. The fast polymerization exhibited an explosive character so that the monomer conversion and molecular weights of the resulting polymers are very dependent on the experimental conditions, such as temperature, stirring manner and rate.

The photoinitiated cationic polymerization of typical vinyl ether monomers, such as isobutyl vinyl ether, di(ethylene glycol) divinyl ether, tri(ethylene glycol) divinyl ether, 1,4-butanediol divinyl ether, and 1,6-hexanediol divinyl ether by use of substituted vinyl halides was studied in the next work. The cationic polymerization of these monomers was initiated at 0 ^{o}C (or room temperature) upon irradiation at λ =

350 nm in CH_2Cl_2 solutions with one of the following compounds: 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene, 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene, and 1-bromo-1,2,2-triphenylethene in the presence of zinc iodide (ZnI_2). A mechanism involving formation of monomer adduct from the photoinduced homolysis of vinyl halide followed by electron transfer is proposed. In the subsequent step, the terminal carbon - halide bond in this adduct is activated by the coordinating effect of ZnI_2. Polymerization exhibited some characteristics of controlled cationic polymerization.

In the fourth study, a photoinitiation approach for Lewis acid-catalyzed cationic polymerization of vinyl ethers, based on *in situ* formation of zinc halide, has been developed. The proposed mechanism of photoinitiation involves photoinduced generation of vinyl cations from subtituted vinyl halide, 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene, by electron transfer and subsequent reaction with the monomer to form an adduct. In the process, zinc bromide, which plays central role in propagation step, was generated simultaneously by the reaction of metallic zinc with the photochemically produced bromine radicals. The living nature of the polymerization was studied by the investigation of time dependence of logarithmic conversion and molecular weights. The capability of the photoinitating system to induce crosslinking was also demonstrated using various difunctional monomers.

The last two studies are application of the photoinitiating systems developed in the frame of this thesis to produce tailor-made macromolecular architectures.

In the first application, poly(isobutyl vinyl ether)-graft-poly(ethylene oxide) graft copolymer with pendant methacrylate groups (PIBVE-*g*-PEO) was obtained by photoinitiated living cationic copolymerization of isobutyl vinyl ether with α-vinyloxy-ω-methacryloyl-poly(ethylene oxide) (VE-PEO-MA) macromonomer. For this purpose, anionically prepared VE-PEO-MA hybrid macromonomer and isobutyl vinyl ether were irradiated in the presence of diphenyl iodonium iodide and zinc iodide as photoacid generator and activator, respectively. Successful graft copolymerization and conservation of pendant double bonds were confirmed by GPC, and ^1H-NMR and FT-IR spectral analysis. The free radical photocross-linking behavior of the graft copolymer was demonstrated.

In the final application, a new synthetic approach for the preparation block copolymers by mechanistic transformation from Atom Transfer Radical Polymerization (ATRP) to visible light induced free radical promoted cationic polymerization is described. A series of halide end functional polystyrenes with different molecular weights synthesized by ATRP was utilized as macro-coinitiator in dimanganese decacarbonyl [$Mn_2(CO)_{10}$] mediated free radical promoted cationic photopolymerization of cyclohexene oxide or isobutyl vinyl ether. Precursor polymers and corresponding block copolymers were characterized by spectral, chromatographic and thermal analyses.

VİNİL ETERLERİN KATYONİK POLİMERİZASYONU İÇİN YENİ BAŞLATICI SİSTEMLER

ÖZET

Işıkla başlatılan polimerizasyon, mor ötesi-görünür bölgedeki ışık altında fotobaşlatıcı ve/veya fotouyarıcı gibi ışığa duyarlı bileşiklerden üretilen reaktif türler vasıtasıyla başlatılan zincir reaksiyonu sonucu monomerin polimere dönüştürüldüğü bir süreç olarak tanımlanır. Son birkaç on yılda, fotopolimerizasyon sahip olduğu üstün özellikleri nedeniyle kaplama, baskı, yapıştırıcı, vernik, elektronik malzemeler, fotolitografi ve boya gibi birçok farklı uygulamada sıkça kullanılan güçlü bir endüstriyel proses haline gelmiştir. Normal ortam sıcaklığında yüksek hız, düşük enerji maliyeti ve çözücüye ihtiyaç duymayan formülasyonlar sağlaması ve dolayısıyla su ve hava kirliliğinin önüne geçmesi önemli avantajlarındandır. Ek olarak yüksek polimerizasyon hızlarına ulaşıldığında zamansal ve mekansal kontrol de sağlanabilmektedir. Mevcut birçok fotobaşlatıcının varlığı ve akrilat temelli monomerlerin yüksek reaktiviteye sahip olmaları serbest radikalik sistemlere çok daha fazla rağbet görmüştür. Yaygın endüstriyel uygulamaların birçoğu ışıkla başlatılan serbest radikal polimerizasyona dayanmasına rağmen bu polimerizasyon türü ile ilgili oksijen inhibisyonu ve son ürünün özelliklerini etkileyen kürleme sonrası kısıtlamalar gibi bazı dezavanajlar vardır. Katyonik fotopolimerizasyon serbest radikalik analoğuna kıyasla çeşitli avantajlara sahiptir. Katyonik polimerizasyon uçucu madde salımı gibi sorunların, moleküler oksijen inhibisyondan kaynaklanan sınırlandırmaların, toksisite problemlerinin ve yüksek viskoziteden kaynaklanan problemlerin üstesinden gelebilmektedir. Ayırca bir kere başlatıldığında vinil eter ve epoksi gibi katyonik olarak polimerleşebilen monomerler, ışıksız ortamda yavaş yavaş polimerleşme olarak bilinen karanlık-polimerizasyona devam edebilmektedir.

Szwarc tarafından 1950 yılında keşfedilen ilk yaşayan polimerizasyon tekniğinden bu zamana çekici özellikleriyle iyi tanımlanmış polimerler kolayca hazırlanmıştır. Son birkaç on yılda, atom transfer radikal polimerizasyonu (ATRP), geri dönüşümlü katılma-parçalanma transfer (RAFT) polimerizasyonu, nitroksit ortamlı radikal polimerleşmesi (NMRP), halka açılma polimerizasyonu (ROP) ve halka açılma metatez polimerizasyonu (ROMP) gibi diğer yeni metotların geliştirilmesi polimer biliminin bu alanında yeni ufuklar açmıştır. Biyomühendislik, tıp, biyokimya, malzeme mühendisliği gibi birçok alanda özel amaçlar için özel olarak tasarlanan malzemlere duyulan muazzam istekten dolayı böyle tasarlanan makromolekül yapıların sentezi polimer bilminin ana konusu haline gelmiştir. Ancak, sıkça kullanılan bu polimerizasyon tekniklerinin polimer camiasının ilgisine ihtiyaç duyan halen bazı dezavajları mevcuttur. Alternatif bir yöntem olarak yaşayan katyonik polimerizasyonun birçok yaklaşımı, serbest radikal polimerizasyonla ilgili dezavantajların üstesinden gelmek amacıyla endüstriyel açıdan önemli monomerlerin polimerlerinin sentezi rapor edilmiştir.

Bu tezde Lewis asidi destekli yönteme dayanan yaşayan katyonik polimerizasyon için yeni fotobaşlatıcı sistemler geliştirilmiştir. Ek olarak yeni geliştirilen metodun çift fonksiyonlu vinil eter monomerlerinin UV ile kürleme ve çapraz bağlama uygulamalarındaki etkinliği değerlendirilmiştir.

Katyonik fotopolimerizasyonlarla ilgili yaygın sorunlar Lewis asitleri gibi tuz türü bileşenlerin çözünürlük problemleri, klasik fotobaşlatıcıların zayıf spektral özellikleri ve Lewis asitlerinin kararlılık problemleridir. Bu nedenle tezdeki çalışmalar yukarıda belirtilen sorunları aşmak için bileşenlerin daha uygun olanlarla değiştirilerek yeni başlatıcı ve polimerizasyon sistemlerinin ileri sürülmesine veya mevcut bileşenlerin farklı kombinasyonuna odaklanmıştır. Bu bağlamda bu tez sonucunda altı ana çıktı mevcuttur:

i. Katyonik başlatıcı olarak difeniliyodonyum halojenürler, çinko halojenür varlığında divinil eterlerin çapraz bağlanma reaksiyonunda başarılı olarak kullanılmıştır.

ii. Sulu ortamda vinil eterlerin katyonik fotopolimerizasyonu gerçekliştirilmiştir.

iii. Yüksek çözünürlük ve iyileştirilmiş spektral özelliklere sahip tuz olmayan türde yeni bir fotobaşlatıcı (vinil halojenürler) vinil eterlerin yaşayan katyonik fotopolimerizasyonuna uygulanmıştır.

iv. Metal halojenür temelli Lewis asitin ($ZnBr_2$) in situ oluşturulması gerçekleştirilmiş ve bu Lewis asit takip eden yaşayan katyonik polimerizasyon veya foto-çapraz bağlamada kullanılmıştır.

v. Metakriloyil yan gruplarla donatılmış poli(etilen oksit)-*graft*-poli(izobütil vinil eter) (PEO-*g*-PIBVE) başarılı bir şekilde sentezlenmiş ve foto-çapraz bağlanma reaksiyonunda kullanılmıştır.

vi. ATRP ve görünür bölge ışıkla uyarılan serbest radikallerle yükseltilen katyonik polimerizasyonun kombinasyonlarını içeren bir mekanistik transformasyonla blok kopolimerler sentezlenmiştir.

İlk olarak yüksek nükleofilliğe sahip karşıt iyon içeren difeniliyodonyum tuzlarının kullanımıyla divinil eterlerin katyonik foto-çapraz bağlanma reaksiyonları çalışılmıştır. Bu yaklaşımda hem direkt hem de indirekt başlatıcı metotlar denenmiştir. Direkt sistemde sadece difeniliyodonyum tuzu ve çinko halojenür başlatıcı çifti olarak kullanılırken indirekt sistemde bunlara ek olarak antresen, perilen, 2,2-dimetoksi-2-fenil asetofenon, benzofenon ve tiyoksanton gibi ışığa duyarlı ve onyum tuzunu aktive eden fotouarıcılar kullanılır. Her iki başlatıcı sistem de belirtilen katyonik polimerizasyonun gayet etkin bir şekilde gerçekleşmesini sağlamıştır.

İkinci çalışmada, yitterbium triflat ($Yb(OTf)_3$) gibi suya karşı dayanıklı Lewis asidi varlığında difeniliyodonyum iyodür ile başlatılan sulu ortamda vinil eterlerin katyonik polimerizasyonu amaçlanmıştır. Heterojen özellikteki sistemin sulu kısmı $Yb(OTf)_3$ ve fotobaşlatıcı içerirken organik faz vinil eter monomeri, asetonitril ve yine fotobaşlatıcı içerebilmektedir. Çok hızlı gerçekleşebilen bu polimerizasyon bazen patlayıcı karakteri gösterdiğinden dolayı oluşan polimerin dönüşüm oranı ve molekül ağırlığı sıcaklık, karıştırma şekli ve hızı gibi deneysel kuşullara oldukça bağımlıdır.

İzobütil vinil eter, di(etilen glikol) divinil eter, tri(etilen glikol) divinil eter, 1,4-butandiol divinil eter ve 1,6-hegzandiol divinil eter gibi tipik vinil eter monomerlerinin fotobalatılmış katyonik polimerizasyonun sübstitüye vinil halojenür kullanımı ile gerçekleştirilmesi bir sonraki çalışmadır. Bu monomerlerin fotopolimerizasyonu 0 ^oC (veya oda sıcaklığında) λ = 350 nm dalgaboyundaki ışıkla CH_2Cl_2 çözeltisi içerisinde çinko iyodür (ZnI_2) varlığında şu başlatıcılar ile

gerçekleştirilmiştir: : 1-bromo-1,2,2-tris(*p*-metoksifenil)eten, 1-bromo-1-(*p*-metoksifenil)-2,2-difenileten ve 1-bromo-1,2,2-trifenileten. Monomer ve fotoliz sonucu elde edilen katyonun katılma ürünün oluşmasını ve sonrasında elektron transferini içeren bir başlama mekanizması önerilmiştir. Bir sonraki aşamada ise terminal karbon-halojenür bağı çinko iyodürün koordinasyon etkisi ile aktif hale getirilerek ilerleme basamağı tetiklenmektedir. Bu polimerizasyon bazı karakterleriyle kontrollü katyonik polimerizasyon özellikleri göstermektedir.
Dördüncü çalışmda ise çinko halojenürün *in situ* oluşturulmasına dayanan Lewis asit katalizli vinil eterlerin katyonik polimerizasyonuna dair bir yaklaşım geliştirimiştir. Burada ilerleme aşamasında merkezi rol alan çinko halojenür başlama basamağında eşzamanlı olarak fotoliz sonucu açığa çıkan brom radikallerinin ortamda bulunan çinko radikallerini oksitlemesi sonucu oluşur. Bu polimerizasyon çeşidinin yaşayan karakteri ve UV kürlemedeki etkinliği de araştırılmıştır.
Son iki çalışma ise geliştirilen başlatıcı sistemlerin özel olarak dizayn edilmiş makromoleküler yapıların sentezlerinde uygulamalarını içermektedir. Bu iki uygulamadan ilkinde metakrilat yan gruplara sahip poli(izobütil vinil eter)-aşı-poli(etilen oksit) (PIBVE-*g*-PEO) sentezi ve bunun UV kürlemesi gerçekleştirilmiştir. İkincisinde ise Atom Transfer Radikal Polimerizasyonu (ATRP) ve görünür bölge uyarılmış serbest radikal temelli katyonik polimerizasyonun kombinasyonuna dayalı mekanistik transformasyon yöntemi ile blok kopolimerler sentezlenmiştir. Bu çalışmada başlatıcı olarak dimanganez dekakarbonil [$Mn_2(CO)_{10}$] kullanılmıştır. Yukarıda belirtilen çıktıları gösteren sonuçlar katyonik polimerizasyon için geliştirilen başlatıcı sistemlerin başarılı bir şekilde uygulandıklarını göstermektedir.

1. INTRODUCTION

There was a time when everything from wheels to houses was made of stone. Fortunately, some of the cave-people discovered coke (carbon) as reducing agent for the reduction of iron oxide to metallic iron [1]. This discovery that all happened several thousands years ago changed not only lives of stoneagers but also ours. However, this was not the last. Could you imagine how our ancestors would ride a car at highways, fly a plane, or drink a fresh dairy milk. Fortunately again, chemists were at there; it was the time we were entering “the Polymer Age”. For instance, natural rubber obtained from *crying trees* was used by South American Indians in the maufacture of waterproof materials for containers, shoes, etc. in the first years of this age. Rubber trees were first stated in *De Orbe Novo* by Pietro Martine d’Anghiera in the early 16th century and then first investigated chemically by Frenchman Macquer in the late 18th century [2]. Enormous contribution of the industrial revolution to the mass production of rubber, cellulose gutta-percha and shellac articles by the invention of processing, mixing and kneading machines opened this new era. After this time, people have needed and wanted more and more polymeric materials because of their elegant properties including high strength, lightness, processability, ease of production and so on. Since the beginning of 20th century, synthetic routes, advanced design and molecular architechture of the polymers have being well-established, which is driven by the desire of polymers for special purposes. Therefore 20th century can be considered as the rise of polymer age due to the great progress and huge amount of use. Nowadays, polymers and polymer science is living its diamond age. However, it still needs attention of polymer community to improve present polymerization methods and develop new polymerization techniques which are more efficient, inexpensive and environmentally-friendly. In some cases, a novel polymer architecture would also require development of a new polymerization approach.

Mechanistically, polymerization methods are divided into two main categories; step-growth and chain polymerizations. In the first class, monomers are transformed to oligomers and then polymeric macromolecules by condensation reactions including esterification, amidation or any other coupling reactions relasing small by-products such as water or methanol. In general meaning, the second method, chain or addition polymerization, transforms vinylic monomers to polymers and can be divided into three sub-classes depending on active species take role in the propagation step: free radical, anionic and cationic. In addition, polymerization techniques can be also classified as conventional or classic and controlled/living according to their mode of action. In another classification based on initiation process, there are several polymerization methods: light-induced (photo-initiated ot photo-), thermal, electro-, redox polymerization, and etc. This thesis focuses on photo-induced cationic living polymerization and crosslinking techniques.

Cationic polymerization is an elegant way for preparation of industrially important materials including many high-, medium-, and low-molecular-weight polymeric materials. Indeed, this branch of the polymer chemistry was widely employed in manufacturing of several derivatives of butyl rubber, namely synthetic rubbers, in first decades of 20th century. Both low-molecular-weight synthetic rubbers used mainly as adhesive, plasticizer, additives for motor oils and transmission fluids, and lubricant [3, 4] and high-molecular-weight rubbers commonly utilized as bulky parts in automotive, tire, sealant and building industries have been produced by cationic polymerization [5]. Polyacetals, poly(tetramethylene glycol), poly(ε-caprolactam), polyaziridine, polysiloxanes, poly(*N*-vinyl carbazol), polyindenes, and poly(vinyl ether)s are other common commercial polymers obtained by different modes of cationic polymerization [6]. Even, some monomers such as viny1 ethers, tetrahydrofuran, ethylene imine and l,3-dioxolane can be polymerized only cationically.

Both vinylic monomers such as vinyl ethers; isobutylene; and styrene derivatives, and heterocyclic monomers involving sulphur; oxygen; nitrogen atoms in their rings may undergo cationic polymerization. Polymerization mechanisms of these monomer types vary; the former ones are polymerized mainly through stabilized carbenium-ions whereas heterocyclic monomers need onium ions for their propagation reactions. Regardless of the mechanisms, cationic polymerizations are employed in important commercial processes, and are remarkable scientific methods for preparation of well-defined polymers and copolymers as well.

1.1 Why Cationic Photopolymerization?

In general understanding, cationic photopolymerization is known as a polymerization technique involving positively charged or electrophilic active centers at the growing chain end, produced from photo-induced chemical reactions. In recent years, it has become a substantial technological, commercial and scientific application. Significance of the cationic polymerization was contrasted after discovery of photo-initiated cationic polymerization and living cationic polymerizations since this new techniques opened new perspectives in polymer science, and has become powerful industrial process widely used in various applications including coatings, inks, adhesives, varnishes, electronics, photolithography, and dyes due to its excellent advantages [7-9]. Especially, living cationic polymerization allows synthesis of polymers with controlled molecular weights and narrow polydispersity, and it provides structural control as well. Although much effort has been devoted to free radical systems [10, 11] mainly due to the availability of a wide range of initiators and the great reactivity of acrylate-based monomers, several advantages of the cationic photopolymerization over its free radical analogues have also been reported [8, 9, 12]. Similar to free radical photopolymerization technique, it offers high rate of polymerization at ambient temperatures, lower energy cost, and solvent-free formulation, thus elimination of air and water pollution [8, 9]. It also allows temporal and spatial control of the polymerization when high initiation rate is reached [13]. Additionally, photo-initiated cationic polymerization overcomes limitations due to molecular oxygen inhibition, toxicity, and problems associated to high viscosity. Furthermore, once initiated, cationically polymerizable monomers undergo dark-polymerization in which they slowly polymerize without radiation.

1.2 Living Cationic Polymerization

Since discovery of the first living polymerization technique by Szwarc in 1950s [14], well-defined polymers with attractive properties have been readily prepared. In recent decades, development of other new methods such as ATRP, RAFT, NMRP, ROP and ROMP has opened new horizons in this line of the polymer science. Because of the enormous desire of tailor-made materials for specific purposes in many fields including bioengineering, medicine, biochemistry, material science, etc., syntheses of such engineered macromolecular structures have become the main subject of the polymer science. However, these common polymerization techniques have still some drawbacks that need attention of polymer community. As an alternative method, various approaches of living cationic polymerization [15-19] have been reported for the synthesis of polymers of industrially important monomers to overcome the disadvantages related to free radical polymerization. In fact, among the ionic polymerization methods, living cationic polymerization has become one of the most attractive technique in recent years.

"Living polymerization" refers a chain polymerization in which chain breaking reactions, namely transfer and termination, are absent. For decades, living cationic polymerization has been principally achieved by tuning nucleophilicity of counteranion generated in the presence of a metal halide, an externally added weak Lewis base, or an added salt [16, 20].

In the Lewis acid-catalyzed method, protonic acid reacts with vinyl ether monomer to form monomer-HX adduct. Terminal carbon-halide bond in this adduct is activated by the coordinating effect of zinc halide leading to generation of suitable nucleophilic counteranion by stabilizing the growing carbocation. Thus, chain breaking processes are prevented and living cationic polymerization of vinyl ether proceeds (Figure 1.1).

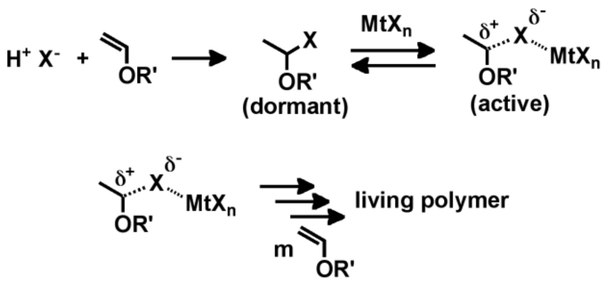


Figure 1.1 : Living cationic polymerization of vinyl ethers.

1.3 Photo-initiated Living Cationic Polymerization

Among the living cationic polymerizations, the Lewis acid-catalyzed approach has been perfectly adapted to the photo-induced polymerization mode as presented in Figure 1.2 [21-26]. In this methodology, cationic species (either carbocation or Brønsted acid) generated photochemically from photosensitive compounds containing halogen atom react with monomer (i.e. vinyl ether) and eventually form a halide-monomer adduct required in the first stage of the propagation. In the subsequent step, addition of new monomers to the adduct is catalyzed by Lewis acid, namely metal halides, by coordination of metal ion with the halogen of the adduct. Propagation and the rest of the polymerization is the same with conventional living cationic polymerization.

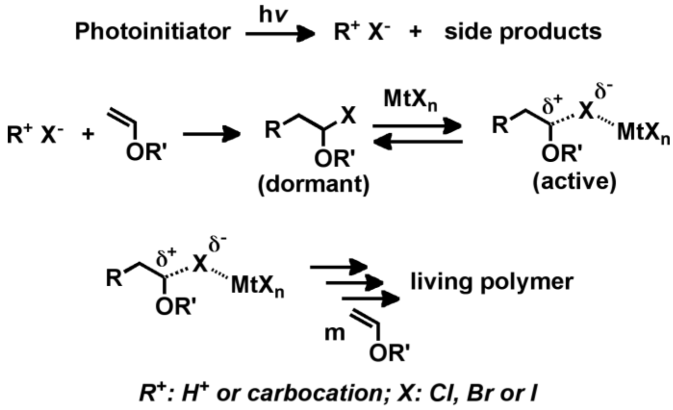


Figure 1.2 : Photo-initiated living cationic polymerization of vinyl ethers.

According to the proposed mechanism and the previous reports, the essential components of the living cationic photopolymerization system are as follows (Figure 1.3):

- *Photoinitiator (PI)* is the organic component that absorbs incident light and directly produces cationic species leading to propagation. Each photopolymerization formulation must contain a photoinitiator.
- *Photosensitizer (PS)* absorbs light, and distinctively, reacts directly or indirectly with the photoinitiator to generate cationic species. This component is not necessary for all polymerization systems. However, it brings some advantages such as extension of absorption range of the photoinitiating system or overcoming solubility problems.
- *Light (hv)* is another essential component of photopolymerizations. UV or visible light can be employed as a light source.
- *Co-activator (MtX_n)*, or metal-salt-based Lewis acid, is required in propagation step for activation of dormant species and addition of monomers.
- *Monomer* refers cationically polymerizable vinyl type monomer, such as vinyl ether, isobutylene or *p*-methoxystyrene.

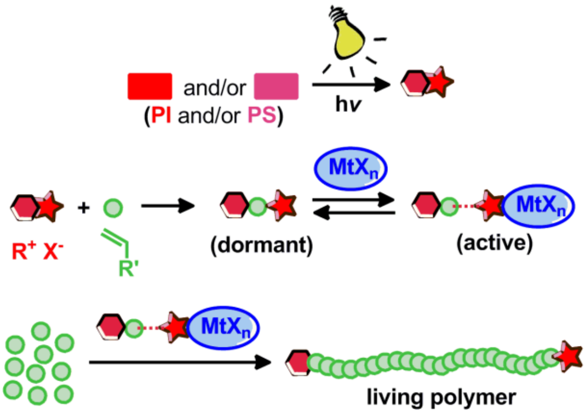


Figure 1.3 : Main components of Lewis acid-catalyzed living cationic photopolymerization.

1.4 Purpose of the Thesis

The main subject of this thesis is study of photo-initiated living cationic polymerization of vinyl ethers. Additionally, efficiencies of the recently developed systems are evaluated in UV curing and crosslinking applications of difunctional vinyl ether monomers.

The common drawbacks associated with cationic photopolymerizations are solubility problems of salt type components such as Lewis acids and photoinitiators, poor spectral properties of usual photoinitiators, and stability issue of Lewis acids. Therefore, the work focuses on introducing new photoinitiating and polymerization systems by replacing the components with new ones or using different combinations of the present components for a specific purpose and overcome the shortcomings.

In this respect, we firstly aimed to develop a new photoinitiating system in order to improve their spectral properties. There are two common approaches to enhance spectral properties; use of photosensitizers, and employment of new class of photosensitive compounds absorbing light at longer wavelengths. In the first methodology, photosensitizers absorbing light at longer wavelengths are used to sensitize classical photoinitiators with poor spectral characteristics. Depending on the second approach conventional photoinitiators are replaced with recently developed photoinitiators, namely vinyl halides, which are functional at longer wavelengths.

The second objective of the thesis is to overcome solubility problems associated with the salt-based components. Classical cationic photoinitiators such as diphenyliodonium halides that are scarcely soluble in monomers can be replaced with completely organic and highly soluble vinyl halides. On the other hand, poly(ethylene glycol) can be added to the formulation as an additive to dissolve metal-salt-based co-activators such as zinc halides by coordination, since they are also barely soluble in organic media. Alternatively, zinc halide can be produced in situ during the photolysis process using a convenient precursor. By this elegant way, both solubility and stability problems of the Lewis acid will be overwhelmed.

The final aim of the thesis is introduction of the newly developed systems in certain applications for specific purposes such as synthesis of graft copolymers, cationic photopolymerization in aqueous media, and crosslinking systems.

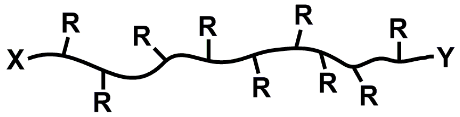
2. THEORETICAL PART

2.1 Controlled/Living Polymerization Methods

The discovery of controlled/living polymerization methods is considered as the most important progress in polymer science by most of the scientist in polymer community, since it opened a rational avenue to the design and synthesis of tailor-made and telechelic macromolecular architectures employed for any purposes [27, 28]. According to IUPAC, living polymerization refers “a chain polymerization from which chain termination and irreversible chain transfer are absent”, while controlled polymerization is defined as a polymerization with controlled kinetic feature yielding structurally precise polymer molecules [29]. In general understanding, living and controlled are used together to refer polymerization techniques producing structurally well-defined polymer chains without termination and chain transfer reactions. Therefore, controlled/living polymerization techniques can be considered as elegant routes to achieve a high degree of control over structural design of polymer chains. Block, comb-shaped, multiarmed, ladder-like, H-shapped, cycle and etc. are the main topologies that can be achieved by such methods. As a consequence of this control over structure, polymers with widely assorted physical and chemical properties can be obtained rom readily available low-cost monomers.

There are several structural factors that define individual characteristics of a certain polymer as illustrated in Figure 2.1. Firstly, molecular weight and molecular weight distribution (MWD) or PDI are the main structural aspects that determine physical properties of polymers. On the other hand, pendant functional moieties (R), end functional groups (X and Y) and steric structure of backbone deeply affect both physical and chemical properties. In addition, three-dimensional shape and sequence of constitutional repeating units along the main chain are the other important factors [20].

Controlled/living polymerization methods offer polymer chemists two principally influential strategies to design polymeric architectures. The first strategy relies on sequential addition of monomers and gives rise segmented block copolymers. The second one allow synthesis of polymers with functional groups at one or both end(s) when living end of propagating chain is terminated with suitable compounds. There are several topologies that can be achieved by these approaches as summarized in Figure 2.2 [30].



- Molecular weight
- Polydispersity
- Side-chain functional group (R)
- End functional group (X and Y)
- Stereoregularity of backbone
- Spatial shape (topology)
- Sequence of repeating units

Figure 2.1 : Structural features that would be controlled during polymer synthesis.

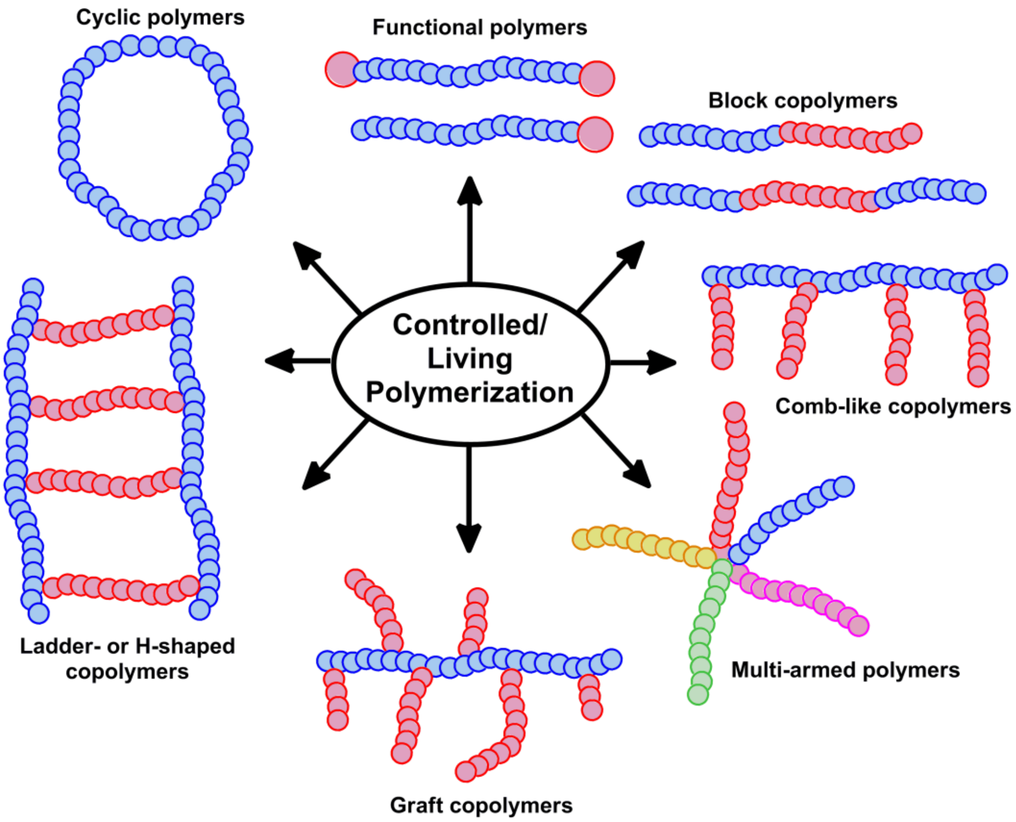


Figure 2.2 : Different polymer architectures that can be produced by controlled/living polymerization techniques.

Anionic polymerization is the first living polymerization method introduced by Szwarc in 1950s and has been utilized as an elegant tool for the synthesis of poylmers with controlled properties [31, 32]. Living anionic polymerization was succesfully acknowledged for the preparation of commercialized products such as footwear, pressure-sensitive adhesives, cables, softtouch overmolding, cushions, lubricants, gels and coatings under the trade name Kraton [27]. Significant contributions to the development of this class of polymeric materials are still found in the current literature [33-35]. However, the concept of controlled/living polymerization was not fully recognized until 1960 [33]. In theory, the well-mannered living systems requires only an initiator and monomer, as observed in the anionic polymerization of styrene, dienes, and ethylene oxide. However, increasing desire for synthesis of complex macromolecular architecture and introduction of new monomers give rise novel approaches involving control over chain transfer and termination kinetics. These systems, so called controlled/living polymerizations, consist of initiators, catalysts, and sometimes chain-end stabilizers.

The discovery of living cationic polymerization in 1980s by Sawamoto, Higashimura, Faust and Kennedy was another milestone of the controlled/living polymerization methods. In the following years, the range of living cationic polymerization was rapidly extended by introduction of new initiating systems, monomers, and synthetic methods [20]. In the last two decades, the last and the most remarkable discovery was observed in polymer science; introduction of controlled/living radical polymerization techniquess [36]. Precise control of functionality, molecular weight, and uniformity (molecular weight distribution) can now be made not only by living ionic polymerization routes but also by newly developed controlled/living radical polymerization techniques. Several controlled/living radical polymerization methods namely ATRP [37, 38], NMRP also called as SFRP [39], and RAFT [40], iniferters [41], ITP [42], CMRP [43], organotellurium-, organostibine-, organobismuthine-mediated polymerization (OMRP) [44] have been developed to produce well-defined macromolecules. Another remarkable development has been achieved in the metathesis polymerization and click chemistry. Many new catalysts have been developed and applied to prepare advanced materials [45-48]. The range of monomers and functional groups used in the preparation of tailor-made polymers has been expanded in recent years as a result of such developments.

2.1.1 Controlled/living free radical polymerizations

Free radical polymerization is flexible and less sensitive to the polymerization conditions and functional groups compared to ionic analogues. However, classical free radical processes yield polymers without control of molecular weight and chain end. Competing coupling and disproportionation reactions and the inefficiency of the initiation step lead to loss of functionalities. Recent developments in controlled/living radical polymerization provided the possibility to synthesize well-defined polymers with controlled functionality also with radical routes [49]. The controlled/living free radical polymerization techniques depends on minimization of chain breaking reactions and growth of all chains at the same time. Therefore, fast initiation and very slow termination reactions are main requirements of such systems in which active propagating radicals are periodically generated. The first examples of these systems were seen consecutively in cationic ring opening [50], carbocationic [51] and anionic polymerizations [52].

Each controlled/living free radical polymerizations method depends on one of the following equilibria between propagating active radicals and dormant species:

(1) Active radicals are reversibly deactivated into dormant species in a process called deactivation/activation (Figure 2.3). In the first approach depending on persistent radical effect, newly formed radicals are immediately stabilized (with a rate constant of deactivation, k_{da}) by a group (i.e. nitroxide) or a transition metal complex (commonly based on Cu, Fe, Co, Mo, Os and Cr) leading to formation of dormant species. Subsequently, dormant species are activated (with a rate constant of activation k_a) thermally [37, 39, 53], photochemically [54, 55], electrochemically [56] or by redox [57] to form active species again. Most of these radical species undergo propagation (k_p), and the others can terminate (k_t).

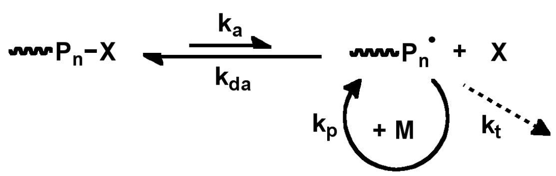


Figure 2.3 : General mechanism of controlled/living free radical polymerization by activation/deactivation process.

The crucial point of the system is that persistent radicals (X) do not react with each other but only cross-couple with the growing species. However, termination by both radical coupling and disproportionation should be also included in the mechanism due to the magnitude of the related rate constant. While, the propagating radicals mostly couple with X whose concentration is 1000 times higher. The amount of radicals decreases when amount of X increases with time leading to drop in the probabilty of termination.

NMRP and transition metal-catalyzed free radical polymerizations including OMRP, ATRP and CMRP are all rely on this mechanism.

(2) In an alternative mechanism [58], radicals are involved in a rapid degenerative exchange process between dormant and active polymer chain ends (Figure 2.4). These processes do not rely on persistent radical effect. The initiation and termination reactions cause a steady state concentration. Sometimes, long-lived intermediates can participate in the exchange process leading to retardation of polymerization or side reactions such as termination of propagating radicals.

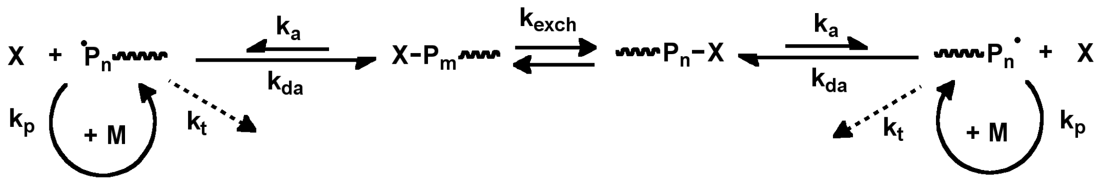


Figure 2.4 : Controlled/living free radical polymerization via degenerative exchange process.

ITP and RAFT are the most widely used techniques that follow degenerative exchange process.

Most commonly used controlled/living polymerizations, namely ATRP; NMRP; and RAFT, will be described briefly here.

2.1.1.1 ATRP

Among the controlled/living radical polymerization strategies, ATRP, coined by Matyjaszewski et al. [59] and Sawamoto et al. [60] in 1995, has turned out to be the most promising method allowing good control on the molecular weight and microstructure of the polymers in a targeted manner. As illustrated in Figure 2.5, a typical ATRP system must contain an initiator (RX), a transition metal halide (Mt^zX_z) coordinated with ligand(s) (L), and obviously, monomer (M). The transition metal of the complex can exist in two different oxidation states. ATRP process begins reaction of the lower oxidation state metal complex (Mt^z/L) with the initiator leading to formation a radical ($R^\bullet$) and the corresponding higher oxidation state metal complex with a coordinated halide anion X-Mt^{z+1}/L, in a process termed activation. In the consequent step namely deactivation, the latter complex transfers the halogen atom back to the radical to re-form the alkyl halide and the lower oxidation state metal complex. However, prior to deactivation some of the active radicals can react with the monomer (M) yielding polymer chains in the propagation step. A little fraction of the radicals can be coupled with each other instead of X-Mt^{z+1}/L. The most important difference of the ATRP compared to conventional radical polymerization is structure of the resulted polymer containing halogen-terminated end. This halide functionality allows preparation of block copolymers when suitable condition for ATRP of another monomer is provided.

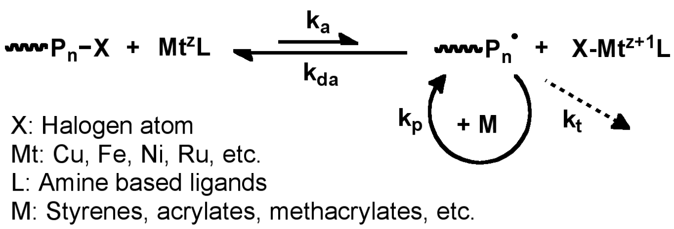


Figure 2.5 : General mechanism of ATRP

In this method, control is achieved by the equilibrium maintained between an active ($P_n^\bullet$) and a dormant chain (P_n-X). The mechanism involves reversible homolytic cleavage of a carbon–halogen bond by a redox reaction between an dormant species and a metal/ligand complex, such as copper (I) complexes with 2,2-bipyridine. ATRP catalyzed by copper complexes has been applied successfully to the controlled/living polymerization of several monomers including styrenes, acrylates, methacrylates, acrylonitrile, and other monomers so far [61]. Table 2.1 summarizes trnasiton metals of complex catalysts system employed in ATRP of diverse monomers.

Table 2.1 : Transition metals used in ATRP of various monomers.

ATRP	Monomer	Ref.
Cu-based	Styrenes, acrylates, methacrylates, acrylonitrile	[61]
Ru/Al-based	Styrenes, acrylates, methacrylates	[62, 63]
Fe-based	Styrenes, methacrylates, vinyl acetate	[64-66]
Ni-based	Methacrylates	[67-69]

2.1.1.2 NMRP

Another controlled/living radical polymerization method developed in recent years is NMRP, also called SFRP by some authors [39, 70]. This type polymerization, which relies on persistent radical effect, can be realized through reversible deactivation of propagating chain end by relatively stable radical nitroxides such as TEMPO (Figure 2.6).

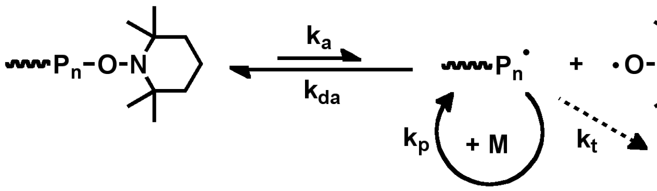


Figure 2.6 : General mechanism of NMRP.

According to general mechanism, the control is assured by the reversible termination of the propagating polymeric chain and reduced concentration of the growing radical chain end. The exceptionally low concentration of reactive radicals ends because of the absence of other reactions leading to initiation of new polymer chains results in decrease in irreversible termination reactions, such as coupling or disproportionation. This allows formation of desired amount of initiating species and growing chains which is observed in a living fashion. Like the other controlled/living radical polymerization, this method produces well-defined polymers due to the these properties. The key to the success of this approach is employment of a wide variety of persistent radicals such as (arylazo)oxy, substituted triphenyls, verdazyl, triazolinyl, nitroxides, etc. in a reaction at near diffusion controlled rates with the carbon-centered free radical of the propagating chain end in a thermally reversible process [39].

2.1.1.3 RAFT

RAFT polymerization is one of the most recent entrants and one of the most efficient methods in controlled/living radical polymerization techniques [40, 71-74]. A major advantage of the RAFT process over other controlled radical polymerization techniques is its tolerance of protic and other functionalities that can be incorporated into the chain transfer agent [72, 75-77]. In this technique, after the initiation, the RAFT agents reversibly deactivate the polymer chains as the rate constant of chain transfer is faster than the rate constant of propagation (Figure 2.4). In the polymerization, the functional group present on the CTA is retained at the end of the polymerization. This enables the incorporation a wide range of functional end-groups such as -OH, -COOH, $-NR_2$, $-CONR_2$ $-SCO_3Na$ etc. α-Functional groups can be introduced via the R group while the Z group of the CTA contribute to the incorporation of ω-functional groups (Figure 2.7).

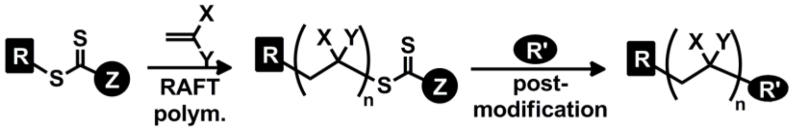


Figure 2.7 : Synthesis of functional polymers by RAFT polymerization.

The key to succesful RAFT polymerization is a order of addition-fragmentation equilibria as presnted in Figure 2.8 [40, 73]. In initiation and termination steps, there is no difference between RAFT and conventional polmerizations. However, after initiation, addition of a propagating radical ($P_n^\bullet$) to the thiocarbonylthio compound [RSC(Z)=S] completely change the nature of the polymerization. In the subsequent step, fragmentation of the intermediate radical yields a macromolecular thiocarbonylthio compound [P_nS(Z)C=S] and a new initiating radical ($R^\bullet$). A new growing radical ($P_m^\bullet$) is generated by the reaction of the radical ($R^\bullet$) with monomer. The crucial point is establishment of rapid equilibrium between the active growing radicals ($P_n^\bullet$ and $P_m^\bullet$) and the dormant polymeric thiocarbonylthio compounds assuring equal possibility for all chains to grow. This situation allows formation of polymers with narrow molecular weight distribution. After completion of the polymerization, polymers with thiocarbonylthio end group are obtained; therefore, this way block copolymers can be synthesized by sequential addition of another monomer without any post-modification process [78].

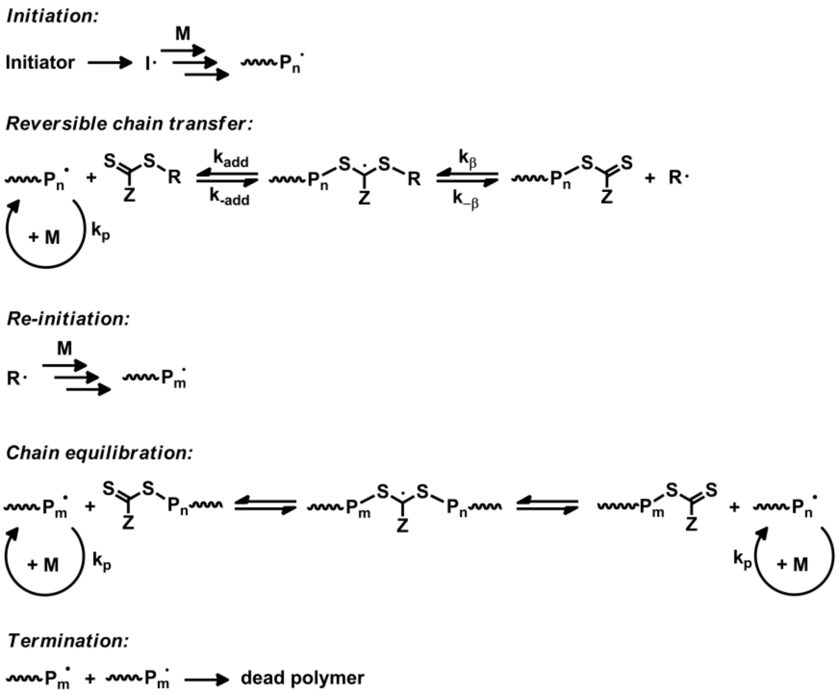


Figure 2.8 : General mechanism of RAFT polmyerization.

RAFT polymerization differs considerably from NMRP and ATRP by the means of the mechanism for achieving control. In ATRP and NMRP, propagating radicals are successively deactivated by atom transfer and radical-radical coupling and activated by homolytic cleavage of the labile bonds of dormant species. The position of the deactivation-activation equilibria and the "persistent radical effect" play key role in the rate of polymerization and, in turn, the control over the kinetics. Whereas, initial radicals are necessary to initiate and retain RAFT polymerization, since radicals are neither generated nor deactivated in this approach.

2.2 Living Anionic Polymerization

Anionic polymerization introduced by Szwarc about a half century ago is the first living polymerization method and has been utilized as an elegant tool for the synthesis of well-defined polymers with narrow polydispersity [31, 32]. The characteristics of anionic polymerization make itself suitable for the synthesis of tailor-made polymers containing reactive terminus at one (monotelechelic) or both ends (telechelic) through post-modification or initiation with functional initiators [79-81]. In this polymerization, the propagating species are organometallic species such as carbanions or oxanions and react through nucleophilic reactions in aprotic media as shown below (Figure 2.9). Although styrene and its non-base-sensitive derivatives have been must studied monomers for living polymerization butadienes, methacylates, acrylates, ethylene oxide, hexamethylcyclotrisiloxane, and lactones are other common monomers that can undergo anionic living polymerization [30].

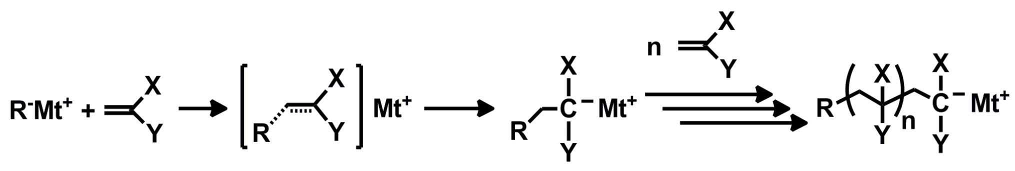


Figure 2.9 : Living anionic polymerization.

Anionic polymerization requires many rigorous experimental conditions including inert atmosphere, absolute purification of most of the reagents used, temperature, solvent, glassware manipulation etc. for complete synthesis. Once succeeded, utilization of one of two different strategies of anionic polymerization allows the generation of functional termini. These include (i) initiation with (protected) functional initiators and (ii) termination with a suitable electrophile and result in various model functional polymers that have been significantly used in many applications [82, 83].

Functional polymers synthesized by living anionic polymerization are transformed to different topologies such as linear, hyperbranched, star, core-shell polymers or further functional polymers depending on aim through other polymerization technique or effective reactions such as click reactions. Reaction of the commonly used initiators such as butyl lithium or sodium naphtalenide with styrene yields polystyrenes with one end (eq. 2.1) or two reactive ends (eq. 2.2), respectively. Further utilization of these macro-anions as initiators produces corresponding block copolymers, AB and ABA copolymers, individually. Alternatively, treatment of reactive macro-anions with ethylene oxide and termination with appropriate reagents results in polystyrenes with hydroxyl groups at one or two end(s). If such hydroxyl functional polymers treated with methacryloyl chloride a macromonomer with methacryloyl functionality will be obtained. A subsequent free radical polymerization of this macromonomer with a second type monomer yields graft copolymers. On the other hand, reaction of anion-ended polymers with polychlorosilanes or divinyl benzene yields star-branched polymers [30].

$$C_4H_9^- \, Li^+ + \text{Styrene} \longrightarrow C_4H_9\text{-polsytrene}^- \, Li^+ \tag{2.1}$$

$$\underset{\text{naphthalenide}}{\text{Sodium}} + \text{Styrene} \longrightarrow Na^+ \, {}^-\text{polsytrene}^- \, Na^+ + \text{Naphthalene} \tag{2.2}$$

2.3 Living Cationic Polymerization

The present thesis is mainly based on photo-initated living cationic polymerization methods. Therefore this section gives the principles of the polymerization in details and discusses more specific developments in new polymerization systems, especially in photopolymerization methods.

In general understanding, cationic vinyl polymerization is known as an addition polymerization mediated by a propagating carbocation (**2**) which is generated by a reaction of a vinyl monomer with an initiator, usually a Brønsted acid or a “cationogen” (**1**) (Figure 2.10). Generally, high reactivity of the propagating cationic chain causes some side reactions including chain transfer and termination reactions that yield unreactive polymeric chains. For instance, in chain transfer, abstraction of inhrently acidic β-proton of growing cation (**2**) by cationically polymerizable monomers, which are principally nucleophilic or basic, leads to unsuppressible undesirable reactions giving polymers with double bond at the end (**3**). Beacause of these side reactions, synthesis of polymers in controlled manner is not possible by such conventional cationic polymerization. Control over structure and architecture of the polymer chains which is important for most of the applications cannot be possible in this process.

Fortunately, the discovery of living cationic polymerization by Higashimura, Sawamoto, Faust and Kennedy opened a new avenue to synthesis of well-defined polymers from cationically polymerizable monomers in 1980s [84-86]. Establishment of the elementary principles of living cationic polymerization was begun after these dates, however, the methodology has been still under development by introduction of new initiating, monomer and catalyst systems, and new synthetic applications as well.

2.3.1 Principles of living cationic polymerization

Controlled initiation and propagating processes are crucial for successful living cationic polymerization. In addition, reversible termination is also essential in some cases. Achievement of the polymerization depends on these three essential steps in which a carbocation is formed, stabilized and/or deactivated-activated reversibly.

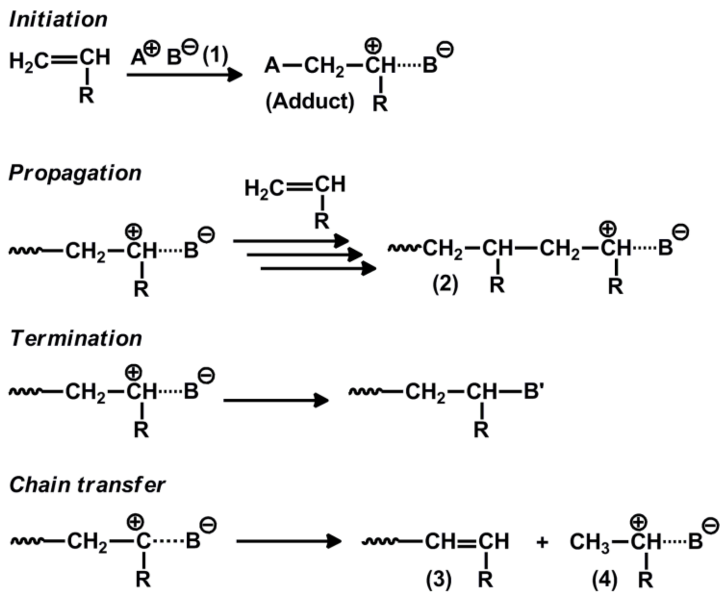


Figure 2.10 : Elementary reactions for conventional cationic polymerization.

2.3.1.1 Well-defined initiation

Controlled initiation can be considered as the utilization of an initiator with a well-defined group, which then becomes head group of the newly generated chain, as it trigger the polymerization. This way head group functionalized polymers can be readily prepared.

Polymerization of IB catalyzed by Ziegler-Natta like catalysts, ethylaluminum dichloride ($EtAlCl_2$), was first described by Kennedy and gives a brief scheme of the initiating reactions in living cationic polymerization [5, 87]. In this initiating system, protons generated from reaction of trace amount of water with the Lewis acid or from a Brønsted acid initiate the polymerization reaction folowed by a propagation which is driven by the Al-based Lewis acid (Figure 2.11).

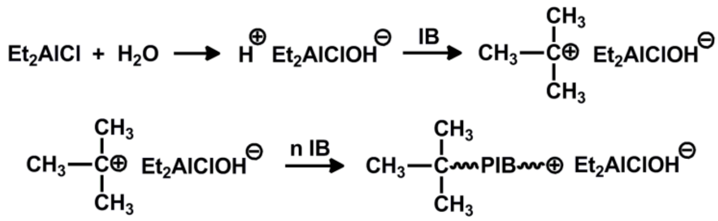


Figure 2.11 : Living cationic polymerization of IB initiated $H_2O/EtAlCl_2$ by initiating system.

Obviously, use of *tert*-butyl chloride in the presence of $EtAlCl_2$, as an initiating system, instead of water or protonic acid based systems, gives the similar carbocation and polymer structure, since *tert*-butyl chloride can be regarded as the adduct of IB with a protonic acid (HCl). The process is presented in Figure 2.12, in which the chloride ion is abstracted from the initiator molecule by $EtAlCl_2$ yielding a carbocation, thus such compound is known as a cationogen. Studies in this line have shown the stability of the produced carbocation from the cationogen deeply affects nature of the polymerization.

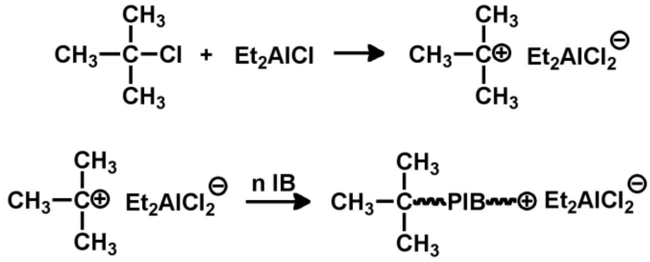


Figure 2.12 : Living cationic polymerization of IB initiated by *tert*-butyl chloride/$EtAlCl_2$ initiating system.

2.3.1.2 Suppressing chain transfer during propagation

The most significant shortcoming of cationic polymerization is instability of cationic site of propagating chain since the β-protons of growing carbocations are labile to be abstracted by cationically polymerizable monomer due to the acidic nature of the β-proton and high nucleophilicity or basicity of the monomer [20]. Therefore, counter-anions of both initiator and propagating chains should be sufficiently stable not to cause termination, but suppress proton elimination (i.e., chain transfer), hence counter-anions promote initiation and propagation in controlled manner. To overcome the problem related to instabile cation, two different approaches based on stabilization of carbocation by nucleophilic interaction via (i) a suitably nucleophilic counteranion (B) [85] and (ii) through an externally added Lewis base (**X**) [86] has been developed.

Both approaches rely on decrease of cationic charge of growing chain (**2**) and, in turn, the acidity of β-protons that suppress chain transfer to the monomer. A characteristic example for the former method is living cationic polymerization of vinyl ethers by the HI/ZnI_2 or HI/I_2 initiating system (Figure 2.13). The highly active chain end is capped with a stable covalent iodide which is activated by a Lewis acid such as zinc iodide or molecular iodine in such systems. In other words, stabilization of carbocationic site of growing chain by nucleophilic iodide anion which is coordinated and activated by a Lewis acid to produce small amount of active complexed carbenium ion plays the key role in this type of polymerization [88, 89]. This active chain end allow insertion of monomer molecules to the chain end without chain transfer or termination.

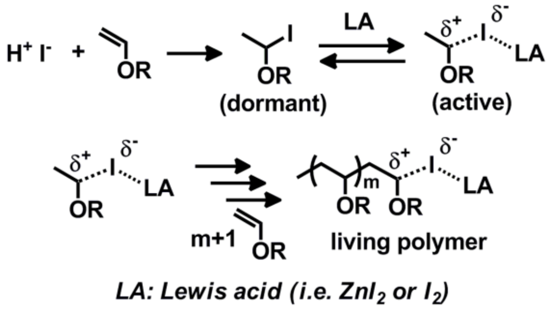
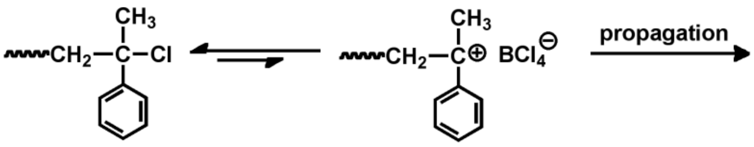


Figure 2.13 : Living cationic polymerization protonic acid/Lewis acid initiating system.

Alternatively, Lewis bases were externally added to polymerization system in the latter method to generate weakly nucleophilic counterions. Polymerization of IB initiated by cationogen/$EtAlCl_2$ in the presence of Lewis bases including esters, ethers or some pyridine derivatives is a good example for the second approach [90, 91]. The key component of this system (**5**) is the externally added Lewis bases (X) since the counterion (B) is not highly enough nucleophile to stabilize the carbocation by itself; so that, non-base-added form of this system is not in living manner. Depending on the both approaches various initiating systems have been developed as their sub-classes.

2.3.1.3 Reversible termination

One of the most important steps in living cationic polymerization is conceptualization of reversible termination, which was first used for polymerization of α-methylstyrene initiated by the $C_6H_5C(CH_3)_2Cl/BCl_3$ system (eq. 2.3) [92]. Such process become the basis of *quasiliving cationic polymerization*, in which transfer and termination reactions are reversible and their rates are higher than that of propagation. However, neither termination nor transfer reactions are observed during ideal living polymerizations [87]. In other words, all the growing chains are operational during whole period of living polymerizations since chain transfer and termination reactions are absent. On the contrary, the presence of reversible transfer and termination reactions do not affect the livingness in quasiliving polymerizations because propagation is the only main consuming process (monomer consumption during initiation is tiny) similar to ideal living systems. Truly living and quasiliving systems are almost identical by the means of kinetics; however, there are some important issues that can be clarified by only the concept of quasiliving [93]. As visualized in Figure 2.14, the most significant diffrence between truly living and quasiliving polymerization relies on the mechanisms of propagation. In quasiliving polymerizations, there are equlibria between active and dormant species at every propagating steps; whereas, dormant species do not exist in ideal living models. In fact, all living carbocationic olefin and alkyl vinyl ether polymerizations proceed according to quasiliving mechanism when such remarkable dissimilarity between ideal and quasiliving systems is considered [93-97].



(2.3)

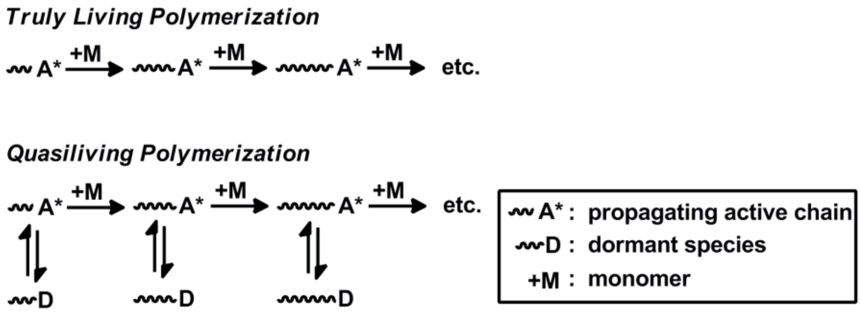


Figure 2.14 : Mechanistic difference between ideal living and quasiliving polymerizations.

2.3.2 Monomers and initiating systems

As schematized in Figure 2.14, the equilibria between active and dormant species define the living nature of the polymerization. Such important equilibria exploit three different methods depending on mainly initiating systems: (i) with nucleophilic counteranions; (ii) with added bases (nucleophiles); and (iii) with added salts [98]. This section, thus, will overview the initiating systems for each type of monomers including vinyl ethers, isobutylene, styrene derivatives and *N*-vinylcarbazole.

2.3.2.1 Initiating systems with suitable nucleophilic counteranions

Vinyl ethers have been the most commonly polymerized monomers by living cationic polymerization which was first reported by Higashimura and his associates in 1984. After this date, several initiating systems based on nucleophilic counteranions (combinations of initiator and Lewis acid activator) have been developed (Table 2.2).

In the first example of this polymerization, alkyl vinyl ethers (CH_2=CH-OR; R: alkyl) was polymerized with a mixture of hydrogen iodide and iodine, which is then called the HI/I_2 initiating system. The polymerization initiated with HI/I_2 in *n*-hexane at temperatures below 0°C yields poly(isobutyl vinyl ether) showing the following characteristics that are typical for "living" polymers.

i. The higher monomer conversion results in higher number-average molecular weight (M_n).

ii. Addition of new monomers into totally polymerized reaction mixture causes further propagation and, in turn, further increase of M_n in line with conversion.

iii. Each initiator triger propagation of only one polymer chain without transfer and termination. Therefore the number of molecules ($[HI]_0$) of hydrogen iodide initially supplied is equal to the number of polymer chains.

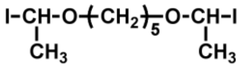
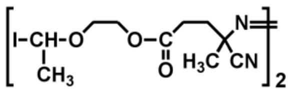
$$M_n = \frac{\text{weight of polymerized monomer}}{[\text{HI}]_0} \quad \textbf{(2.4)}$$

iv. The polymerization rate can be increased by an increase of initial amount of iodine (I_2); however, it does not affect the molecular weight.

v. The polydispersity index is very low and the molecular weiht distribution is almost monodisperse during the polymerization.

As stated by Kennedy, this first report on living polymerization of alkyl vinyl ethers (R: methyl, ethyl, n-butyl, i-octyl, n-hexadecyl, etc.) "opened a most fruitful chapter in polymer synthesis" [87, 99]. Further studies have shown that such living polymerization is possible usually at considerably low temperatures (<0 °C) in both nonpolar (*n*-hexane, toluene, etc.) and fairly polar (methylene chloride, etc.) solvents [85, 99, 110].

Table 2.2 : Initiating systems based on nucleophilic counteranion.

Initiator	Activator	References
HI	I_2	[85, 99]
HI	ZnX_2 (X: Cl, Br, I)	[100, 101]
HI	SnX_4 (X: Cl, Br, I)	[101]
HCl	SnX_2 (X: Cl, I)	[102]
HI	$R_4N^+ A^-$ (R: C_2H_5, *n*-C_4H_9, *n*-$C_{12}H_{25}$, etc.; A: ClO_4, PF_6, BF_4, NO_3, BPh_4, I)	[103]
$HOP(O)(OPh)_2$	ZnX_2 (X: Cl, I)	[104]
Me_3Si-I	ZnX_2 (with RR'C=O or RCHO)	[105, 106]
$Me_3SiOCH_2CH_2OCH_2I$	I_2	[107]
	I_2	[108]
	*n*-Bu_4NClO_4	[109]

As depicted in Figure 2.13, addition of hydrogen iodide into vinyl ether monomers an adduct is immediately and quantitatively generated from reaction of hydrogen iodide with double bond of the monomer. However, the adduct is inactive (dormant) unless molecular iodine is present in the medium. In the consequent step, I_2 added into the mixture coordinates with the iodine atom of the adduct and the bond between iodine and the terminal carbon atom becomes labile to insertion of new vinyl monomers. This activated terminal is subjected to repetitive attack by the monomer molecules leading to living polymer. In addition to molecular iodine, some mild metal halides (ZnX_2 and SnX_2; X: I, Br, Cl) act as Lewis acid activators and are employed widely in this polymerization.

According to Figure 2.13, in general hydrogen iodide acts as an “initiator” that produces the first dormant adduct through its reaction with a monomer molecule, and in turn generates the first living propagating center with the nucleophilic iodide anion. In the subsequent step, Lewis acid (I_2, ZnX_2 or SnX_2) serves as an ”activator”, or “coinitiator”, which triggers activation of the latent carbon-iodine bond through coordination. Because of the high nucleophilicity of iodide, in the first vinyl ether monomer molecules are nonreactive towards the adduct. Nonetheless, interaction of Lewis acids with the iodide decreases its nucleophilicty and the binary counteranionic moiety has the suitable nucleophilic character for insertion of the monomer molecules. As a consequence, the chain end is active for propagation but still nucleophilic enough to stabilize the cationic center leading to living polymerization [20].

Regarding active-dormant equilibrium in this kind of polymerization, the dormant species are neutral, in contrast to the fact that the active species are at least partly ionic. This issue is studied by Higashimura and his coworkers [111], and summarized in Figure 2.15. The Lewis acid activator (I_2 or ZnX_2) does its job by not only interaction with the terminal carbon-halogen bond of propagating chain but also undergoes a rapid halogen (counteranion) exchange with the terminal halogen. However, such exchange (i.e. ether methylene exchange) can not be observed when $CF_3CO_2H/ZnCl_2$ is used as initiating system. Thus, this outcome intensely suggests that the active species are at least partly ionic, and the living propagation proceeds via an ionic intermediate.

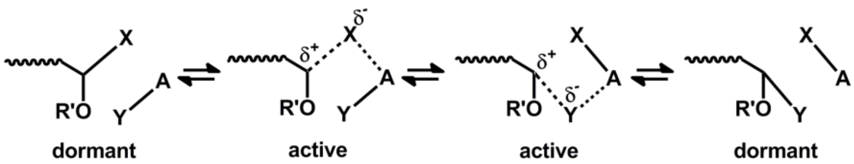


Figure 2.15 : Ion-exchange process at carbon-halogen terminal during living cationic polymerization based on stabilization of a carbocation by a counteranion.

Although most of the living cationic polymerizations of alkyl vinyl ethers are carried out at temperatures below 0 °C, Sawamoto and his associates reported living polymerization of alkyl vinyl ethers at room temperature or above using the HI/ZnI_2 initiating system [88]. Alternatively, $HOP(O)(OPh)_2$ can form an adduct by its reaction with a monomer and trigger the polymerization in the presence od ZnI_2 as depicted in Figure 2.16 [104].

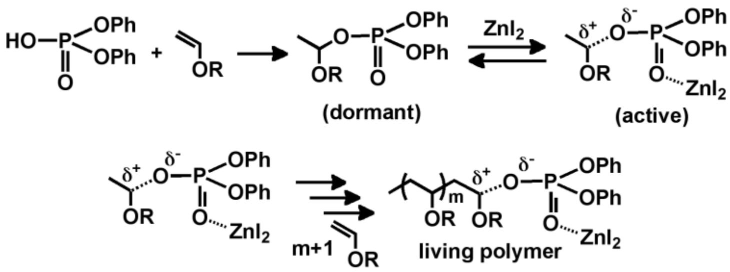


Figure 2.16 : Living cationic polymerization of vinyl ethers using $HOP(O)(OPh)_2/ZnI_2$ initiating system.

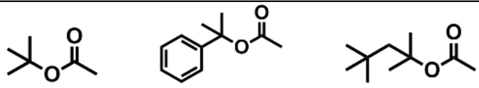
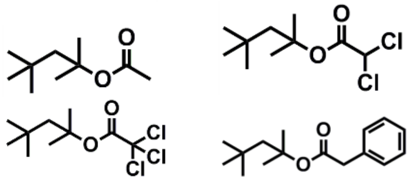
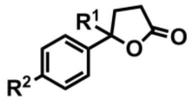
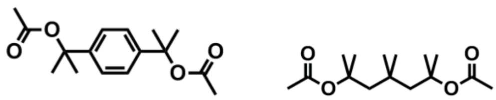
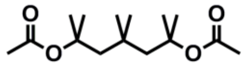
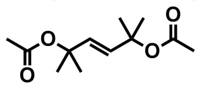
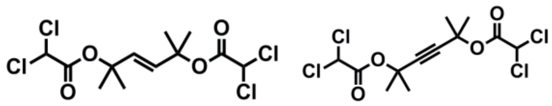
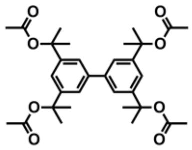
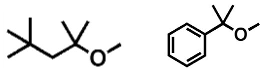
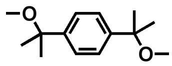
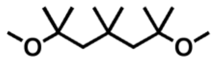
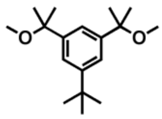
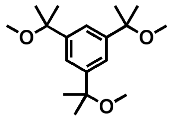
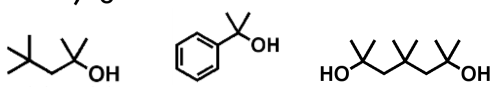
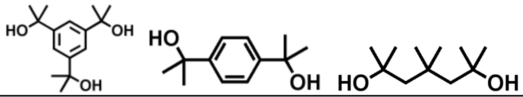
In addition, bifunctional living polymers allowing synthesis of ABA-type triblock copolymers and telechelic polymers with a narrow molecular weight distribution in a high blocking efficiency can be produced using a bifunctional adduct in I_2 catalyzed living cationic polymerization [108].

Another industrially important monomer which is cationically polymerizable is IB. Its first living cationic polymerization initiated by tertiary acetates and catalyzed by boron trichloride (BCl_3) was reported in 1986 by Faust and Kennedy [86, 112]. After this pioneering work, several initiating systems for living cationic polymerization of IB have been developed (Table 2.3).

This initiating system can be divided into three sub-groups, in which carbocation is stabilized by a nucleophilic anions derived from an activator and BCl_3; the initiating couples include tertiary ester/BCl_3, tertiary ether/BCl_3 and tertiary alcohol/BCl_3. A typical example of initiation mechanisms based on cumyl derivatives is depicted in

Figure 2.17. In this system, cationogen (alcohol, ether or ester) and the Lewis acid (BCl_3) are known as initiator and activator (coinitiator), respectively. Design of the initiator allow synthesis of different topologies such as ABA-type block copolymers [113, 114] or star-shaped polymers [115, 116].

Table 2.3 : Various initiating system based on BCl_3 for living polymerization of IB.

Initiating System	Initiator	Reference
Ester / BCl_3		[86, 112]
Ester / BCl_3		[86, 112, 131]
Ester / BCl_3		[132]
Ester / BCl_3		[133]
Ester / BCl_3		[134]
Ester / BCl_3		[135-137]
Ester / BCl_3		[138]
Ester / BCl_3		[115]
Eter / BCl_3		[139]
Eter / BCl_3		[113, 114]
Eter / BCl_3		[140]
Eter / BCl_3		[141]
Eter / BCl_3		[142]
Alcohol / BCl_3		[143]
Alcohol / BCl_3		[116]

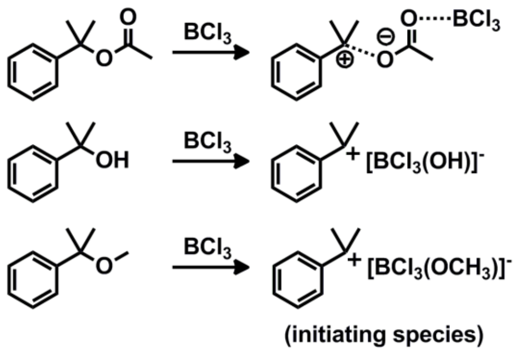


Figure 2.17 : Initiating methods based on activator/BCl_3 system.

The system usually yields a living polymers in wide range of fairly polar solvents (e.g. CH_2Cl_2) at -80 ^oC – 0 ^oC. However, the polydispersities are a little bit higher than unity (PDI > 1.2) [20]. Alternatively, titanium halide salts (i. e. $TiCl_4$, $TiBr_4$) instead of BCl_3can be used as a coinitiator [117]. In this case usually a alkyl chloride[117-119] or trace amount of water [120] is used as an initiator.

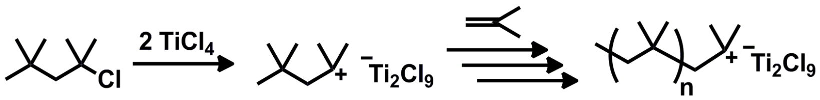


Figure 2.18 : Living cationic polymerization of isobutylene by titanium chloride based catalyst.

Although styrene derivatives are less reactive and generate less stable cationic propagating species compared to vinyl ethers several aromatic vinyl monomers including styrene [121], *p*-methylstyrene [122, 123], *p*-methoxystyrene [124, 125], *p*-*t*-butoxystyrene [126], cholorostyrene [127, 128], have been polymerized by this living polymerization method also. Both ZnI_2 [122, 124-126, 129] and BCl_3 [123] can be used as Lewis acid in such polymerization. In recent years, $AlCl_3OBu_2$ has been employed as a coinitiator in controlled cationic polymerization of styrene [130].

2.3.2.2 Initiating systems with added bases

As discussed in earlier sections, the key to achieving living cationic polymerization of vinyl ether is overcoming the generation of the additional active species, the unstable propagating carbocation frequently causing unpreferred side reactions such as chain transfer or temination. Therefore, a fine equilibrium between the dormant and active species should be established. In addition to adjustment of the equilibrium by a nucleophilic counteranion formed by coordination of the atom attached to the initiating or propagating ends using a proper Lewis acid, employement of weak Lewis bases, esters, or ethers in activation process is another alternative way to attain such polymerization method [102]. This approach is summarized in Figure 2.19.

Vinyl ethers can be rapidly polymerized by $EtAlCl_2$ in combination with metal halides of strong Lewis acidity. However the polymerizations are not living fashion, since such powerful Lewis acids can not generate counteranions with suitable nucleophilicity for stabilization of carbocations. As reported by Aoshima and Higashimura, addition of a Lewis base of suitable basicity to such systems can switch the polymerization from non-living to living state [144].

Regarding IBVE, the living polymerization initiated with the IBVE-HCl adduct in the presence of added bases in toluene at 0 °C proceeds for almost all Lewis acids ($MtCl_n$; Mt: Fe, Ga, Sn, In, Zn, Al, Hf, Zr, Bi, Ti, Si, Ge, Sb) [98]. Although the rate of the polymerization can differ significantly due to the type of metal atom almost all resulted polymers show very narrow polydispersity ranging from 1.02 to 1.10. In a typical example, the time for completion of living polymerization catalyzed by $FeCl_3$ is in seconds; whereas, the polymerization time can be extended to weeks in the case of $SiCl_4$ and $GeCl_4$. This significant variation in polymerization time completely depends on the type of metal atom determining the strength of the interaction between the Lewis acid and the propagating end.

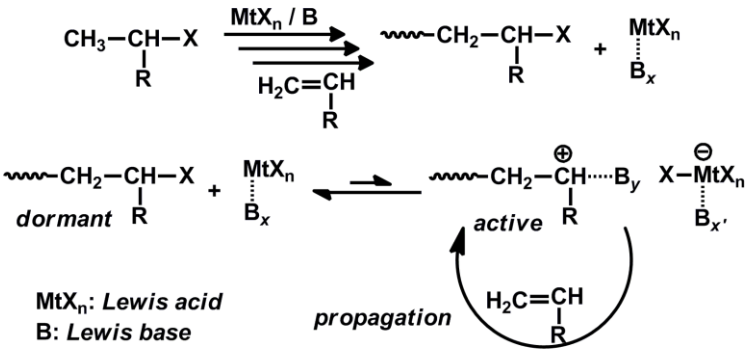


Figure 2.19 : Living cationic polymerization catalyzed by a Lewis acid (MtX_n) in the presence of a weak Lewis base (B).

Polymerization rate in the presence of ethyl acetate as an added Lewis base differs quite significantly for all the metal halides for IBVE [102]:

$GaCl_3$, ~$FeCl_3$ > $SnCl_4$ > $InCl_3$ > $ZnCl_2$ > $AlCl_3$ ~ $HfCl_4$ ~ $ZrCl_4$ > $EtAlCl_2$ > $BiCl_2$ > $TiCl_4$ >> $SiCl_4$ ~ $GeCl_4$ ~ $SbCl_3$

As a consequence, role of the weak Lewis base includes formation of Lewis acid complex by coordination, fine-tuning of the metal halide activity, and stabilization of carbocation at the propagating site and counteranion [102]. Thus, choice of suitable Lewis base usually depends on nature of each Lewis acid. In other words, suitable basicity of the added base depending on the nature of metal halide is the key point for determining activity of each metal halide, and in turn, attaining control over the polymerization. To be exemplified, a controlled reaction could be desingned by the combination of THF (a stronger Lewis base) with $FeBr_3$ or $GaCl_3$ (stronger Lewis acids). In such acid/base pair, equilibrium between active and dormant species is provided from a strong acid-base interaction when the base acts to suitably adjust the equilibrium. Thus, basicity of the added base is a quite substantial factor. Living polymerization with $SiCl_4$,$GeCl_4$, and $SbCl_3$ can be achieved by the different role of the added base. Polymerization proceeds very slowly with these mild catalysts, even in the absence of an added base. This means the counteranions produced by these acids are not strong enough to stabilize the propagating carbocation by themselves. In order to adjust the counteranion reactivity, an added base should be involved in the formation of the counteranion.

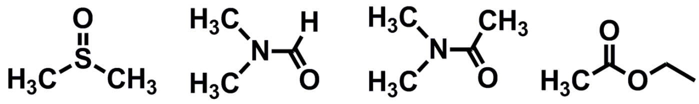
There have been several reports on living cationic polymerization by addition of Lewis bases, which are listed in Table 2.4 [20, 102]:

Table 2.4 : Initiating systems and added Lewis bases for living cationic polymerization.

Initiator/Activator	**Added Lewis Base**
$H_2O/EtAlCl_2$	Ester: CH_3COOEt
$H_2O/AlCl_3$	Ester: PhCOOEt
$CH_3CO_2H/EtAlCl_2$	Ester: CH_3COOEt
$CH_3CO_2H/EtAlCl_2$	Ether: Et_2O
IBVE-HCl/ $EtAlCl_2$ or $AlCl_3$	Ether: 1,4-dioxane
$CH_3CH(O\textit{i}Bu)OCOCH_3/EtAlCl_2$	Ether: 1,4-dioxane, THF
$CH_3CH(O\textit{i}Bu)OCOCF_3/EtAlCl_2$	Amine: 2,6-dimethylpyridine
CF_3SO_3H (no activator)	Sulfide: Me_2S, Et_2S, etc.

In the case of IB, the initiating system for living cationic polymerization consists of an initiator/Lewis acid activator (BCl_3 or $TiCl_4$) couple in conjunction with an externally added Lewis base (Table 2.5) [20].

The utilized Lewis acids concern tertiary chlorides, esters, ethers and alcohols. The applicibility of Lewis bases with the following structures are also reported.

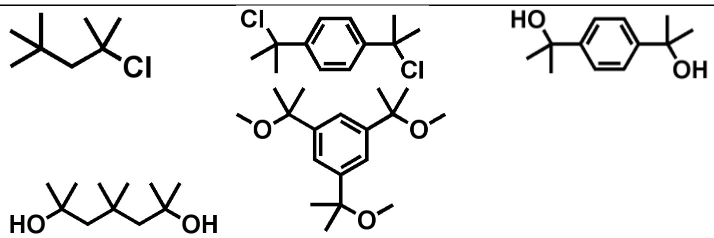
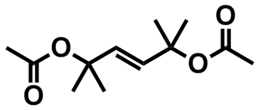
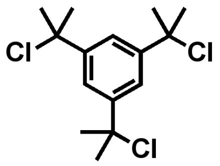
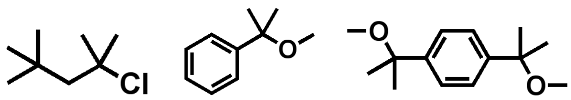
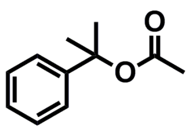


Lewis bases can be applied to the following systems:

i. Tertiary chlorides (e.g. cumyl chloride) in conjunction with BCl_3 is reported to be an efficient "inifer" system with chain transfer and termination steps. External addition of a Lewis base on the other hand converts the non-living nature of the system into a living polymerization. For initiators such as tertiary esters and ethers, addition of bases only improves the polymerization characteristics and allows synthesis of polymers with lower polydispersities.

ii. $TiCl_4$ is not an appropriate initiator for living cationic polymerizations due to its excessive activity probably, resulting from the hardly removable trace amount of water. Use of tertiary ethers in conjunction with $TiCl_4$; however, results with *in situ* formation of electron donor species ($TiCl_3OCH_3$) which regulates the rate of polymerization [145].

Table 2. 5 : Inititiators for Lewis base-assisting living cationic polymerization of IB.

Initiating System	Initiator	Reference
Cationegen / BCl_3 / Lewis base		[145]
Cationegen / BCl_3 / Lewis base		[146]
Cationegen / BCl_3 / Lewis base		[147]
Cationegen / $TiCl_4$ / Lewis base		[145]
Cationegen / $TiCl_4$ / Lewis base		[148]

iii. Living polymerization of isobutylene requires electron donating structures with higher basicity compare to the systems dealing with vinyl ethers. Moreover, it needs a lower concentration of base (nearly equal to the concentration of initiator) whereas vinylether systems seek for excess amount of Lewis bases [149].

iv. The most significant development is that such living system with added Lewis bases at -80 °C yielded almost monodisperse PIB (PDI<1.1) [145]. Such controlled manner is not possible using these initiating systems without added base.

2.3.2.3 Initiating systems with added salts

Another noteworthy initiating system, which is based on hydrogen iodide and a tetraalkylammonium salt ($R_4N^+A^-$; R: *n*-alkyl; A^-: ClO_4^-, PF_6^- etc.), allowing living polymerization of IBVE in CH_2Cl_2 at -15 to -40 °C was reported by Nuyken and Kröner [103, 150]. Such polymerization also relies on the iodide counteranion derived from hydrogen iodide, but no Lewis acid activator is employed for activation of carbon-halogen bond of the growing end. In fact, the role of the ammonium salt is not very well understood.

A variety of combinations of 1-phenylethyl halide (PhE-X; X = C1, Br), metal halides (MX_n, = $SnCl_4$, $SnBr_4$, $EtAlCl_2$), and added salts ($n$$Bu_4N^+Y^-$; Y^- = Cl^-, Br^-, I^-, ClO_4^-) were employed as new initiating systems for living styrene polymerization by Sawamoto and coworkers [151, 152]. The concept for the living cationic polymerization of styrene with added salt relies on the nucleophilic stabilization of the unstable growing carbocation and related control of its ionic dissociation, as demonstrated on the example of the PhE-Cl/$SnCl_4$ initiating system (Figure 2.20).

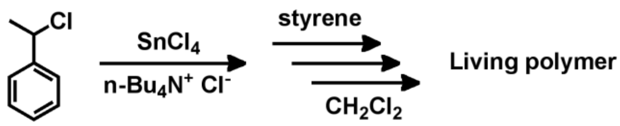


Figure 2.20 : Living cationic polymerization of styrene triggered by PhE-Cl/$SnCl_4$ initiating system in the presence of a salt.

Styrene and derivatives can be polymerized this system. In a typical example, initiating system consitsts of l-phenylethyl chloride, $SnCl_4$ and *tetra-n*-butylammonium chloride (n-Bu_4NCl). This system is considered as the first cationic initiating system for preparation of PSt with narrow molecular weight distribution (~1.1). $C_6H_5CH(CH_3)$-Cl/$SnCl_4$ (+n-Bu_4NCl), HSO_3CH_3/ $SnCl_4$ (+n-Bu_4NCl) and

CH3CO-ClO4/none (+n-Bu_4NCl) are good example of such initiating system for living cationic polymerization of styrene.

N-Vinylcarbazole is another monomer can be polymerized by this initiating system.

2.4 Photo-initiated Polymerizations

Photo-initiated polymerization, or briefly photopolymerization, is usually described as a typical process that transforms functional monomers,oligomers, and polymers into higher molecular weight polymers by a chain reaction initiated by reactive species (free radicals or ions), which are generated from photo-sensitive compounds, namely photoinitiators (PIs) and/or photosensitizers (PSs), by UV-Vis light irradiation. The great advantages of photopolymerization offers high rate of polymerization at ambient temperatures, lower energy cost, and solvent-free formulation, thus elimination of air and water pollution.[8, 9] It also devotes temporal and spatial control of the polymeriztion when high initiation rate is reached.[13]

In recent decades, photopolymerization has become powerful industrial process widely used in various applications including coatings, inks, adhesives, varnishes, electronics, photolithography, printing plates, optical waveguides and dyes due to its excellent advantages [7-9, 153]. Photopolymerization is employed in production of laser videodiscs, curing of acrylate dental fillings [154], and fabrication of 3D objects [155] as well. “Many studies involving various photopolymerization processes have been continuously conducted in biomaterials for bones and tissue engineering, microchips, optical resins and recoding media, surface relief gratings, anisotropic materials, polymeric photo-optical control materials, clay and metal nanocomposites, photoresponsive polymers, liquid crystalline materials, interpenetrated networks, microlenses, multilayers, surface modification, block and graft copolymerization, two-photon polymerization, spatially controlled polymerizations, topochemical polymerization, solid-state polymerization, living/controlled polymerization, interfacial polymerization, mechanistically different concurrent polymerizations, pulsed laser polymerization, polymerizations in microheterogenous media, and so forth” as reviewed in the thesis by Aydogan [153].

In a usual photopolymerization, the wavelength or range of wavelengths of the initiating source is determined by the reactive system including the monomer(s), the initiator(s), and any photosensitizers, pigments or dyes which may be present. Principally, emission wavelength range of light source must overlap wavelegth range of light absorption by the PIs to produce reactive species efficiently [156]. In this process the PI is switched to an electronically excited state (PI*):

$$PI \xrightarrow{h\nu} PI^* \qquad \textbf{(2.4)}$$

The lifetime of PI* is too short, usually less than 10^{-6} sec it can be decomposed into initiating species (I•, I^+ or I^-) or decay back to PI (with emission of light and heat):

$$PI^* \begin{cases} \longrightarrow PI \\ \longrightarrow I\bullet,\ I^+ \text{ or } I^- \end{cases} \qquad \textbf{(2.5)}$$

These reactive species (I•, I^+ or I^-) can react with a quencher (Q) and be quenched or can react with monomer (M) initiate propagation of a polymer chain:

$$I\bullet,\ I^+ \text{ or } I^- \begin{cases} \xrightarrow{Q} I\!-\!Q \\ \xrightarrow{M} \text{polymer} \end{cases} \qquad \textbf{(2.6)}$$

Upon generation of active centers, photopolymerizations propagate and terminate in the same manner as traditional (i.e. thermal) polymerizations. Although photopolymerization can be initiated radically, cationically and anionically, much effort has been devoted to free radical and cationic systems mainly due to the availability of a wide range of photoinitiators and the great reactivity of monomers.

2.4.1 Photo-initiated free radical polymerization

Photoinitiated free radical polymerization is one of the most widely employed route in industrial applications because of its applicability to a wide range of formulations based on acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV or visible range.

It consists of four distinct stages: Photoinitiation, propagation, chain transfer and termination.

i) Photoinitiation step involves absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit.

ii) Propagation step involves repeated addition of monomer units to the chain radical produces the polymer backbone.

iii) Chain transfer step involves termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and formation of new radicals capable of initiating other chain reactions.

iv) Termination step involves termination of chain radicals by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

Photoinitiation:

$$PI \xrightarrow{h\nu} PI^*$$

$$PI^* \longrightarrow R_1^{\cdot} + R_2^{\cdot}$$

$$R_1^{\cdot} + M \longrightarrow R_1{-}M^{\cdot}$$

Propagation:

$$R_1{-}M^{\cdot} + M \longrightarrow R_1{-}MM^{\cdot}$$

$$R_1{-}MM^{\cdot} + (n\text{-}2)M \longrightarrow R_1{-}M_n^{\cdot}$$

Transfer:

$$R_1{-}M_n^{\cdot} + R{-}H \longrightarrow R_1{-}M_n{-}H + R^{\cdot}$$

$$R^{\cdot} + M \longrightarrow R{-}M^{\cdot}$$

Termination:

$$R_1{-}M_n^{\cdot} + R_1{-}M_m^{\cdot} \longrightarrow R_1{-}M_{n+m}{-}R_1$$

$$R_1{-}M_n^{\cdot} + R_2^{\cdot} \longrightarrow R_1{-}M_n{-}R_2$$

$$R_1{-}M_n^{\cdot} + R_1{-}M_m^{\cdot} \longrightarrow R_1{-}M_n + R_1{-}M_m$$

$$R_1{-}M_n^{\cdot} + R_2^{\cdot} \longrightarrow R_1{-}M_n + R_2$$

Figure 2.21 : Elementary reactions in free radical photopolymerization.

The role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light.

In most cases of photoinduced polymerization, initiators are used to generate radicals. Photoinitiators are generally divided into two classes, *Type I* and *Type II*, according to the process by which initiating radicals are formed.

2.4.1.1 *Type I* photoinitiators (unimolecular photoinitiator system)

Photoinitiators termed unimolecular are so designated because the initiation system involves only one molecular species interacting with the light and producing free-radical active centers. These substances undergo a homolytic bond cleavage upon absorption of light (eq. 2.7). The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction (eq. 2.8).

$$PI \xrightarrow{h\nu} PI^* \xrightarrow{k} R_1\cdot + R_2\cdot \qquad \textbf{(2.7)}$$

$$\frac{d[R_1^\bullet]}{dt} = \frac{d[R_2^\bullet]}{dt} = k[PI^*] \qquad \textbf{(2.8)}$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ($\phi_{R\bullet}$) (eq. 2.9).

$$\Phi_{R\cdot} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \qquad \textbf{(2.9)}$$

Hypothetically, cleavage type photoinitiators should have a $\phi_{R\bullet}$ value of two since two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the excited state to other, ground state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to monomer thus initiating polymerization. The other radical usually undergoes either combination or disproportionation. The initiation efficiency of photogenerated radicals (f_P) can be calculated by the following formula:

$$f_P = \frac{\text{Number of chain radicals formed}}{\text{Number of primary radicals formed}} \qquad \textbf{(2.10)}$$

The overall photoinitiation efficiency is expressed by the quantum yield of photoinitiation (ϕ_P) according to the following equation:

$$\Phi_P = \Phi_R \cdot x\ f_P \qquad \textbf{(2.11)}$$

Regarding the energy neccessity, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to ensure long term storage stability.

Initiating radicals, formed by direct photofragmentation process (α or less common β cleavage) of *Type I* photoinitiators upon absorption of light, are capable of triggering polymerization. As illustrated in Figure 2.22, the photoinitiator forms an excited singlet state, which then undergoes rapid intersystem crossing to form a triplet state. In the triplet state, two radicals (benzoyl and benzyl radicals) are generated by α-cleavage fragmentation. The benzoyl radical is the major initiating species, while, in some cases, the benzyl radical may also contribute to the initiation.

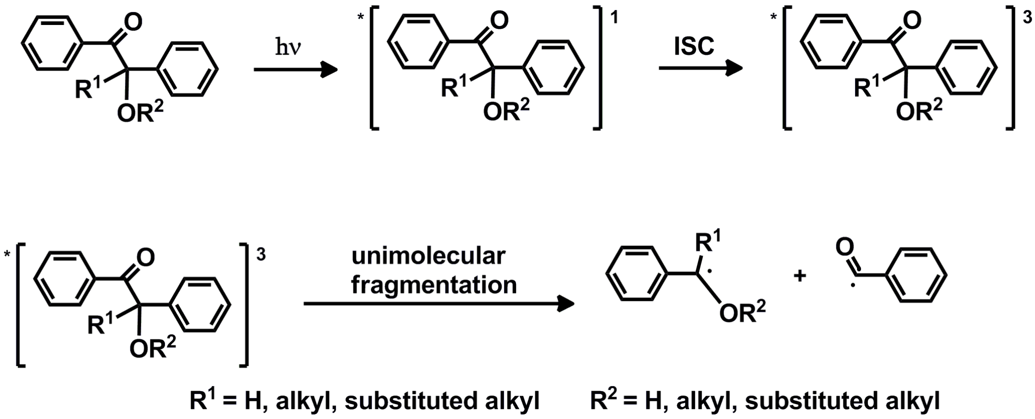


Figure 2.22 : Formation of initiating radicals from decomposition of a *Type I* photoiniator.

Most of the *Type I* photoinitiators are aromatic carbonyl compounds with appropriate substituents. Benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α-aminoketones and acylphosphine oxides are the most efficient ones (Table 2.6) [157-160].

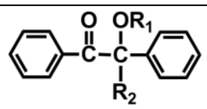
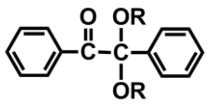
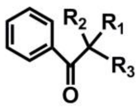
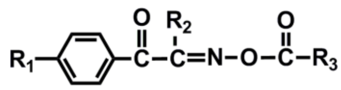
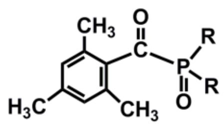
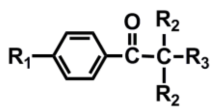
2.4.1.2 *Type II* photoinitiators (bimolecular photoinitiator systems)

The excited states of certain compounds do not undergo *Type I* reactions because their excitation energy is not high enough for fragmentation (i.e., their excitation energy is lower than the bond dissociation energy). The excited molecule can, however, react with another component of the polymerization mixture (co-initiator

(COI)) to produce initiating radicals (eq. 2.12). In this case, radical generation follows second-order kinetics (eq. 2.13).

Classic *Type II* photoinitiators include aromatic carbonyls such as benzophenone and derivatives [161-164], thioxanthone and derivatives [165-169], benzyl [162], quinines [162], and organic dyes [170-175], whereas alcohols, ethers, amines, and thiols are used as hydrogen donors. Recently, thiol and carboxylic acid derivatives of thioxanthones have been reported to initiate photopolymerization without co-initiators as they contain functional groups with H-donating nature [176-178].

Table 2.6 : Structures of typical *Type I* radical photoinitiators.

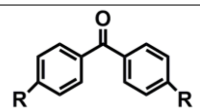
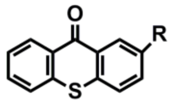
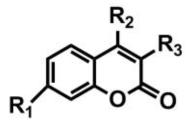
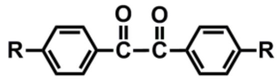
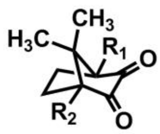
Photoinitiators	Structure	λ_{max} (nm)
Benzoin ethers	 R_1 =H, alkyl R_2 =H, substituted alkyl	323
Benzil ketals	 R =CH_3, C_3H_7, CH_2	365
Acetophenones	 R_1 = OCH_3, OC_2H_5 R_2 = OCH_3,H R_3 = C_6H_5,OH	340
Benzyl oximes	 R_1=H, SC_6H_5 R_2= CH_3,C_6H_{13} R_3= C_6H_5, OC_2H_5	335
Acylphosphine Oxides	 R= C_6H_5, OCH_3	380
Aminoalkyl phenones	 R_1 = SCH_3, morpholine R_2 = CH_3,CH_2Ph, C_2H_5 R_3 = $N(CH_3)_3$, morpholine	320

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^* + \mathrm{COI} \xrightarrow{k} \mathrm{R_1}\cdot + \mathrm{R_2}\cdot \quad \mathbf{(2.12)}$$

$$\frac{d[R_1^{\bullet}]}{dt} = \frac{d[R_2^{\bullet}]}{dt} = k[PI^*][COI] \quad \mathbf{(2.13)}$$

Alternative approach concerns the attachment of both chromophoric and hydrogen donating groups into polymer chains [179-193]. This way, the odor and toxicity problems observed with the conventional photoinitiators and amine hydrogen donors were overcome.

Table 2.7 : Structures of typical *Type II* photoinitiators.

Photoinitiator	**Structure**	**λ_{max} (nm)**
Benzophenones	 R = H, OH, $N(C_2H_5)_2$, C_6H_5	335
Thioxanthones	 R = H, Cl, isopropyl	390
Coumarins	 R_1 = $N(C_2H_5)_2$, $N(CH_3)_2$ R_2 = CH_3,eyelopentane R_3 = benzothiazole, H	370
Benzils	 R = H, CH_3	340
Camphorquinones	 R_1 = CH_3, H R_2 = H, CH_3	470

A novel thioxanthone based photoinitiator have also been developed possesssing anthracene group that does not require an additional hydrogen donor for radical formation and initiates the polymerization of both acrylate and styrene monomers in the presence of air [194]. In addition, TX-A possesses excellent optical absorption properties in the near-UV spectral region, ensuring efficient light absorption. Quite recently, thioxanthone-fluorene carboxylic acid (TX-FLCOOH) and its sodium salt

(TX-FLCOO$^-$ Na$^+$) were synthesized as efficient photoinitiators in visible light [195]. In fact, photoinitiators with higher wavelength absorption characteristics are desired as they cost lower energy and are defined to be "green".

Typical photoinitiators for *Type II* system are listed in Table 2.7.

Radical generation by Type II initiating systems has two distinct pathways:

Hydrogen abstraction from a suitable hydrogen donor

Bimolecular hydrogen abstraction is limited to diaryl ketones [196]. The free radical generation process is the H-abstraction reaction of triplet photoinitiator from hydrogen donors (R-H) such as amines and alcohols. The radical derived from the donor can initiate the polymerization, whereas ketyl radicals stemming from aromatic carbonyl compound are usually not reactive toward vinyl monomers because of bulkiness, the delocalization of the unpaired electrons, or both. The overall process is depicted in the example of benzophenone in Figure 2.23.

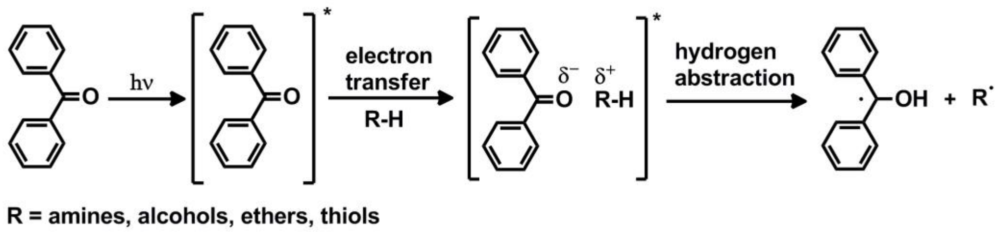


Figure 2.23 : Formation of initiating radicals from photolysis of *Type II* photoinitiator in the presence of suitable hydrogen donor.

Photoinduced electron transfer reactions and subsequent fragmentation

Photoinduced electron transfer is a more general process, which is not limited to a certain class of compounds and is more important as an initiation reaction comprising the majority of bimolecular photoinitiating systems. The photoexcited compounds (sensitizer) can act as either an electron donor with the coinitiator as an electron acceptor or vice-versa. The radical ions obtained after the photoinduced electron transfer can generally undergo fragmentation to yield initiating radicals (eq. 2.14-2.16).

The electron transfer is thermodynamically allowed, if Gibbs Energy Change (ΔG) calculated by the Rehm-Weller equation (eq. 2.17) is negative [197].

$$PS \xrightarrow{h\nu} PS^{*} \tag{2.14}$$

$$PS^{*} + A \longrightarrow PS^{\cdot +} + A^{\cdot -} \longrightarrow R_1^{\cdot} + R_2^{\cdot} \tag{2.15}$$

$$PS^{*} + D \longrightarrow PS^{\cdot -} + D^{\cdot +} \longrightarrow R_1^{\cdot} + R_2^{\cdot} \tag{2.16}$$

$$\Delta G = F\,[E_{1/2}^{ox}\,(D/D^{+\cdot}) - E_{1/2}^{red}\,(A/A^{-\cdot})] - E_S + \Delta E_c \tag{2.17}$$

where
F = Faraday constant
$E_{1/2}^{ox}\,(D/D^{+\cdot})$, $E_{1/2}^{red}\,(A/A^{-\cdot})$ = redox potentials of the donor and acceptor
E_S = excitation state of the reactive state of the sensitizer; $E_S = h\nu$
ΔG = Coulombic stabilization energy

Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems. Dyes comprise a large fraction of visible light photoinitiators because their excited electronic states are more easily attained. Coinitiators, such as tertiary amines, iodonium salts, triazines, or hexaarylbisimidazoles, are required since dye photochemistry entails either a photo-reduction or photo-oxidation mechanism. Numerous dye families are available for selection of an appropriate visible initiation wavelength; examples of a thiazine dye (with an absorption peak around 675 nm), acridine dyes (with absorption peaks around 475nm), xanthene dyes (500–550 nm), fluorone dyes (450–550 nm), coumarin dyes (350–450 nm), cyanine dyes (400–750 nm), and carbazole dyes (400 nm) [198-201]. The oxidation or reduction of the dye is dependent on the co-initiator; for example, methylene blue can be photo-reduced by accepting an electron from an amine or photo-oxidized by transferring an electron to benzyltrimethyl stannane [199]. Either mechanism will result in the formation of a free-radical active center capable of initiating a growing polymer chain.

2.4.2 Photo-initiated anionic polymerization

Anionic photopolymerization had received less attention compared to cationic and free radical counterparts [156]. However, anionic photopolmerization recieve further attention after introduction of a new initiating system depending on *trans*-$Cr(NH_3)_2(NCS)_4^-$(Reineckate anion). In fact, irradiation of ligand field absorption bands of transition metal complexes results in ligand substitution reactions. This process can be employed for the controlled photogeneration of anions from a stable precursor. *trans*-$Cr(NH_3)_2(NCS)_4^-$ is considered as an ideal anion source since

$K^+[trans\text{-}Cr(NH_3)_2(NCS)_4^-]$ is readily soluble in a variety of organic solvents, resistant to thermal substitution in nonhydroxylic media, and its quantum efficiency is quite high (> 10%) for releasing of NCS^- (eq. 2.18) upon ligand field excitation with near-UV/Vis light [202-204]. In the presence of a monomer containing electron-withdrawing substituents to stabilize the negative charge, such as ethyl α-cyanoacrylate, anionic polymerization is initiated.

$$\textit{trans}\text{-}Cr(NH_3)_2(NCS)_4^- \xrightarrow[\text{solvent}]{h\nu} Cr(NH_3)_2(NCS)_3(\text{solvent}) + NCS^- \qquad \textbf{(2.18)}$$

In another report, acyl-substituted ferrocenes, namely benzoylferrocene and 1,1'-dibenzoylferrocene, were utilized as photoinitiator for the anionic polymerization of ethyl α-cyanoacrylate [205]. Generation of anionic initiating species is schematized in Figure 2.24.

$Pt(acac)_2$ or a cyclopentadienyl complex of Fe or Ru have been also utilized as anionic photoinitiators [206].

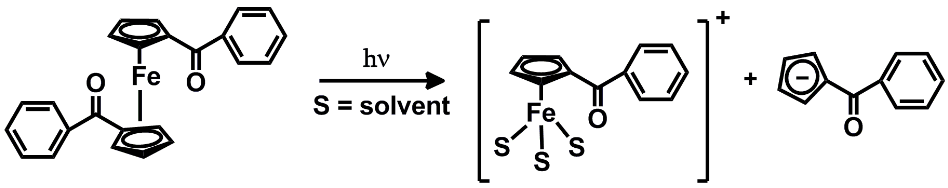


Figure 2.24 : Generation of anionic species from photolysis of 1,1'-dibenzoylferrocene.

2.5 Photo-initiated cationic polymerization

Much effort has been devoted to free radical photopolymerizations [10, 11] mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers. Although the most popular industrial applications are based on the photo-initiated free radical polymerization there are some drawbacks associated with this type of polymerization. For instance, free radical species are inhibited by molecular oxygen and inhbites almost polymerization based on free radicals. Moreover, post-cure limitations, which may affect the properties of the final product and toxicity of the monomers are another drawbacks. Several advantages of the photo-initiated cationic polymerization over the photo-initiated free radical polymerization have also been reported [8, 9, 12]. Cationic photopolymerization overcomes volatile emissions, limitations due to molecular oxygen inhibition, toxicity, and problems associated to high viscosity. Furthermore, once initiated, cationically polymerizable monomers such as vinyl ethers and epoxides undergo dark-polymerization in which they slowly polymerize without radiation.

General scheme for photo-induced cationic polymerization is depicted in Figure 2.25. A photo-sensitive compound, namely photoinitiator (PI), absorbs incident light and undergoes decomposition leading to production of initiating species. Active species, namely a radical cation ($R^{+\cdot}$) in turn, react with cationic polymerizable monomers (M), and yield polymer (Figure 2.25).

$$PI \xrightarrow{h\nu} H^{+} + R^{+\cdot} + \text{other products}$$

$$R^{+\cdot} + M \longrightarrow \text{polymer}$$

$$H^{+} + M \longrightarrow \text{polymer}$$

Figure 2.25 : General scheme of photo-initiated cationic polymerization.

2.5.1 Direct initiating systems for cationic photopolymerization

Since the most significant element of photo-initiated cationic polymerization is the cationic PIs, their synthesis and initiation mechanism is one of the most important research area for polymer science. A compound can be said to be a useful PI if it has high absorbtion of light in the UV-Vis region and high quantum yield which can be defined as the number of initiating species formed per photon absorbed. Additionally, the reactivity of the initiating species is an important issue for an efficient photoinitiator.

Onium salts are the most widely used cationic photoinitiators. They contain chromophopric groups as the light sensitive body with heteroatoms as cationic centers in the structure. As counterions, mostly inorganic metal complex anions are used [207]. In recent years, onium salts with highly nucleophilic counterions such as Cl^{-}, Br^{-} and I^{-} have also been used in conjuction with Lewis acids [21-23, 25].

So far, the most frequently used onium salts are aryldiazonium, diaryl iodonium, triarylsulfonium and tetra alkyl phosphonium salts with non-nucleophillic counter ion (Figure 2.26).

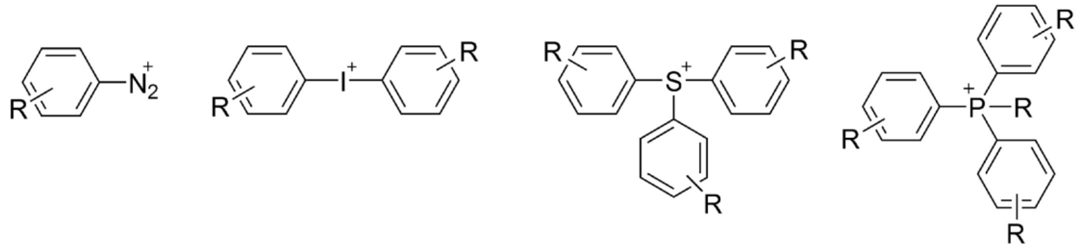


Figure 2.26 : Chemical structures of common onium salt PIs.

Recently, other onium salts like *N*-alkoxy pyridinium [208], allylic onium [209, 210], trialkyl phenacyl ammonium [211], and dialkyl phenacyl sulfonium salts [212, 213] of the following structures (Figure 2.27) are shown to be convenient for producing the initiating species for cationic polymerization.

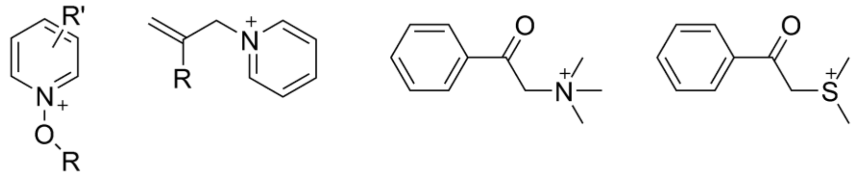


Figure 2.27 : Phenacyl based onium salts.

Generally, these onium salts generate initiating species upon irradiation at appropriate wavelengths. The mechanism usually refered to as direct photoinitiation [207], and represented in Figure 2.25. The cationic polymerization of suitable monomers is initiated by both radical cation and/or protonic acid that are generated photochemically upon photolysis of cationic photoinitiators. Most photoinitiators, used in cationic photopolymerization mainly absorbs light between 225 to 350 nm. For practical applications, however, they are expected to absorb light at quite longer wavelengths. Several attempts have been described to overcome this problem. Three modes of indirect initiation are possible depending on the role played by the additives in the initiation of the polymerization (*vide infra*).

2.5.1.1 Aryldiazonium salts

Being easily obtained starting from the aniline derivates, these salts produce Lewis acids upon irradiation which can initiate polymerization itself or react with a hydrogen donor compound in the reaction mixture to yield Brønsted acid which is capable of initiating appropriate monomers.

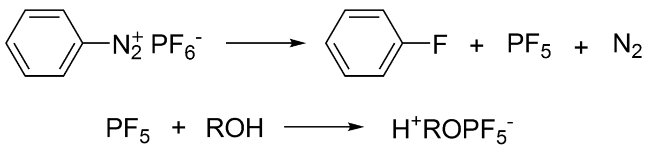


Figure 2.28 : Photoinitiating mechanism of aryldiazonium salts.

Despite having high quantum yields changing in the range 0.3 and 0.6 [214], aryldiazonium salts suffer from their thermal instability which limits their practical applications as a long time storage is quiet impossible. Furthermore, evolution of nitrogen gas during polymerization causes bubbling to yield porous materials (Figure 2.28).

2.5.1.2 Diaryliodonium salts

Diaryliodonium salts (Figure 2.29) are the most frequently used halonium salts as they are easy to obtain and quite reactive [215-217]. The nucleophillic halogen counter-ion must be replaced by a non-nucleophillic anion in order to prevent the termination of cationic polymerization.

As they generally have low spectral sensitivity, an electrophillic substitution reaction can be applied on the aromatic rings to posses electron donating species which can move absorption bands to lower energies. Alternatively, some special additives, namely photosensitizers, can be used to carry out polymerization at longer wavelengths.

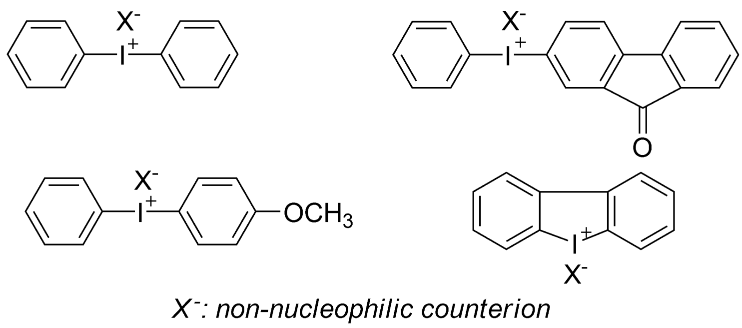
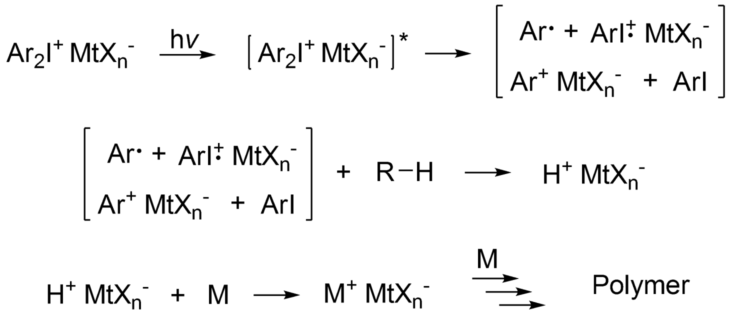


Figure 2.29 : Commonly used diaryl iodonium PIs.

Photolysis of diaryliodonium salts take place either through homolytic or heterolytic cleavage of the halogen-aryl bond to form species which react with a hydrogen donor compound to yield a Brønsted acid that initiates polymerization (Figure 2.30).



RH: solvent or monomer
MtX_n^-: PF_6^-, SbF_6^-, AsF_6^-, etc.

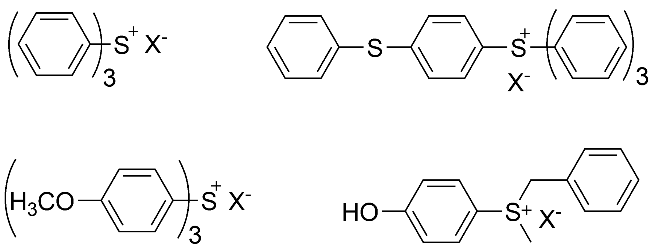
Figure 2.30 : Photo-initiated polymerization by irradiation of diphenyliodonium hexafluorophosphate.

Notably, the electron donating subtituents on the aromatic structures not only shifts absorption bands to longer wavelengths, but also favors photolysis of diaryliodonium salts to afford higher polymerization rates.

2.5.1.3 Sulphonium salts

Triaryl sulphonium salts (TPS) are generally produced by the method of Pitt [218]: a Friedel–Crafts condensation of aromatic hydrocarbons with sulphur dichloride, followed by chlorination and further condensation. Various alkylaryl sulphonium salts may be synthesized by an alkylation of mercaptobenzene [219].

Sulphonium salts that have been the most common utilized for cationic polymerizations are compiled in Figure 2.31 [220-222].



X^-: non-nucleophilic counterion

Figure 2.31 : Common sulphonium salts.

The photolysis mechanism is similar with the diaryliodonium salts. When irradiated in appropriate wavelengths, TPS's undergo either a homolytic or a heterolytic cleavage followed by a proton release after some additional steps which are summarized in (Figure 2.32).

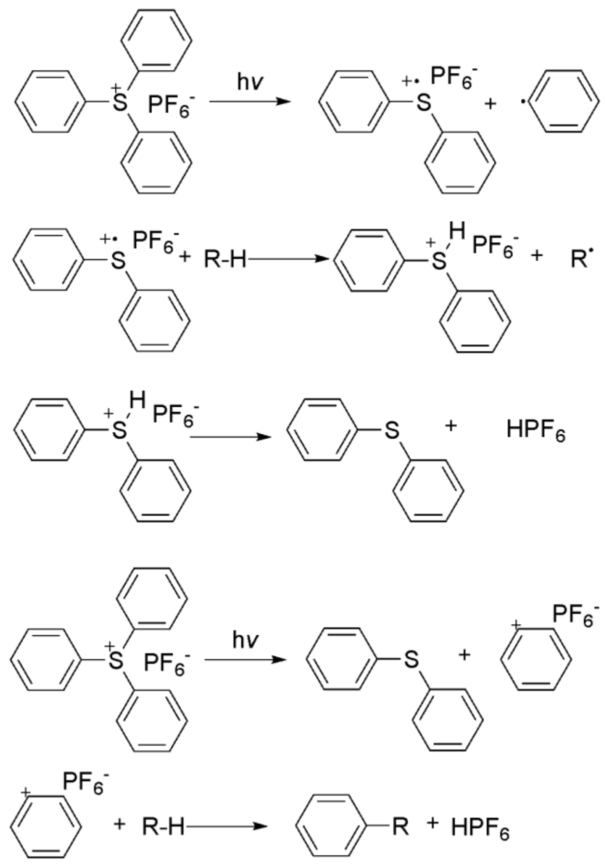


Figure 2.32 : Photochemically generation of protons from triarylsulphonium hexafluorophosphate.

In some special cases, a Brønsted acid does not need to be the only initiating species. If heterolytical cleavage of one of the alkyl groups results with a stable carbocation, polymerization can possibly be initiated by this intermediate structure.

Recently, Endo and coworkers have developed novel sulfonium type initiators which can initiate polymerization either upon irradiation or thermal treatment. In addition, these photoinitiators are shown to be functional for both cationic and radical polymerization. This dual activity is particularly important in hybrid curing systems for coatings and adhesions [223].

Recently, Crivello and coworkers have developed synthesis of a new initiating system called *S*,*S*-dialkyl-*S*-(3, 5-dimethyl-4-hydroxyphenyl)-sulfonium salts (4HPS) [224-226] with absorption maxima in the middle UV region. More recently, the same group also reported a facile synthesis of its isomeric counterparts, *S*,*S*-dialkyl-*S*-(3, 5-dimethyl-2-hydroxyphenyl) sulfonium salts (2HPS).

Being poorly soluble in common monomers used in photocationic curing, these sulfonium compounds attract little attention. However, derivating the structure with possessing different alkyl groups, improved solubility characteristics can be achieved. Notably, these salts are demonstrated to be of high photosensitivity (Φ=0,12-0,31) and good thermal stability.

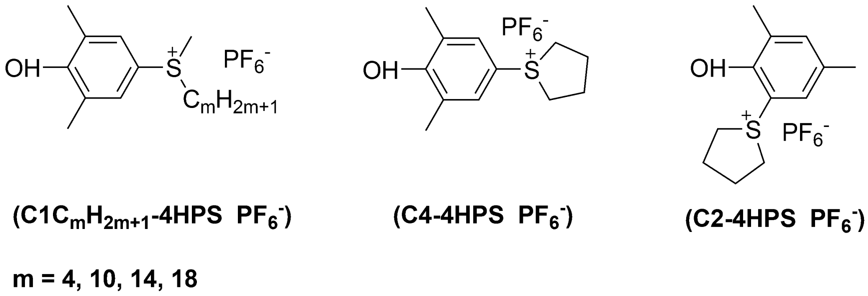


Figure 2.33 : Chemical structures of HPS salts.

2.5.1.4 Phosphonium salts

The preparation of phosphonium salts is based on the reaction of chloromethylated or bromomethylated aryl compounds with the corresponding phosphines [227-231]. As illustrated in Figure 2.34, phosphonium salts with absorptions acceptable for direct photolysis have been synthesized.

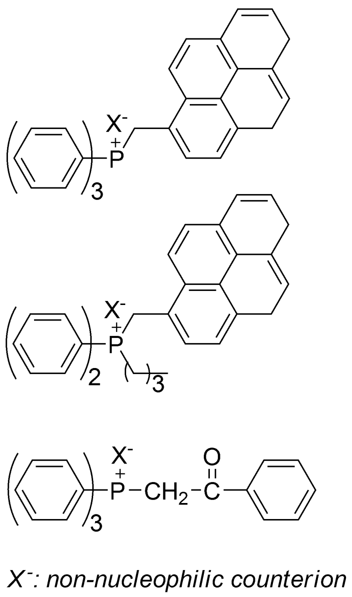


Figure 2.34 : Novel phosphonium salts.

Benzyl or pyrenylmethyl groups containing phosphonium salts produce the respective carbon centered cations after a heterolytic bond rupture according to Figure Figure 2.35 [232-234]. These cations are assumed to be the initiating species in cationic polymerization.

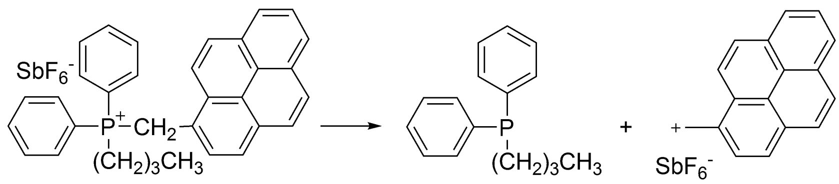


Figure 2.35 : Generation of cationic species upon photolysis of pyrene substituted phosphonium salt.

Because of releasing very stable cations upon irradiation, phosphonium salts containing pyrenylmethyl groups are excellent initiators for photopolymerization of convenient monomers like epoxides and vinyl monomers [230, 234].

2.5.1.5 *N*-Alkoxy pyridinium salts

N-Alkoxy Pyridinium salts are obtained with relatively high yields by a reaction of pyridine *N*-oxides with a triethyloxonium salt in methylene chloride or chloroform [208]. Quinolinium salts can also be prepared from the corresponding *N*-oxides [235]. In both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions. The most frequently used photoinitiators of this type are shown in Figure 2.36. The spectral response of these salts is in 260-310 nm range [208].

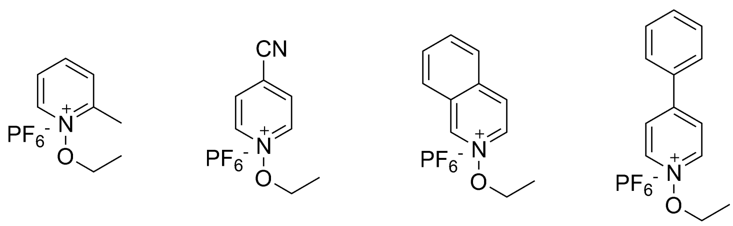


Figure 2.36 : Widely used *N*-alkoxy pyridinium salts.

When irradiated in suitable wavelengths, these salts readily initiate polymerization of appropriate monomers according to the following mechanism as exemplified for the case of *N*-ethoxy–2-methylpyridinium hexafluorophosphate (EMP^+ PF_6^-) in Figure 2.37.

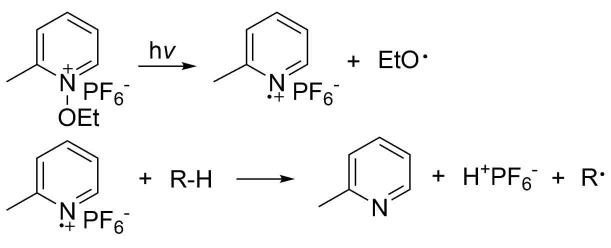
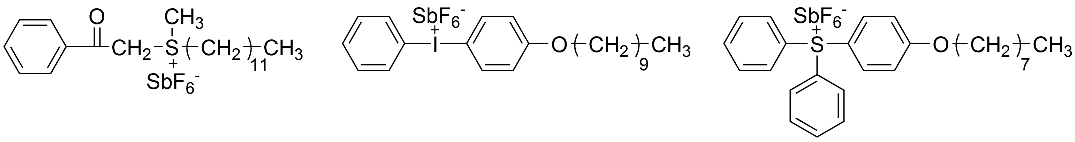


Figure 2.37 : Formation of protonic acid during photo-induced decomposition of EMP^+ PF_6^-.

2.5.1.6 Phenacyl sulfonium salts

Being thermally rather stable and highly photoresponsive, phenacyl sulfonium salts are significantly attractive for photo-induced cationic polymerization [236, 237]. Despite being easily obtained, they suffer from their poor solubility in common monomers which make them unpreferable. However, novel phenacyl sulfonium salts were synthesized via deriving the structure with alkyl substituents to improve solubility properties [212]. Similar strategy was also followed to improve the solubility of iodonium and sulphonium salts. The following chart contains the chemical structures of the salts having good solubility (Figure 2.38).



(DPS-12) **(IOC-10)** **(SOC-8)**

Figure 2.38 : Chemical structure of phenacyl sulfonium salts.

2.5.1.7 Phenacylammonium salts

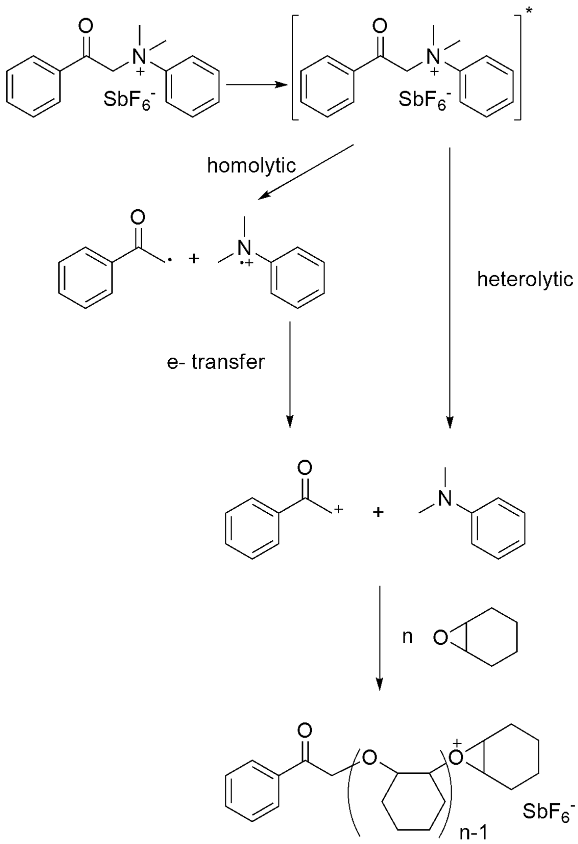


Figure 2.39 : Photo-initiated cationic polymerization of CHO using a phenacylammonium salt as a PI.

Phenacyl anilinium salts have light absorbtion 300–350 nm which make them preferable for photo-induced cationic polymerization. Upon irradiation these salts undergo either a heterolytic cleavage or a homolytic cleavage followed by an elecron transfer to yield a cation intermediate which in turn can initiate polymerization of appropriate monomers [211]. Figure 2.39 shows the mechanism in detail. As can clearly be seen, the photolysis of phenacylammonium salts are irreversible and different than their sulfonium analogs [238].

2.5.1.8 Polymer bound onium salts

Onium salts may be incorporated into polymers. These polymeric initiators often show good miscibility with monomers and polymers generated in the course of the polymerization. Furthermore, a lower order of toxicity is found owing to the inability of high molecular weight polymers to be absorbed by biological systems.

Incorporating iodonium and sulfonium salts to the polymer backbone was achieved and used as macrophotoinitiators [239, 240]. Easy to incorporate, *N*-oxides also found applications in this area [241-243]. In a recent study, Yagci and coworkers introduced *N*-oxide functions to the chain end of PSt via substitution reaction of halogen terminated polystyrenes obtained by ATRP (Figure 2.40).

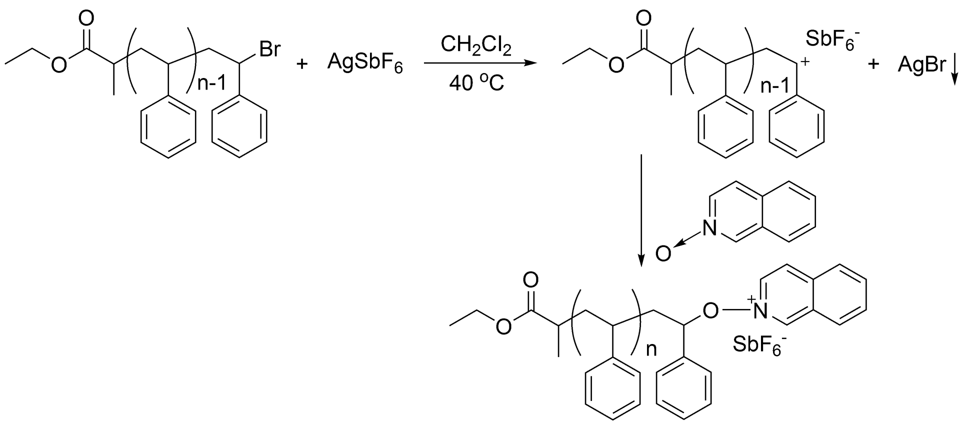


Figure 2.40 : Synthesis of *N*-oxide functionalized PSt by ATRP.

Although being cationic photoinitiators, these polymers were used to form block copolymer via a free radical mechanism when irradiated in the presence of MMA [244].

In another study, the same group attached 4-phenyl-pyridinium *N*-oxide as pendant groups to the polychloromethyl styrene and its block copolymer with PSt via nucleophillic substitution with chloride as leaving group. The obtained macrophotoinitiators were used to obtain graft copolymers by grafting from method of MMA, and hydroxyl functionalization [245].

2.5.1.9 Iron arene complexes based photoinitiators:

Iron arene complexes or ferrocenium salts are attractive photoinitiators for cationic polymerization of epoxides [246] since they are readily prepared from non-expensive starting materials and their photolysis is extremely efficient in the UV and visible regions [247]. Iron arene complexes are usually prepared from ferrocene by exchange of one cyclopentadienyl moiety for a neutral aromatic species in the presence of a Lewis acid, followed by metathesis with a salt possessing an appropriate counter anion [248-250]. In addition, their spectral responses are localized in the middle region of UV spectrum which can be extended easily to visible light regions by exchange of their ligands.

Upon irradiation, ferrocenium salts lose their arene ligands leading to generation of iron-based Lewis acids that coordinate with epoxide monomers. One of the monomers undergoes ring-opening followed by addition of a new monomer. Arene complex initiators are convenient for polymerization of only epoxides, which are able to coordinate with iron. Vinyl monomers can not be polymerized with this type of initiators. The photo-initiated cationic polymerization of epoxides by iron complexes is indicated in Figure 2.41.

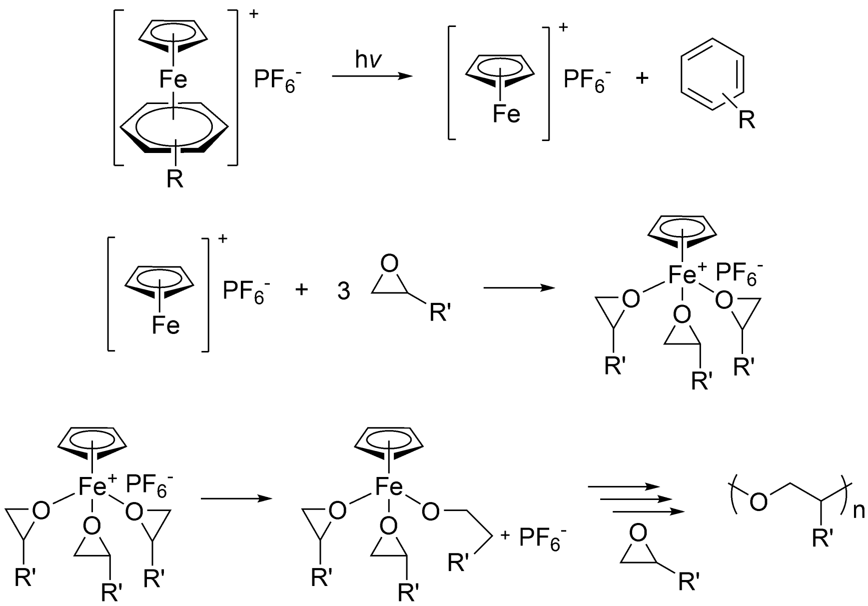


Figure 2.41 : Photo-initiated cationic polymerization of epoxides by iron complexes.

Iron arene complexes have been successfully applied in photopolymerization and UV curing of various epoxides [251-256]. Multifunctional solid novolac resins were also polymerized by using iron arene complexes were successfully. The irradiation of these formulations gives a latent image; the crosslinking itself is started only after heating for 3 min at 100 ^{o}C. The fact that thermal curing can be applied long time after the irradiation has also been utilized in dark curing adhesives for opaque substrates.

2.5.1.10 Non-salt photointiators for cationic polymerization

As stated several times in the text, onium salts are the most commonly used photoinitiators in cationic photopolymerization. However, their disadvantages including limited spectral response characterized under 300 nm, poor solubility in organic solvents and the emerging of undesirable and toxic materials such as arsenic or antimony force development of non-ionic or non-salt photoinitiators. This type of initiators does not contain metal atoms or show any ionic character which is the main property of conventional cationic photoinitiators. High solubility in organic solvents, elimination of metal atoms (As, Sb, etc.) and absorption characteristics well-suited for deep-UV exposure are some advantages of such photoinitiators.

Non-salt photoinitiators are widely used in cationic photopolymerization based crosslinking, curing and lithography applications due to their great advantages. Upon photolysis, photochemically active nitrobenzyl esters [257, 258], sulfonyl ketones [259], phenacyl sulfones, phenyl disulfones [260] generate strong organic acids. In addition to sulfur containing photoinitiators, selenide [261] and organosilane [262-264] based photoinitiators were employed to initiate cationic photopolymerization.

2.5.1.11 Other photoinitiators

Photosensitive tosylate esters of nitrobenzyl [257] and benzoin [265]; sulfonyl ketones [259, 260]; and diphenyl disulfones [260] can be employed in cationic photopolymerization, especially in photolithography and chemical amplification processes. The advantages of these photoinitiators are the ease of synthesis, the absorption wavelengths suitable for deep-UV curing and the high yield of acid formation [257].

Upon their photolysis, corresponding sulfonic or sulfinic acid formed and initiates cationic polymerization. Although each type of photoinitiators has different photolysis process the active species for cationic polymerization are same for each compound.

Silanol are also capable of initiating of cationic polymerization of cyclohexene oxide in the presence of aluminum(III) complexes of β-diketones, β-ketoesters or *ortho*-carbonylphenolate upon UV irradiation or moderate heating (40 ^{o}C) [262, 264]. The release of Brønsted acid is strongly accelerated by UV light due to the formation of light sensitive intermediates, when the ligands are 1,3-diketones [263].

In more recent years, diphenyldiselenide (DPDS) as non-salt initiator was used for photosensitized cationic polymerization of NVC [261]. Diselenide compounds in the presence of aromatic nitriles are well-known photosensitization system for *in situ* generation of electrophilic selenium species.

2.5.2 Indirect initiating systems for cationic photopolymerization

Without absorption of the incident photon energy, photochemical processes cannot occur. Medium and high pressure mercury lamps that are frequently used as light sources provide emissions at 313 and 366 nm. If daylight is to be used for curing a coating formula, light absorption at wavelengths longer than 400 nm is highly desired. Rather than introducing electron donating substituents to the structure as mentioned before, some electron rich compounds like trimethoxybenzene or hexamethylbenzene can be added to polymerization mixture to form CTCs with initiators in the electronic ground state which have absorptions at longer wavelengths. Moreover, some special additives can be used in conjunction with photoinitiators to carry out polymerization at longer wavelengths. Notably, in general the additives are the light absorbing species here. Provided the systems thus obtained do initiate cationic polymerizations, the initiation can be explained through one of the following mechanisms:

1. Classical energy transfer: The electronic excitation energy is transferred from the excited additive (sensitizer) to the onium salt initiator producing the excited state of the latter. The route of onium salt decomposition often differs from that observed for direct photolysis of the onium salt [266-270].

2. Free radical promoted: Many photolytically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerizations [271-273].

Polymerizations initiated via addition-fragmentation reactions can also be classified as an initiation process involving radicalic species. The principle of this class of reactions consists in the reaction of a photolytically formed radical with an allyl–onium salt generating a radical cation intermediate. These reactive species undergo a fragmentation giving rise to the formation of initiating cations.

3. Electron transfer via exciplexes: Sensitizers such as anthracene, perylene or phenothiazone form exciplexes with onium salts. Being formed in the consequence of light absorption by the sensitizer, these energy rich complexes consist of non-excited onium salt and electronically excited sensitizer molecules. In the complexation state, electron transfer to the onium salt is observed, giving rise to positively charged sensitizer species [274, 275].

Notably, above decsribed initiation methods do not involve the electronic excitation of the onium salt. Consequently, the initiation mechanisms are entirely different from that found for direct photolysis of onium salts [276-279].

2.5.2.1 Sensitization by classical energy transfer

This mechanism involves the electronic excitation of the ground state of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state. Energy may be transferred from the excited sensitizer (S*) to the onium salt (I) by either resonance excitation or exchange energy transfer (Figure 2.42). Depending on the two components involved, the energy transfer may proceed either in the excited singlet or in the triplet state.

$$S \longrightarrow S^*$$

$$S^* + I \longrightarrow S + I^*$$

Figure 2.42 : Sensitization mechanism by classical energy transfer.

In consequence of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I*) are formed. The further reactions may also differ from those, taking place when the onium salt is excited by direct absorption of light. This conclusion has been drawn on the bases of product analyses [280-282]. An obvious explanation for this difference is the spin multiplicity: in the below discussed sensitized excitations triplet states of the onium salts are populated. In contrast to this, through direct irradiation of the onium salt, electrons are excited primary to the singlet state. A sufficient energy transfer requires the excitation energy of the sensitizer E*(S) to be at least as large as the excitation energy of the photoinitiator E*(I). The photopolymerization with most onium salts can be sensitized by commonly used photosensitizers, such as acetophenone or naphthalene. However, in many cases this reaction does not proceed via energy transfer, since most onium salts are capable of oxidizing these sensitizers in an exciplex formed between sensitizer and onium salt.

Diphenyl iodonium salts are shown to take action of energy transfer with suitable additives like *m*-trifluoromethyl acetophenone [283]. However, energy transfer using TPS salts are shown to be impossible because of unfavorable thermodynamic conditions. Energy transfer sensitization did not turn out to be technically useful, although being a possible pathway in starting the decomposition of onium salts. The reason is that the high triplet energies required allow only the use of sensitizers absorbing at wavelengths below 350 nm. Other multicomponent initiating systems (vide infra) show a more practical spectral response.

2.5.2.2 Free radical promoted cationic polymerization

Many photochemically formed radicals can be oxidized by onium salts leading to generation of cations which are considered as initiating species for cationic polymerization according to the following mechanism as shown in Figure 2.43 [271, 273]. In this mechanism only vinyl ether type monomers reacts with the radical (R·) generated photochemically from PI and give rises a new radical (R-M·) which is also oxidized by the diaryliodonium salt, whereas cyclic monomers do not undergo such oxidation process. Polymerization of cyclic monomers is initiated by only primary radicals; on the other hand, polymerization of vinyl ether monomers is initiated by both primary and secondary radicals.

This process is usually termed as the free radical promoted cationic polymerization. This so-called free radical promoted cationic polymerization is an excellent and fairly flexible type of indirect initiation of cationic polymerization. In more recent years, a new method has been developed for cationic photopolymerization applications, especially high resolution requiring processes. This method is known as “two-photon absorption” and regarded as simultaneous absorption of two photons by a molecule.

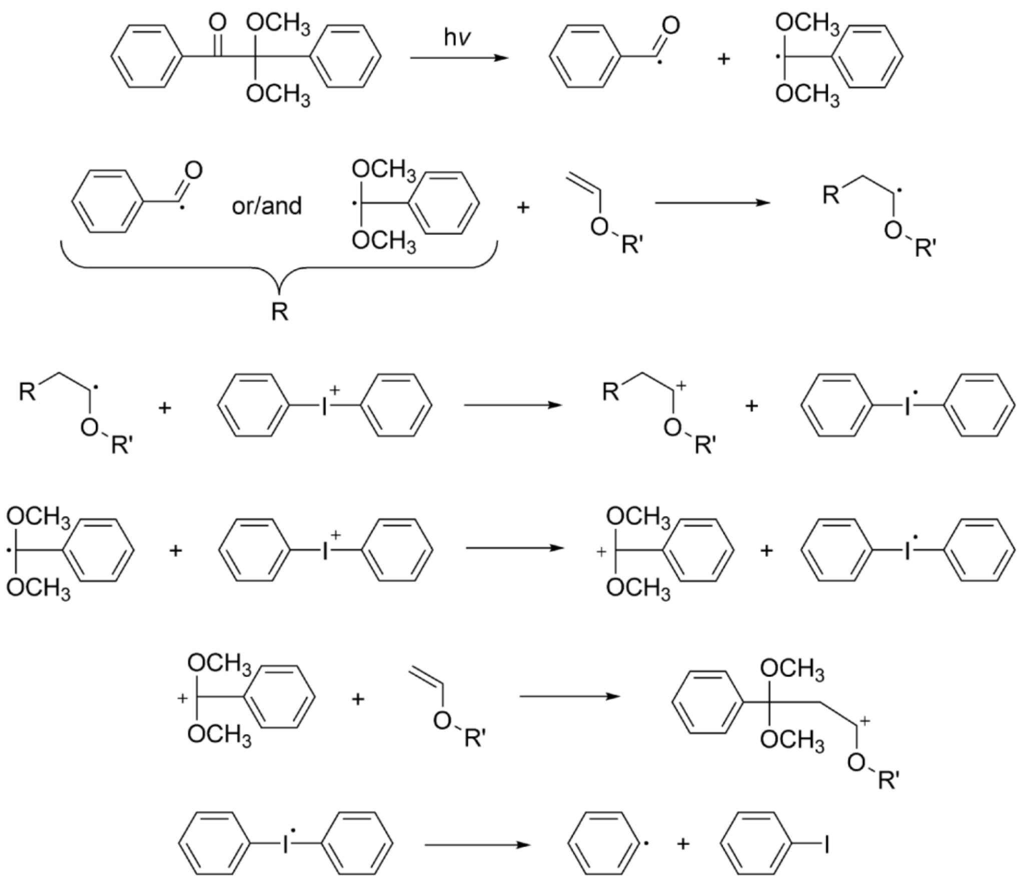


Figure 2.43 : Typical free radical promoted cationic polymerization.

The key for successful two-photon absorption is employment of pulsed lasers that provide high energy required for the absorption process. The main difference between single-absorption and two-absorption is rate of light absorption which is directly proportional to the incident intensity for former, and proportional to the square of the incident intensity for latter [284-286]. Two-photon absorption processes provide the means to activate chemical and physical processes with high spatial resolution due to the non-linearity of light absorption. Therefore, two-photon absorption processes are widely used for a variety of applications, such as photopolymerization [284-286], three-dimensional (3D) microfabrication [287-290], optical data storage [291], imaging [292], and the controlled release [293] of biological systems. In these reported applications, simultaneous two-photon absorption is utilized, where two photons of lower energy are absorbed by the chromophore simultaneously to populate the excited state.

In addition, non-linearity of light absorption can also be achieved by stepwise two-photon absorption. In this process, the first photon is absorbed to generate a long-lived excited state or reaction product [294]. In the second step, a photon of the same or different wavelength is absorbed by the long-lived excited state or reaction product to generate the final photo product. Likewise to simultaneous two-photon absorption, stepwise two-photon absorption occurs with high spatial resolution.

Benzodioxinone and naphtadioxinone were used in stepwise two-photon absorption process in the presence of diphenyliodonium hexafluorophosphate to initiate cationic polymerization of CHO [294]. In fact, this process can be considered as a typical example of two-photon absorption appraoach in free radical promoted cationic polymerization. Upon absorption of light, benzodioxinone decomposes according to Figure 2.44. If benzodioxinone or naphtodioxinone absorbs the first photon the molecule releases the benzophenone which then absorbs the second photon to reduce the iodonium salt yielding in protonic acids for initiation of cationic polymerization. According to experimental results, epoxides can readily be polymerized by the photolysis of benzodioxinones in the presence of suitable oxidants such as iodonium salts [294]. (It is obvious that vinyl ethers may also be polymerized with same system.) The process is based on two-photon absorption in which benzophenone is released by the photolysis of benzodioxinone. Subsequent absorption of the benzophenone thus formed eventually produces protonic acids capable of initiating cationic polymerization by successive hydrogen abstraction and redox processes.

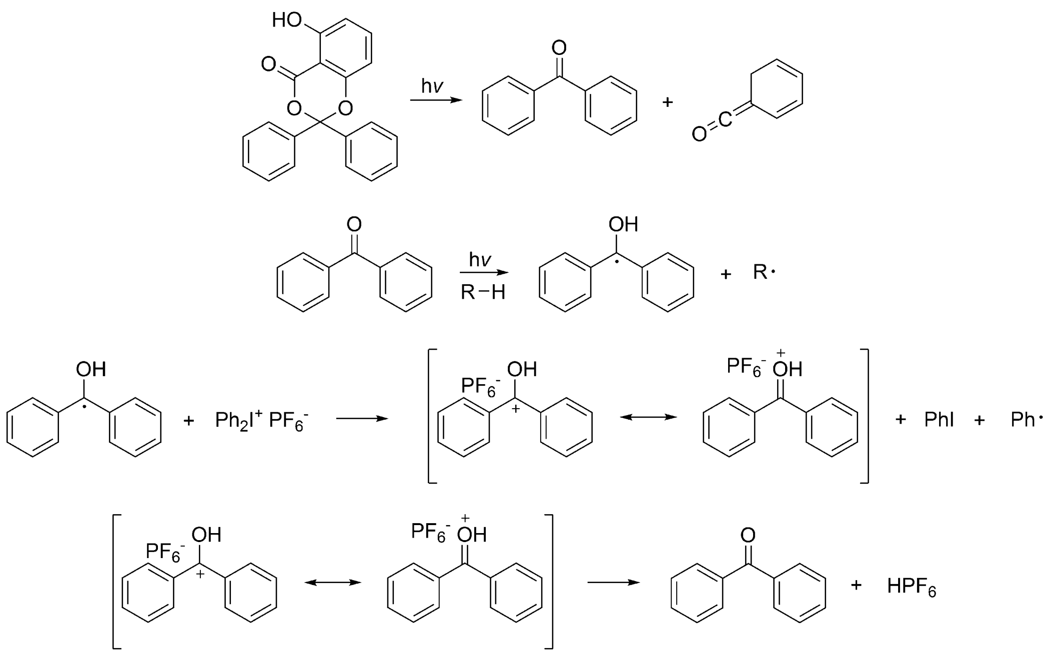


Figure 2.44 : Photodecomposition of benzodioxinone and subsequebt formation of protonic acid in the presence of Ph_2I^+ PF_6^-.

2.5.2.3 Sensitization via exciplexes

The use of photosensitizers is critical to the success of cationic photopolymerizations in many applications in which photopolymerizations are employed as it accelerates the rates of reactions and requires less energy as they provide polymerizations in longer wavelengths [295].

Electron-rich polyaromatic compounds like anthracene, pyrene, and perylene[296] are suitable as photosensitizers as they give redox reactions with DPI salts through exciplex to finally yield the initiating species for photo-induced cationic polymerizations. Figure 2.45 demonstrates the mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt.

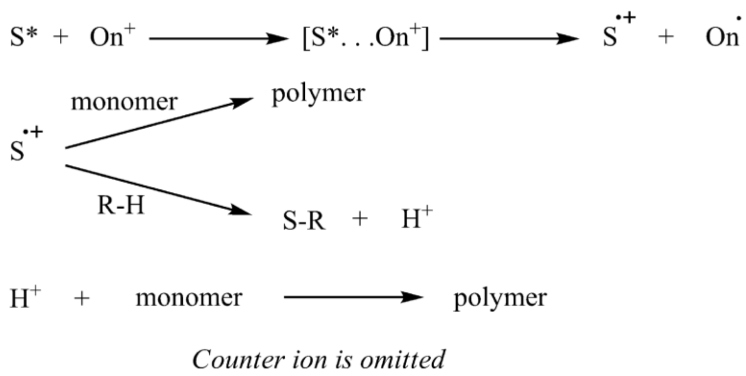


Figure 2.45 : Mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt.

However, because that they are poorly soluble in many monomers and are toxic, photosensitizers received little attention. In addition, because of their high vapor pressure, polyaromatic compounds can be lost from thin coatings during polymerization.

For these reasons, functionalizing these electron rich compounds in a way to improve solubility and less toxicity without affecting their absorption and photosensitizing characteristics can be a convenient solution Figure 2.46.

By attaching formyl groups [295] and reducing them to hydroxymethyl moieties, benzylic alcohol functions can be formed [297], which enhances the polymerization rates when used with epoxides in Brønsted-acid-catalyzed ring-opening cationic polymerizations. As termed by Penczek and Kubisa, the polymerization follows a mechanism called “the activated monomer mechanism” (Figure 2.47) [298-301].

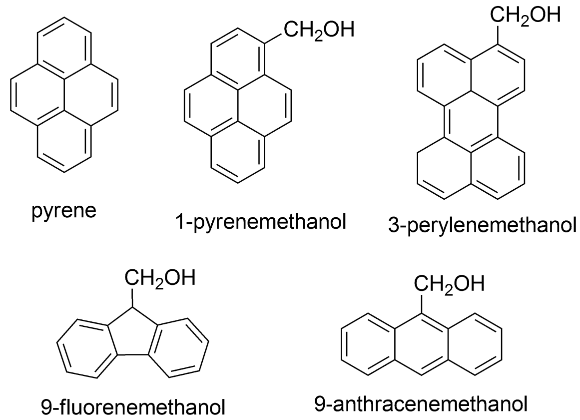


Figure 2.46 : Functionalized polyaromatic sensitizers.

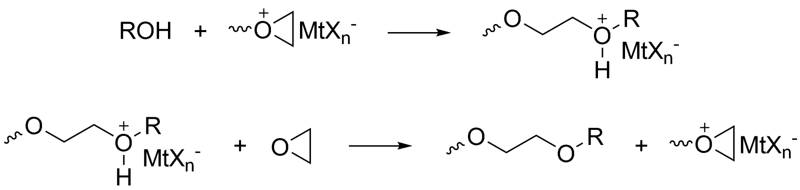


Figure 2.47 : The activated monomer mechanism.

It is interesting to note that these compounds are linked to the polymer chain as terminal groups, thus decreasing its toxicity since migration rates of polymers in the formulation is incomparatively low than their low molecular weight analogs.

In the recent decay, there is a considerable interest in making green photopolymerizations using photosensitizers. One way to obtain non-toxic polymers through sensitization is to copolymerize compounds which can behave either as a photosensitizer and monomer with different monomers [302]. Another way is to polymerize these monomeric photosensitizers and afterwards subject them to sensitize the polymerization of convenient monomers. In both ways non-toxic and odorless polymers can be obtained after polymerization. Compounds introducing phenothiazine moiety and their polymeric analogs were found the display high efficiency in photoinitiated cationic polymerization of vinyl ethers and epoxides.

2.5.2.4 Ground state CTCs

Although it is not considered to be a general method for the indirect initiation, certain salts can undergo decomposition upon irradiation in their appropriate CTC. For example, pyridinium salts are capable of forming ground state CTCs with electron-rich donors such as methyl- and methoxysubstituted benzene [274]. Notably, these complexes absorb at relatively high wavelengths, where the components are virtually transparent. For example, the complex formed between *N*-ethoxy-4-cyano pyridinium hexafluorophosphate and 1, 2, 4-trimethoxybenzene possesses an absorption maximum at 420 nm.

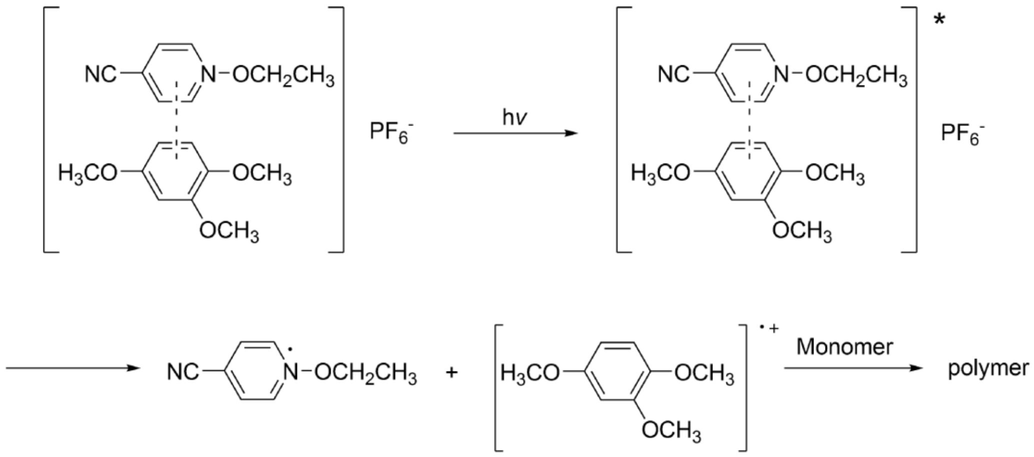


Figure 2.48 : Photoinitiation by CTCs.

The following mechanism shows the action of a CTC as photoinitiator (Figure 2.48). Since polymerization takes place even in the presence of a proton scavenger like 2, 6-di-*tert*-butylpyridine an initiation through Brønsted acid formation can totally be excluded.

2.6 Cationic Polymerization in Aqueous Media

Lewis acid-assisted cationic polymerization is terminated or decelerated by the presence of very small amounts of water and so such polymerization must be carried out under stringently dry conditions, which require more effort and time. In fact, most reactions involving the use of ionic species, such as Lewis acids and coordination compounds, are very sensitive to even traces of moisture because it deactivates or decomposes the intermediates or catalysts into less effective compounds. Accordingly, cationic polymerizations requiring catalyst of Lewis acids [101, 303-306] are also terminated, or undergo chain transfer reactions as a result of the deactivating effect of water. However, the use of water as a solvent in chemical reactions is environmentally-friendly and it provides easy handling and control of the reaction. Furthermore, water can also contribute energetically and economically by acting as a cooling agent (i.e., because of its high heat absorption).

One solution to this quandary is the selection of a water-stable Lewis acid. In 1994, Kobayashi *et al*. [307] introduced lanthanide triflates as a new type of Lewis acid that is water-tolerant and active in the presence of water. These Lewis acids have been used in the thermally activated cationic polymerization of certain monomers including IBVE and *p*MOS in a two phase monomer-aqueous system [308-312]. In these studies, behaviour close to living polymerization was observed but the polymerization rates were uncontrolled, probably due to the heterogeneous nature of the polymerization. Several examples of cationic polymerization in aqueous media have been reported since introduction of Lewis acids based on triflate [309, 310, 313-319]. An example of these polymerizations is schematized in Figure 2.49.

Reversible activation of the C-Cl bond at the dormant polymer terminus in the presence of water by lantanite triflates is the crucial issue in such living/controlled cationic polymerizations [308, 320].

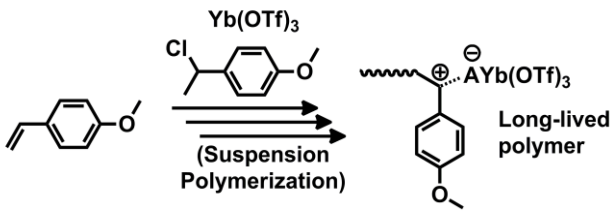


Figure 2.49 : Cationic suspension polymerization of styrene using water tolerant Lewis acid.

2.7 Vinyl Cations

Recently vinyl cations, which can be generated upon irradiation of VHs in a two-step process, have been involved in cationic polmerizations [321-324]. In the primary step of the photo-decomposition, the photoinduced homolysis of carbon-bromine bonds leads to the formation of vinyl/bromine radical pairs (Figure 2.50). Some of the radicals undergo electron transfer forming vinyl cations and bromide ions, while others escape the solvent cage. It appears that the vinyl cations formed in this way are incapable of initiating the cationic polymerization as is shown by the fact that monomer formulations containing only vinyl bromide are not polymerized.[325] This is due to the high nucleophilicity of bromide ions which readily react with vinyl cations inside the solvent cage or due to termination of the cationic polymerization at a very early stage. However, the addition of onium salts with non-nucleophilic counterions to the formulations containing the vinyl halide provides an alternative mechanism of initiating cationic polymerization of various cyclic and vinylic monomers.[326] In this case, the vinyl radicals undergo an electron transfer reaction with the onium cation to form vinyl cations (Figure 2.51). Naturally, the subsequent propagation reaction requires a non-nucleophilic counterion to avoid termination of the polymerization.

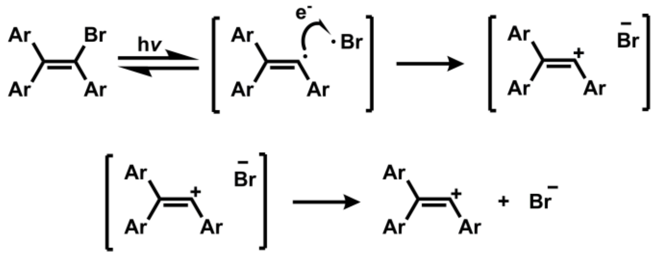


Figure 2.50 : Photoinduced vinyl cation formation [321-324].

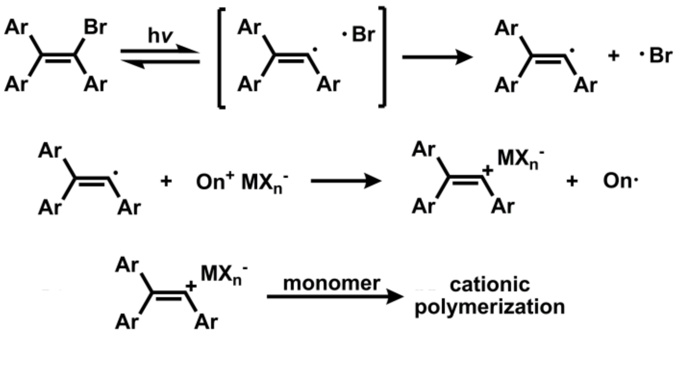


Figure 2.51 : Free radical promoted cationic polymerization by using vinyl halides in the presence of onium salts

The photoinitiating system described above has limitations in that the most active anions tend to be toxic and it does not provide an advantage over the use of a radical source to decompose the iodonium salt to form the initiating cations.

2.8 Use of Photo-initiated Free Radical Promoted Cationic Polymerization in Synthesis of Block Copolymers

The development and successful applications of block copolymers have attracted broad scientific and technological interest in nanotechnology [327], biology [328], medicine [329-331], physics [332], materials science [333-335] and many other related fields. Indeed, the unique properties of block copolymers have been well-established over years and will enhance their novel application as pioneering candidates in advanced technologies. Among the several synthetic methodologies for the preparation of segmented copolymers of various monomers, sequential monomer addition technique is considered as the simplest and straightforward route. However, limited combination of monomers that are polymerizable by the same mechanism is the main infirmity of this technique that precludes its use in certain applications. In other words, specifically designed macromolecular architectures with certain physical and structural properties usually require polymerizations of diverse monomers by distinct polymerization mechanisms. Mechanistic transformation reactions are well-designed techniques that allow combination of two or more polymerization methods to produce block copolymers of assorted monomers [336, 337]. Several strategies such as dual functional initiator [338-342] and propagating chain end switch [343-347] have been proposed and successfully applied. Several transformation approach involving combinations of free radical systems with anionic [348], activated monomer [349], cationic [241, 350, 351], free radical promoted cationic [352-354], and condensation[242] polymerizations have been developed. In some cases, same polymerization mechanisms but different initiating systems were also employed [244, 355].

According to Bamford [356-359], $Mn_2(CO)_{10}$ in conjunction with organic halides is ideal for use as components of photochemical free radical generation process since it absorbs light in the visible range and is soluble in a wide variety of reactive monomers. Such initiation process can be employed for the mechanism transformation from ATRP to visible light radical polymerization leading to the formation of block copolymers. In this case, initiating macro-radicals were produced from the polymeric halide obtained by ATRP (Figure 2.52).

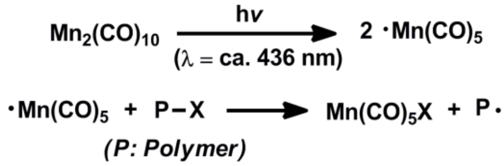


Figure 2.52 : Photoinduced free radical generation from polymeric halides by using dimanganese decacarbonyl.

Principally, it is possible to generate virtually any cations from radicals formed by photochemical [23, 360], thermal [361, 362], or any other means [363] with the aid of onium salts providing favorable thermodynamic conditions [364-366]. Low-molecular-weight-initiators such as thioxanthones [367], acyl germanes [354, 368], acetophenones [23, 369], bisacylphosphine oxides [360], or benzophenone [23] are commonly used as simple free radical sources for so called free radical promoted cationic polymerization. Polymeric radicals can also be oxidized to corresponding macro-cations by a similar redox process [365, 366, 370]. In this case, block copolymers from monomers that can be polymerized by different mechanisms are formed. A typical example of such transformation utilizing polymers with benzoin end groups and iodonium salt was reported previously (Figure 2.53).

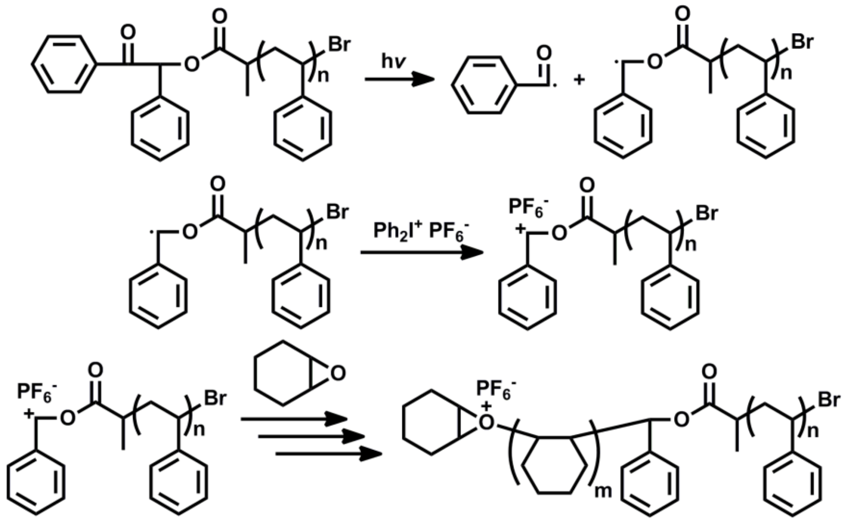


Figure 2.53 : Synthesis of block copolymers by combination of ATRP and free radical promoted cationic photopolymerization.

3. EXPERIMENTAL PART

3.1 Materials and Chemicals

3.1.1 Monomers

Isobutyl vinyl ether (IBVE, 99%, Aldrich):

It was distilled from calcium hydride (CaH_2) in vacuo before use.

Di(ethylene glycol) divinyl ether (DEGDVE, 99 %, Aldrich):

It was used as received.

Tri(ethylene glycol) divinyl ether (TEGDVE, 98%, Aldrich):

It was used as received.

1,4-Butanediol divinyl ether (BDVE, 98 %, Aldrich):

It was used as received.

1,6-Hexanediol divinyl ether (HDVE, 97 %, Aldrich):

It was used as received.

α-Vinyloxy-ω-methacryloyl-PEO (VE-PEO-MA):

The macromonomer was kindly provided by Koichi Ito, and its detailed synthesis is described in literature [371].

Cyclohexene oxide (CHO, 98%, Aldrich):

It was distilled over CaH2 under reduced pressure before use.

Styrene (St, 99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use.

Methyl methacrylate (MMA, 99%, Aldrich):

It was passed through basic alumina column to remove the inhibitor.

3.1.2 Photoinitiators and catalysts (Lewis acids)

Diphenyliodonium iodide (Ph_2I^+ I^-, 98%, Alfa Aesar), diphenyliodonium bromide (Ph_2I^+ Br^-, 98 %, Alfa Aesar), diphenyliodonium chloride (Ph_2I^+ Cl^-, 97 %, Fluka):

Diphenyliodonium based photoinitiators were used as received.

Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, 98%, Alfa Aesar):

It was used as received.

Benzophenone (BP, 99 %, Acros):

It was used after being recrystallized from ethanol.

Thioxanthone (TX, ≥97.0%, Fluka):

It was used as received.

2,2-Dimethoxy-2-phenyl acetophenone (DMPA, Ciba Specialty Chemicals) and 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure 2959, Ciba):

Type I photoinitiators were used as received.

Anthracene (Acros Organics) and perylene (Aldrich):

Polyaromatic photosensitizers were also used as received.

1-Bromo-1,2,2-tris(p-methoxyphenyl)ethene (AAAVB); 1-bromo-1-(p-methoxyphenyl)-2,2-phenylethene (PPAVB); and 1-bromo-1,2,2-triphenylethene (PPPVB):

Substituted vinyl halides were kindly provided by Wolfram Schnabel and prepared as described in the literature.[372-374] The melting points are as follows. AAAVB: 122-124 ^oC (lit.[375] 118-119 ^oC), PPAVB: 130-132 ^oC (lit.[374] 130-131^oC), PPPVB: 116-118 ^oC.

The ^1H-NMR (250 MHz, $Si(CH_3)_4$) spectra are as follows. AAAVB: δ ($CDCl_3$) 7.25 (dd, *J* = 7.9 and 7.9 Hz, 4H, Ar*H*), 6.86 (dd, *J* = 8.6 and 8.6 Hz, 4H, Ar*H*), 6.64 (dd, *J* = 26.2 and 8.6 Hz, 4H, Ar*H*), 3.82 (s, 3H, Ar\`-OC$H_3$) 3.76 (s, 3H, Ar\`\`-OC$H_3$), 3.70 (s, 3H, Ar\`\`\`-OCH_3). PPAVB: δ ($CDCl_3$) 7.35 (br, 5H, Ar*H*), 7.22 (br, 2H, Ar*H*), 7.07 (br, 3H, Ar*H*), 6.97 (br, 2H, Ar*H*), 6.69 (d, *J* = 8.5 Hz, 2H, Ar*H*), 3.75 (s, 3H Ar-OCH_3). PPPVB: δ ($CDCl_3$) 7.36 (br, 5H, Ar*H*), 7.30 (br, 2H, Ar*H*), 7.16 (br, 3H, Ar*H*), 7.05 (br, 3H, Ar*H*), 6.94 (br, 3H, Ar*H*).

Zinc iodide (ZnI_2, anhydrous, Merck), zinc chloride ($ZnCl_2$, anhydrous, Aldrich), zinc bromide ($ZnBr_2$, anhydrous, Aldrich):

Zinc based Lewis acids were used as received.

Metallic zinc powder (particle size < 45 μm, ≥ 95%, Merck):

ZnO layer was carefully cleaned by treating with diluted HCl solution followed by washing water, ethanol (96 %), diethyl ether, then dried under vacuum and cleaned Zn was stored under nitrogen atmosphere.

Ytterbium trifluoromethanesulfonate ($Yb(OTf)_3$, 97%, Fluka):

It was used as received.

Dimanganese decacarbonyl, $Mn_2(CO)_{10}$ (Aldrich):

It was purified by sublimation and stored in a refrigerator in the dark.

3.1.3 Solvents

Dichloromethane (J.T. Baker):

It was dried with calcium chloride and distilled over P_2O_5. It was stored over molecular sieves for use as a solvent in the photopolymerization experiments.

Methanol (Technical):

It was used for the precipitation of polymers without further purification.

Toluene (99.9%, Sigma-Aldrich):

It was dried with calcium chloride and distilled over sodium wire.

Tetrahydrofuran (THF, 99.8%, J.T.Baker):

(a) It was used as eluent for chromatography as received (High Performance Liquid Chromatography Grade).

(b) For use in the chemical reactions, it was dried and distilled over benzophenone/sodium.

n-Hexane (95%, Aldrich):

It was used without further purification.

Diethyl ether (J.T. Baker):

It was dried with calcium chloride and distilled over sodium wire.

Acetonitrile (98%, Aldrich):

It was used without further purification.

3.1.4 Other chemicals

Poly(ethylene glycol) (PEG, M_n =1500 g/mol, Fluka):

It was used as received.

N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich):

It was used as a ligand in ATRP and distilled prior to use.

CuBr (98%, Acros), ethyl-2-bromopropionate (>99%, Aldrich):

It was used as received.

Calcium chloride ($CaCl_2$, J. T. Baker):

It was used as received.

Calcium hydride (CaH_2, Acros):

It was used as received.

Ethyl-2-bromopropionate (>99%, Aldrich):

It was used as received.

3.2 Equipment

3.2.1 Photoreactors and light sources

3.2.1.1 Rayonet

A Rayonet merry-go-round photoreactor was used to perform the polymerizations in which the sample was surrounded by a circle of 16 lamps emitting light nominally at either 300 or 350 nm.

3.2.1.2 Rofin Polilight PL400 Forensic Plus

A Rofin Polilight light source emmitting light at 350, 415, 430, 450, LP530, 490, 505, 515, 530, 550, 560, LP560, 570, 590, 620, 650 (with a bandwidth of ca. ±20 nm), white, half white and blank was used for photobleaching and photopolymerizations.

3.2.1.3 Ker-Vis blue photoreactor

It is a merry-go-round photoreactor in which the sample was surrounded by a circle of 6 lamps emitting light nominally at 400-500 nm (Phlips TL-D 18W Blue).

3.2.2 Radiometer

Light intensities of the light sources at the location of polymerization sample were measured by a Delta Ohm model HD-9021 radiometer or a USB2000 Fiber Optic Spectroradiometer (Ocean Optics, Inc.).

3.2.3 UV-Vis spectrometer

A Cary 3000-Bio (Varian) spectrometer was used to measure the UV-Vis absorption spectra of the compounds and the photobleaching behavior of the formulation.

3.2.4 DSC

DSC measurments were accomplished with a Perkin-Elmer Diamond DSC with a heating rate of 10 $^{o}C \cdot min^{-1}$ under nitrogen flow.

3.2.5 Photo-DSC

Kinetics of some photocuring experiments was performed on a photo-DSC. The polymerizations were carried out under a N_2 atmosphere in a modified Perkin Elmer DSC-7 to allow for irradiation of the sample and reference pans by use of a bifurcated fiber optic guide leading to minimization of the thermal heating effect of the light source.[376] Heat flow and temperature calibrations of the DSC instrument were performed with zinc and indium standards. The Rofin Polilight PL400 was employed as an UV light source in the photo-DSC studies using wavelengths of 350±20nm. The irradiation time was controlled by a shutter between the radiation source and the light guide.

3.2.6 GPC

Molecular weights and PDIs of the linear polymers were determined by two different GPC equipmnts: Waters™ and Viscotek™.

3.2.6.1 GPC (Waters)

The Waters GPC consists of a Waters 410 Differential Refractometer detector, a Waters 515 HPLC pump, and Waters styragel columns (HR series 2, 3, 5E) with GPC-grade THF as the eluent at a flow rate of 0.3 mL/min.

3.2.6.2 GPC (Viscotek)

In some cases, molecular weights and PDIs of the linear polymers were determined at 30°C by GPC using a Viscotek GPCmax Autosampler system consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR} and G4000H_{HR}) (7.8 mm internal diameter, 300 mm length), a Viscotek UV detector and a Viscotek differential refractive index (RI) detector with tetrahydrofuran as eluent with a flow rate of 1.0 $mL\cdot min^{-1}$. The effective molecular weight separation of the columns ranged over 456–42,800 $g\cdot mol^{-1}$ for G2000H_{HR}; 1050–107,000 $g\cdot mol^{-1}$ for G3000H_{HR}; and 10,200–2,890,000 $g\cdot mol^{-1}$ for G4000H_{H}. Both detectors were calibrated with PSt standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers therefore are expressed in terms of polystyrene equivalents. Data were analyzed using Viscotek OmniSEC Omni-01 software.

3.2.7 FT-IR

The molecular bond characterizations of polymers were performed by FT-IR technique using a Perkin Elmer Spectum One B FT-IR Spectrometer.

3.2.8 ^{1}H-NMR

^{1}H-NMR spectra were recorded with $Si(CH_3)_4$ as an internal standard using a Bruker AC250 (250.133-MHz) instrument.

3.3 Methods

3.3.1 Photoinduced cross-linking of divinyl ethers using diphenyliodonium halides

For investigation of gel content and gelation time, following procedure was employed in each curing process. A Quartz or Pyrex reaction tube was flushed with dry nitrogen. Photonitiator and/or photosensitizer (2.45×10^{-3} $mol\cdot L^{-1}$), and zinc halide (2.45×10^{-3} mol·L^{-1}) were dissolved in the tube containing methylene chloride (0.39 mL). Difunctional vinyl ether monomer (3.84 mol·L^{-1}) was added into the reaction tube containing components of the initiating system. Two different photoreactors were used for direct and indirect initiation. In direct system, almost homogenous mixture was irradiated at room temperature in a Rayonet photoreactor emitting light nominally at 300 nm. The light intensity of Rayonet reactor was 1.04×10^{-3} W·cm^{-2} as measured by Delta Ohm model HD-9021 radiometer. During photopolymerization, reaction mixtures were irradiated continuously, and gelation process was monitored. Gelation was followed qualitatively by simply inverting the tube and noting any viscosity increase. The system was said to have gelled when there was no flow of solution on inverting the tube. The gel content was determined by measuring the weight loss after 48 hours extraction with methylene chloride at room temperature. In indirect systems, similar experimental procedures were followed except that the reactor containing lamps emitting light around at 350 nm was used.

3.3.2 Photoinitiated cationic polymerization of vinyl ethers in aqueous medium

Rayonet merry-go-round photoreactor was used to perform the polymerizations in which the sample was surrounded by a circle of 16 lamps emitting light nominally at either 300 or 350 nm. The light intensities at the location of the photocuring sample were measured by a Delta Ohm model HD-9021 radiometer. Two photopolymerization methods were used. The “direct method” employed only diphenyliodonium iodide as the photoinitiator absorbing at ca. 300 nm [325]. In the “indirect method”, Irgacure 2959 was used to sensitize [291] the decomposition of the diphenyliodonium salt with 350 nm radiation where the iodonium salt is fully transparent [325].

The polymerizations were heterogeneous, consisting of an aqueous phase containing the Lewis acid and photoinitiator system, and an organic phase containing the monomer. The solutions contained in Quartz or Pyrex ampoules for direct and indirect methods sealed off. The iodonium salt with or without the free radical photoinitiator, and the $Yb(OTf)_3$ were dissolved in a certain amount of water and acetonitrile or methylene chloride in an ampoule. These solvents were used as a co-solvent with water because they are also miscible with the vinyl ethers and should aid transfer of initiating components from one phase to the other. The monomer was added to this mixture which was then irradiated for a certain period at either 0, 10 °C or at room temperature (nominally 25°C). Two conditions of phase mixing was used - in one case the mixture was stirred with a magnetic stirrer and Teflon® coated bar for the first 30 s of irradiation while in the second method the mixture was stirred continuously during the irradiation.

Most of the photopolymerizations resulted in large exotherms (so-called "explosive polymerization") which heated the air in the ampoule and blew its cap off. When IBVE was used, the polymer mixture was splashed around the sides of the ampoule but the irradiation was continued for a total of 2 h. In the case of the BDVE polymerization, this exotherm occurred almost simultaneously with gelation causing the gel to fracture and at this point the irradiation was terminated. The specific amounts of reactants and other details of polymerization are given in the tables.

After irradiation, the contents in the ampoule was quantitatively transferred into excess methanol to quench the reaction [308] and to precipitate the resulting polymer (a poor solvent for polyvinyl ethers). This precipitate was then washed with methanol and the mass of polymer determined gravimetrically after evaporation of the solvent to yield the conversions of monomer to polymer. In the case of the crosslinked BDVE, the gel contents (the weight percentage of monomer converted to gel) were determined gravimetrically from the mass of polymer remaining after extraction of the gel with CH_2Cl_2.

3.3.3 Photoinitiated cationic polymerization of vinyl ethers using VHs

3.3.3.1 Photopolymerization

A typical photopolymerization procedure of IBVE was as follows. A Pyrex tube was heated *in vacuo* with a heat gun, and flushed with dry nitrogen. AAAVB (1.3 mg, 3.1×10^{-6} mol) was dissolved in IBVE (1.0 mL, 7.7×10^{-3} mol) in the Pyrex tube followed by addition of 1.0 mL of a stock solution containing 4.0 mg of zinc iodide (1.3×10^{-5} mol) and 10.0 mg of PEG (6.7×10^{-6} mol) in CH_2Cl_2. PEG was used in polymerization mixture to improve solubility of ZnI_2 by coordination effect [377]. The tube was sealed off under nitrogen atmosphere and exposed to light continuously at 0 ^{o}C for 240 minutes in a Rayonet merry-go-round photoreactor emitting light nominally at 350 nm (I = 3.0 mW·cm^{-2}).

In the cases of difunctional vinyl ethers, a typical photocuring procedure was as follows. AAAVB (1.3 mg, 3.1×10^{-6} mol) was dissolved in BDVE (0.5 mL, 3.2×10^{-3} mol) in a Pyrex tube followed by addition of 1.0 mL of a stock solution containing 4.0 mg of zinc iodide (1.3×10^{-5} mol) and 10.0 mg of PEG (6.7×10^{-6} mol) in CH_2Cl_2. The tube was sealed off and irradiated around 350 nm at room temperature (~22 ^{o}C) in the Rayonet photoreactor. The gelation time was determined by periodically inverting the tube and noting any viscosity increase and the system was considered to have gelled after 9 minutes since no flow of the solution was observed.

For both monofunctional and difunctional monomers, the polymerization was quenched by addition of a small amount of methanol. Since only the monomer is soluble in methanol additional methanol was used to quantitatively transfer the polymer solution or gel into another container and to precipitate the polymer (linear polymer and/or gel) so that the conversion of monomer to polymer could be determined gravimetrically. For difunctional monomers, the gel content was determined by measuring the weight loss after 24 hours extraction of the crosslinked polymer at room temperature with dichloromethane (a good solvent for the linear polymer).

3.3.3.2 Photobleaching

For the photobleaching experiment, very thin quartz cells (with 0.5 mm path length) consisting of two quartz slides and silicone rubber were employed. Empty cells were used to zero the instrument baseline, and a cell with monomer was used as reference for the formulated monomer systems. Samples were irradiated for certain periods (up to 2400 sec) with 350 nm radiation (with a bandwidth of ca. ±20 nm) using a Rofin Polilight PL400, and the photobleaching behavior was observed by monitoring changes in the absorbance with irradiation time. The incident light intensity was measured by a USB2000 Fiber Optic Spectroradiometer (Ocean Optics, Inc.).

3.3.3.3 NMR analysis

For further analysis of the mechanism of the initiation process, the photochemical formation of the adduct from vinyl halide and IBVE in the absence of zinc iodide was investigated by ^{1}H-NMR spectroscopy. For this purpose, AAAVB (5.0 mg, 1.2×10^{-5} mol) was dissolved in 0.4 mL of $CDCl_3$ in a NMR tube (Aldrich, Tube L diam. 7 in. 5 mm, Thift, grade Series 300), and IBVE (0.10 mL, 7.7×10^{-4} mol) was added to this solution. ^{1}H NMR spectra of the solution were recorded with $Si(CH_3)_4$ as an internal standard using a Bruker AC250 (250.133-MHz) instrument before and after 150 minute-irradiation.

3.3.3.4 Photo-DSC

A typical procedure for photo-DSC studies is as follows. The polymerizations were carried out under a N_2 atmosphere in a modified Perkin Elmer DSC-7 to allow for irradiation of the sample and reference pans by use of a bifurcated fiber optic guide leading to minimization of the thermal heating effect of the light source.[376] Heat flow and temperature calibrations of the DSC instrument were performed with zinc and indium standards. The Rofin Polilight PL400 was employed as an UV source in the photo-DSC studies using wavelengths of 350±20nm. The irradiation time was controlled by a shutter between the radiation source and the light guide.

The polymerization mixture (2-5 mg) was weighed into a DSC pan, and the pan immediately placed into the pan holder of the DSC set at a predetermined temperature. Two 0.05-mm-thick-PET-covers (6 mm diameter) with two vent holes were used to prevent sample from evaporation and to provide a stable baseline by covering the DSC pan holders. After placement of the sample, the equipment was stabilized for a period of 3-10 minutes and to allow purging of air from the cell. Once stabilized, the DSC run was begun but for the first 60s, a shutter prevented irradiation of the sample to stabilize the light source and to establish the heat flow baseline. When the shutter was quickly removed, a short induction period was observed before the polymerization commenced and an exotherm was observed. Irradiation was continued after the exotherm peak until no change was observed in the heat flow. To remove the slight imbalance of the thermal heating effect on the sample and reference pans, the cured sample was again irradiated with the same conditions to produce a background which was subtracted from the data of the first run. The rate of conversion ($d\alpha/dt$) can be defined as given in Equation 1 since the measured heat flow in DSC is proportional to the conversion rate. The heat flow curves were integrated to obtain the polymerization heat (H) as a function of time and this was transformed into the percentage of vinyl conversion (α) (Equation 2) by use of the value for the heat of polymerization (ΔH_{tot}) of 60 J/mol.[378, 379]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{\Delta H_{\mathrm{tot}}}\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)_T \qquad \textbf{(3.1)}$$

$$\alpha = \frac{1}{\Delta H_{\mathrm{tot}}}\int_0^t\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)_T \mathrm{d}t \qquad \textbf{(3.2)}$$

3.3.4 Photoinitiated cationic polymerization of vinyl ethers using instantly formed zinc halide from metallic zinc

In a typical photopolymerization procedure of IBVE, a Pyrex tube equipped with magnetic bar was heated *in vacuo* with a heat gun, and flushed with dry nitrogen. Metallic zinc powder (6.12×10^{-2} mol·L^{-1}) and AAAVB (6.12×10^{-3} mol·L^{-1}) was dispersed in IBVE (1.00 mL, 7.68 mol·L^{-1}) in the Pyrex tube under vigorous stirring and then the tube was sealed off under nitrogen atmosphere. The formulation was stirred and exposed to light continuously at 0 °C for 7 hours in a Rayonet photoreactor emitting light nominally at 350 nm (I = 3.0 mW·cm^{-2}). At the end of the photoirradiation, the resulted polymer was dissolved with a little amount of dichloromethane and precipitated in excess amount of methanol (conv.: 38.8%; M_n: 22,500 g/mol; PDI: 1.36).

A typical photocuring procedure for difunctional vinyl ethers was as follows. Zn powder (6.12×10^{-2} mol·L^{-1}) and AAAVB (1.22×10^{-2} mol·L^{-1}) was added into TEGDVE (0.50 mL, 4.90 mol·L^{-1}) in a Pyrex tube, which was previously heated with a heat gun under vacuum and flushed with dry nitrogen. The mixture was bubbled with nitrogen for 2-3 minutes and sealed off. The tube was exposed to light (λ ~ 350 nm) at room temperature (~22 ^{o}C) in the Rayonet photoreactor. The gelation time was determined when stirring was completely stopped since viscosity of the solution increased and flow of the solution was ceased. The polymerization was quenched by addition of a small amount of methanol. Since only the monomer is soluble in methanol additional methanol was used to quantitatively transfer the polymer solution or gel into another container and to precipitate the polymer (linear polymer and/or gel) so that the conversion of monomer to polymer could be determined gravimetrically. The gel content was determined by measuring the weight loss after 24 hours extraction of the crosslinked polymer at room temperature with dichloromethane (a good solvent for the linear polymer) (Entry 1 in Table 4.9).

3.3.5 Synthesis of PIBVE-*g*-PEO copolymer with pendant methacrylate functionality and its photo-curing behavior

3.3.5.1 Synthesis of PIBVE-*g*-PEO copolymer with pendant methacrylate functionality

A quartz tube was heated in vacuo with a heat gun and flushed with dry nitrogen. ZnI_2 (3.20×10^{-3} mol L^{-1}), the macromonomer (VE-PEO-MA, 6.20×10^{-2} mol·L^{-1}), IBVE (0.38 mol·L^{-1}) and Ph_2I^+ I^- (6.60×10^{-3} mol·L^{-1}) were dissolved in CH_2Cl_2 (2 mL) under nitrogen. The tube was sealed off and put in a photoreactor (Rayonet merry-go-round) equipped with 16 lamps emitting light nominally at 300 nm and an overnight polymerization was conducted with continuous stirring at room temperature. In the applied direct photopolymerization method, diphenyliodonium iodide was used as the photoinitiator absorbing at ca. 300 nm [325]. The resulted polymer was precipitated in methanol and dried under vacuum.

3.3.5.2 Photo-curing of PIBVE-*g*-PEO in the presence of MMA

Photo-curing of PIBVE-*g*-PEO (2.96×10^{-3} mol·L^{-1}) in the presence of MMA (1.17 mol·L^{-1}) in CH_2Cl_2 (2 mL) was conducted by using DMPA (9.75×10^{-3} mol·L^{-1}) as photoinitiator. All components of the photo-curing formulation were put into a Pyrex tube degassed and flushed with nitrogen gas. The tube, sealed off prior to irradiation, was exposed to light in the photoreactor emitting light nominally at 350 nm and the curing was kept going on for three hours at room temperature. After curing, the polymer was precipitated in methanol and soluble linear PMMA was separated by extraction with CH_2Cl_2.

3.3.6 Synthesis of block copolymers by combination of ATRP and visible light-induced free radical promoted cationic polymerization

3.3.6.1 General procedure for ATRP

Three different polystyrenes with various molecular weights [PSt(1): 2250 g·mol^{-1}; PSt(2): 3250 g·mol^{-1}; PSt(3): 5630 g·mol^{-1}] were synthesized by ATRP.

In a typical ATRP procedure, monomer (St, 87.3 mmol), ligand (PMDETA, 0.87 mmol), catalyst (CuBr, 0.87 mmol), initiator (ethyl-2-bromopropionate, 0.87 mmol) and deoxygenated solvent (toluene) were added, consecutively, to a Schlenk tube equipped with a magnetic stirring bar. The tube was degassed by three freeze-pump-thaw cycles, left under vacuum, and placed in a thermostatic oil bath (110 ^{o}C) for 25 minutes. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove copper salt. The excess of THF and unreacted monomer were evaporated under reduced pressure. The resulted polymer, ω-bromo-end-functionalized PSt, was dissolved in a small amount of THF, and precipitated in ten-fold excess methanol. The polymer was dried under vacuum at room temperature (Yield = 18.0%; $M_{n,GPC}$ = 2250 g·mol^{-1}; PDI = 1.12). Properties of the synthesized precursor PSt is listed in Table 3.1.

Table 3.1 : Conditions and results for synthesis of polystyrenes by ATRP.

Polystyrene	Time (min.)	Conv. (%)[d]	M_n (g·mol^{-1})[e]	PDI[e]
PSt(1)[a]	25	18.0	2250	1.12
PSt(2)[b]	60	33.0	3250	1.09
PSt(3)[c]	60	24.1	5630	1.09

[a][M]/[I]/[CuBr]/[PMDETA]: 90/1/1/1; temperature: 110 °C. [b][M]/[I]/[CuBr]/[PMDETA]: 100/1/1/1; temperature: 90 °C. [c][M]/[I]/[CuBr]/[PMDETA]: 200/1/1/1; temperature: 100 °C. Ethyl-2-bromopropionate and PMDETA were used as initiator (I) and ligand, respectively. [d]Conversions were determined gravimetrically. [e]Molecular weights and PDIs were determined with GPC.

3.3.6.2 General procedure for visible light induced block formation.

A representative cationic photopolymerization procedure for CHO is as follows. $Mn_2(CO)_{10}$ (14 mg, 7.2×10^{-2} mol·L^{-1}), $Ph_2I^+PF_6^-$ (0.7 mg, 3.3×10^{-3} mol·L^{-1}) and 0.3 mL of CHO (5.9 mol·L^{-1}) were added to a solution of PSt(1) (40 mg, 3.6×10^{-2} mol·L^{-1}) in 0.20 mL of deoxygenated and dried toluene in a Pyrex tube which was previously heated with a heat gun under vacuum and flushed with dry nitrogen. The solution was also flushed with nitrogen for 4-5 min and sealed off. The formulation was stirred and exposed to light continuously at ambient temperature for 2 hours in a Ker-Vis blue photoreactor emitting light nominally at 400-500 nm (Phlips TL-D 18W Blue). At the end of the photoirradiation, the resulted polymer was precipitated in excess amount of methanol (Conv. = 24.7%). Since PCHO is soluble in hexane, homopolymers of CHO possibly formed after block formation was removed by extraction with hexane to purify block copolymers ($M_{n,GPC}$ = 5200 g·mol^{-1}; PDI = 1.07).

Distinctively, an end chain stabilizer, thiolane, was used to prevent dominating IBVE homo-polymerization due to the both hydride abstraction and chain transfer reactions in the photo-induced block formation of PSt-*b*-PIBVE. Therefore, thiolane (10 mg,

2.3×10^{-1} mol·L^{-1}) was added into the polymerization formulations under the same conditions.

4. RESULTS AND DISCUSSION

4.1 Photoinduced Cross-linking of Divinyl Ethers Using Diphenyliodonium Halides

The classical way to initiate UV-radiation curing or cross-linking of vinyl ether monomers and oligomers is based on the use of Brønsted acids photochemically generated from onium salts such as diphenyliodonium compounds containing metal salts such as PF_6^-, SbF_6^-, AsF_6^- or BF_4^-, as a counter anion. Moreover, onium salts can be photochemically activated in a broad wavelength range with the aid of various sensitizers and free radical photoinitiators [268, 270, 380, 381]. In direct initiation, iodonium salts directly absorb incident light around 300 nm and undergo decomposition generating active species capable of initiating cationic polymerization of vinyl ethers. In the indirect initiation, however, the light at higher wavelength is mainly absorbed by free radical photoinitiators or photosensitizers and initiating species are formed by various electron transfer reactions.

Although, both direct and indirect systems are efficiently applied for curing of epoxy and vinyl ether based formulations, the nature of the non-nucleophilic counter anions limits the use of onium salts in wider applications. The limitations associated with the non-nucluophilic counter ion of onium compounds, especially SbF_6^- nad AsF_6^-, include high toxicity and low cost-efficiency due to their central heavy metals. Duan *et al.* and Gebel reported that long-term exposure of these metal salts to human skin led to increased incidences of various cancers [382, 383]. Furthermore, preparation of such initiators originating from corresponding onium salts with halides requires additional steps, i.e. counter anion exchange, thus this makes them expensive [207, 216].

In the current study, employment of diphenyliodonium salts with highly nucleophilic counter anion is described in direct and indirect photoinitiated cationic cross-linking of divinyl ethers. The direct system comprises only a diphenyliodonium salt with highly nucleophilic counter anion and a zinc halide, while indirect systems, in addition to direct system components, consist of a polynuclear aromatic photosensitizer such as AN and PER or an aromatic carbonyl compounds such as DMPA, BP and TX.

The methodology relies on an elegant approach developed by Sawamoto and Higashimura about two decades ago. In their system, Brønsted acid such as hydrogen iodide in conjuction with zinc halide are utilized for initiation of living cationic polymerization of vinyl ethers [88, 101, 384]. However, the use of protonic acids as initiator arises some problems associated with handling of them. To overcome such problems, photoinitiated living cationic polymerization [21-23] of IBVE using diphenyliodonium halides were reported. In our concept, the adducts were generated photochemically, and react with IBVE to form halide-monomer adduct (Figure 4.1). Coordinating effect of the zinc halide employed as a catalyst allows activation of terminal carbon-halide bond of the adduct and triggers generation of suitable nucleophilic counter anion by stabilizing the growth of carbocation, which leads to insertion of weakly basic monomer. The main difference of our system is related to the origin of the cationic species and the rest of the polymerization proceeds in the same manner as described by Sawamoto and Higashimura.

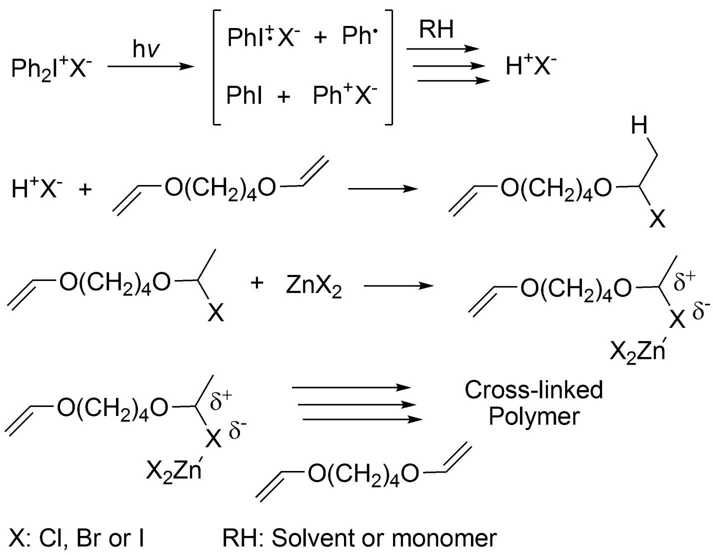


Figure 4.1 : Photoinduced crosslinking of vinyl ethers.

In general, low temperature is required to overcome chain transfer reactions and to achieve living polymerization. On the other hand, in high-speed curing systems, elevated temperature would be an enhancer (or an advantage) rather than a problem, because the crucial point in curing applications is high-rate initiation and polymerization, not preventing the chain transfer process. Therefore, in spite of chain transfer reactions, the described systems for IBVE can be successfully employed in photoinitiated polymerization of difunctional vinyl ethers at room temperature. Overall photoinduced crosslinking process is illustrated in Figure 4.1.

Both direct and indirect acting systems were investigated. For this purpose, initiating efficiencies of direct photolysis of the diphenyliodonium halide; photosensitization of the diphenyliodonium salt with an exciplex-electron-transfer sensitizer such as PER and AN; initiation by a hydrogen-abstraction sensitizer such as BP and TX; and oxidation of a free radical photoinitiator such as DMPA by the iodonium salt in the presence of zinc bromide were examined. Initiation activities of all systems were monitored by gelation time. It should be pointed out that all systems employed in cationic cross-linking of divinyl ethers resulted in effective initiation and quite vigorous polymerizations were observed (Table 4.1 and 4.2). However, the rate of polymerization depends exclusively on the nature of components of the initiating systems.

Table 4.1 : Photo-induced[a] crosslinking of BDVE in the presence of diphenyl iodonium iodide and ZnI_2 by using various free radical PIs or PSs at room temperature.

Entry	Type of PS or PI	t_{gel} (s)	Gel Cont. (%)
1[b]	-	48	98
2	DMPA	21	94
3	BP	40	98
4	TX	49	98
5	AN	61	93
6	PER	80	100

Concentrations; [BDVE] = 3.84 mol·L^{-1}, [PS or PI] = [$PhI_2^+ I^-$] = [ZnI_2] = 2.45×10^{-3} mol·L^{-1}. [a] λ = 350 nm. [b] λ = 300 nm.

The initiating system consisting of DMPA and diphenyliodonium salt appeared to be the most efficient in photo-induced cationic crosslinking of BDVE (Table 4.1, Entry 2). DMPA is a high-quantum-yield *Type I* photoinitiator and it is generally faster than *Type II* initiators such as benzophenone and thioxanthone [176]. In this case, DMPA absorbs incident light and instantly undergoes homolytic cleavage yielding radicals which are subsequently oxidized to the corresponding cation by the diphenyliodonium salt (Figure 4.2).

Table 4.2 : Photo-Induced crosslinking of vinyl ethers in the presence of diphenylonium and zinc halides by using various photosensitizers or free radical photoinitiators at room temperature.

Entry	PS / PI	Onium salt	ZnX_2	M	t_{gel} (s)	Gel Cont. (%)
1 [a]	-	$PhI_2^+ I^-$	ZnI_2	HDVE	237	97
2 [a]	-	$PhI_2^+ I^-$	ZnI_2	EGDVE	142	85
3 [a]	-	$PhI_2^+ I^-$	ZnI_2	BDVE	48	98
4 [a]	-	$PhI_2^+ Br^-$	ZnI_2	BDVE	52	100
5 [a]	-	$PhI_2^+ Cl^-$	ZnI_2	BDVE	53	97
6 [a]	-	$PhI_2^+ I^-$	$ZnBr_2$	BDVE	120	96
7 [a]	-	$PhI_2^+ Br^-$	$ZnBr_2$	BDVE	140	95
8 [a]	-	$PhI_2^+ Cl^-$	$ZnBr_2$	BDVE	325	89
9 [a]	-	$PhI_2^+ I^-$	$ZnCl_2$	BDVE	158	88
10 [a]	-	$PhI_2^+ Br^-$	$ZnCl_2$	BDVE	165	98
11 [a]	-	$PhI_2^+ Cl^-$	$ZnCl_2$	BDVE	No	No
12 [b]	DMPA	$PhI_2^+ Cl^-$	$ZnBr_2$	BDVE	45	92
13 [b]	TX	$PhI_2^+ Cl^-$	$ZnBr_2$	BDVE	65	97
14 [b]	BP	$PhI_2^+ Cl^-$	$ZnBr_2$	BDVE	125	94
15 [b]	AN	$PhI_2^+ Cl^-$	$ZnBr_2$	BDVE	305	91
16 [b]	PER	$PhI_2^+ Cl^-$	$ZnBr_2$	BDVE	1220	78

Concentrations; [M] = 3.84 $mol \cdot L^{-1}$, [PS or PI] = 2.45×10^{-3} $mol \cdot L^{-1}$ and [ZnX_2] = 2.45×10^{-3} $mol \cdot L^{-1}$. [a] The irradiation was carried out at 300 nm. [b] The irradiation was carried out at 350 nm.

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{Ar_2I^+} \longrightarrow \mathrm{R^+} + \mathrm{Ar_2I}\cdot$$

$$\mathrm{Ar_2I}\cdot \longrightarrow \mathrm{ArI} + \mathrm{Ar}\cdot$$

Figure 4.2 : Indirect initiation by oxidation of photochemically generated free radicals.

In the cases of BP and TX, bimolecular process is employed; and after exposure to light, they have to encounter other compounds, namely co-activator. Therefore, these types of photosensitizers are slower than *Type I* photoinitiators. Rehm-Weller Equation is a valuable tool to understand feasibility of electron transfer from photosensitizers such as PER, AN, BP and TX, to onium salts [385]. In principle, the electron transfer is energetically allowed, if the free energy change (ΔG), calculated by equation given below, is negative.

$$\Delta G = 97\ \mathrm{kJ \cdot mol^{-1} \cdot V^{-1}}\ [E_{1/2}^{ox}(PS) - E_{1/2}^{red}(On^+)] - E(PS^*) \quad \mathbf{(4.1)}$$

where $E_{1/2}^{ox}(PS)$ and $E_{1/2}^{red}(On^+)$ are the halfwave oxidation and reduction potentials of the photosensitizer and the diphenyliodonium salt (in V), respectively; and $E(PS^*)$ is the excitation energy of the sensitizer. The ΔG values listed in Table 4.3 suggest that electron transfer from excited states of the sensitizers to the diphenyliodonium salt was favourable in the cases of AN, PER and TX. In the case of BP, sensitization was favourable but with a very low probability. However, gelation time values (t_{gel}) listed in Table 4.1 indicated that polynuclear aromatic photosensitizers, namely AN and PER, were significantly less effective sensitizers than TX and BP.

Table 4.3 : Gibbs free energy changes in electron transfer from sensitizer to diphenyliodonium salts.

PS	$E(PS^*)$ (kJ · mol^{-1}) [268]	$E_{1/2}^{ox}(PS)$ (V)	ΔG (kJ · mol^{-1})^b
BP	290	2.7 ref. [386]	-8.7
TX	277	1.7 ref. [387]	-92.7
AN	319	1.1 ref. [388]	-192.9
PER	277	0.9 ref. [388]	-170.3

^{a} $E^{red}(Ar_2I^+)$: - 0.2 V .[29] ^{b} ΔG was calculated using Rehm-Weller equation.

Apparently, this result is to the reverse of the empiric results derived from the Rehm-Weller equation. This is because there are two mechanisms in the sensitization process depending upon type of sensitizer. In the first mechanism, a polynuclear aromatic photosensitizer such as AN and PER absorbs radiation and form an exciplex with a dipenyliodonium salt. In the exciplex, electron transfer from the excited state photosensitizer to the iodonium salt leads to formation of corresponding radical cation, which is capable of initiation of the polymerization (Figure 4.3). Lifetime of the excited state polynuclear aromatic photosensitizer is the most important factor in the electron transfer process; in that it has to be long enough to allow the sensitizer to encounter a diphenyliodonium salt and form an exciplex. Therefore, these types of initiating systems would be expected to be less efficient compared to sensitizers that work via free radical promoted mechanism (Figure 4.4). If the gelation time of direct acting and free radical driven systems are compared, it is obvious that the indirect systems containing DMPA and BP are more efficient than the direct system (Table 4.1, Entry 1-4). In the indirect systems, in addition to active species (i.e. R^+, $PS^{+}\bullet$ or H^+), which initiate polymerization, there is an additional species, Ar•, which forms active carbocation and new iodinium radical ($Ar_2I\bullet$). In contrast to the indirect systems, only protonic acid is generated which initiates the polymerization in the direct system. The effect of counter anion of diphenyliodonium and zinc halides was, also, investigated. Terminal C-X bond of the X-monomer adduct have to be polarized sufficiently for successive insertion of new monomer [101].

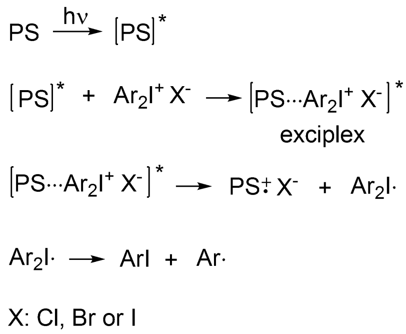


Figure 4.3 : Indirect initiation by electron transfer reactions in exciplex.

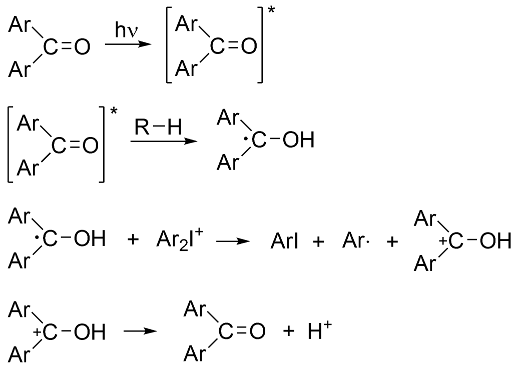


Figure 4.4 : Indirect initiation by hydrogen abstraction of excited aromatic carbonyl compounds followed by electron transfer reactions.

The polarization of the C-X bond resulted from coordination effect of ZnX_2, thus X determines the rate of polymerization. According to Table 4.2 (Entry 3-11), the rate of polymerization increases in the order of $Cl^- << Br^- < I^-$. Accordingly, in the case of diphenyliodonium chloride and zinc chloride, no gelation was observed. This was probably due to low leaving and high nucleophilic characteristics of the chloride ion. The nucleophilicty of halide ions increases in the order $I^- < Br^- < Cl^-$, and leaving-group ability decreases in the order of $I^- > Br^- > Cl^-$ [389].

4.2 Photoinitiated Cationic Polymerization of Vinyl Ethers in Aqueous Medium

The most common method of photoinitiated cationic polymerization uses onium (iodonium, sulphonium, phosphonium) salts with non-nucleophilic anions (e.g. AsF_6^-, SbF_6^-, PF_6^-) [325] either alone and requiring deep UV radiation for curing, or in combination with PSs which allow curing with near visible or visible radiation. Recently, a cationic photoinitation method has been developed for the living polymerization [22, 23] and cross-linking [25] of vinyl ethers. These utilize initiation by diphenyliodonium halides in the presence of a zinc halide Lewis acid ($ZnCl_2$, $ZnBr_2$ or ZnI_2), and these systems eliminate the use of toxic AsF_6^- and SbF_6^- anions. It should be noted that in comparison to the Group 5 fluoroanions, the halides are relatively high nucleophilic and so do not allow the generation of carbocations on irradiation of their iodonium salts [325]. The formation of one of the components of the photoinitiation system occurs when an iodonium salt is photolysed to produce a hydrohalide acid (HX) which reacts with the vinyl ether to form the monomer HX-adduct [325]. Subsequently, zinc halide coordinates with this adduct leading to activation of the C-X bond and insertion of a new monomer unit (Figure 4.5). Unfortunately, this type of polymerization is terminated or decelerated by the presence of very small amounts of water and so such polymerization must be carried out under stringently dry conditions, which require more effort and time. In fact, most reactions involving the use of ionic species, such as Lewis acids and coordination compounds, are very sensitive to even traces of moisture because it deactivates or decomposes the intermediates or catalysts into less effective compounds. Accordingly, cationic polymerizations requiring catalyst of Lewis acids [101, 303-306] are also terminated, or undergo chain transfer reactions as a result of the deactivating effect of water. However, the use of water as a solvent in chemical reactions is environmentally-friendly and it provides easy handling and control of the reaction. Furthermore, water can also contribute energetically and economically by acting as a cooling agent (i.e., because of its high heat absorption).

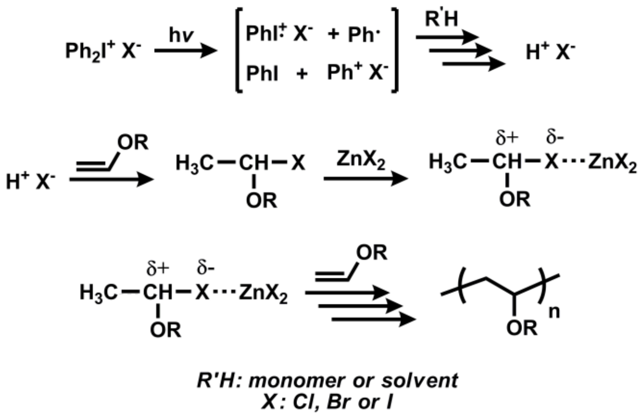


Figure 4.5 : Photoinitiated living cationic polymerization of vinyl ethers.

One solution to this quandary is the selection of a water-stable Lewis acid. In 1994, Kobayashi *et al.* [307] introduced lanthanide triflates as a new type of Lewis acid that is water-tolerant and active in the presence of water. These Lewis acids have been used in the thermally activated cationic polymerization of certain monomers including IBVE and *p*MOS in a two phase monomer-aqueous system [308-312]. In these studies, behaviour close to living polymerization was observed but the polymerization rates were uncontrolled, probably due to the heterogeneous nature of the polymerization.

Therefore, heterogeneous photoinitiated cationic polymerization of mono and divinyl ethers in the presence of the relatively water-tolerant Lewis acid, $Yb(OTf)_3$, rather than the water sensitive ZnI_2, in an aqueous medium is described in the frame of the thesis. Although there have been several reports [308, 310, 311, 316] on cationic polymerization, this is the first study on light-induced cationic polymerization in the presence of large amount of water.

As shown in Table 4.4 (Entry 1), heterogeneous photoinduced polymerizations of BDVE in a aqueous-acetonitrile medium were successfully performed by direct photolysis of the iodonium iodide in conjunction with the water-resistant Lewis acid, $Yb(OTf)_3$ and resulted in the formation of a crosslinked polymer gel. The photo-induced polymerization was very rapid and occurred in an explosive and highly exothermic fashion because of the high Lewis acidity of the ytterbium compound [308].

Table 4.4 : Photoinduced crosslinking of BDVE (0.5 mL) in the presence of diphenyliodonium iodide (5.77×10^{-3} mol · L^{-1}, 0.26 wt%) and $Yb(OTf)_3$ (2.99×10^{-2} mol·L^{-1}, 2.04 wt%) in aqueous media (V_{water} : $V_{acetonitrile}$: V_{IBVE} = 3:4:10; total volume 0.85 mL) at room temperature. The mixture was only stirred at 1000 rpm at the beginning of polymerization for 30 seconds.

Entry	Mode of Inititiation	LI (mW·cm^{-2})	$t_{irrad.}$ (min)	Co-initiator	$t_{gel.}$ (min)	Residual monomer (%)[a]	Conv. (%)[a]	Gel content (%)[b]
1	Direct (~300 nm)	3.00	4.3	-	4.3	25.0	75.0	44.5
2	Indirect (~350 nm)	1.04	4.1	Irgacure 2959[c]	4.1	44.9	55.1	30.5

[a]Monomer conversion: determined from weight of the precipitated polymer in proportion to weight of the monomer. Note that this differs from the conversion of vinyl groups in the divinyl monomer.
[b]Gel content: determined by measuring the weight loss after 48 hours extraction with methylene chloride at room temperature.
[c][Irgacure 2959] = 8.46×10^{-3} mol·L^{-1} (0.21wt%)

Although direct photolysis results in polymerization, it has some limitations for practical applications due to its poor spectral absorbance at wavelength around 350 nm where most commercial radiation sources emit. Therefore, indirect modes of initiation such as electron transfer reactions or oxidation of radicals is often employed to extend the spectral response to longer wavelengths [325]. In this work, a water soluble radical photoinitiator, Irgacure 2959, was used for this purpose. On exposure to 350 nm radiation, this photoinitiator produces benzoin-type free radicals which can be oxidized by diphenyliodonium salt leading to generation of initiating cationic species [23, 325]. Table 4.4 (Entry 2) lists the photopolymerization results for BDVE using this indirect photopolymerization method. As discussed above, this reaction was also highly exothermic.

Regardless of the initiation mode, the BDVE network polymers exhibited a macroporous structure (Figure 4.6), due to the incorporation of water into the sample. The observed yellow-brown color is the characteristic for poly(vinyl ethers) obtained by such initiation and probably due to the elimination of alcohol moieties yielding polyene [390].

Figure 4.6 : Picture of photochemically cross-linked BDVE.

Table 4.4 also lists the gel time, the fraction of residual divinyl monomer, the fraction of the divinyl monomer polymerized and the fraction of polymer gel formed after a certain period of polymerization. The gel times were similar for both systems however the monomer conversion varied. The disagreement of conversions may simply be due to differences in the level of phase intermixing discussed above and as will be discussed below. For both the direct and indirect photopolymerization method, the difference between the weight fractions of polymer and gel formed (approximately 25-40 wt% as shown in Table 4.4) indicates that much of the polymer is soluble and unconnected from the network. This level appears to be larger than would normally expected in chain growth polymerization of divinyl monomers and may suggest that the length of the polymerizing chain is relatively short due to chain transfer reactions or that the polymerization involves considerable levels of cyclization of the divinyl monomer resulting in primary cycles rather than crosslinks [391].

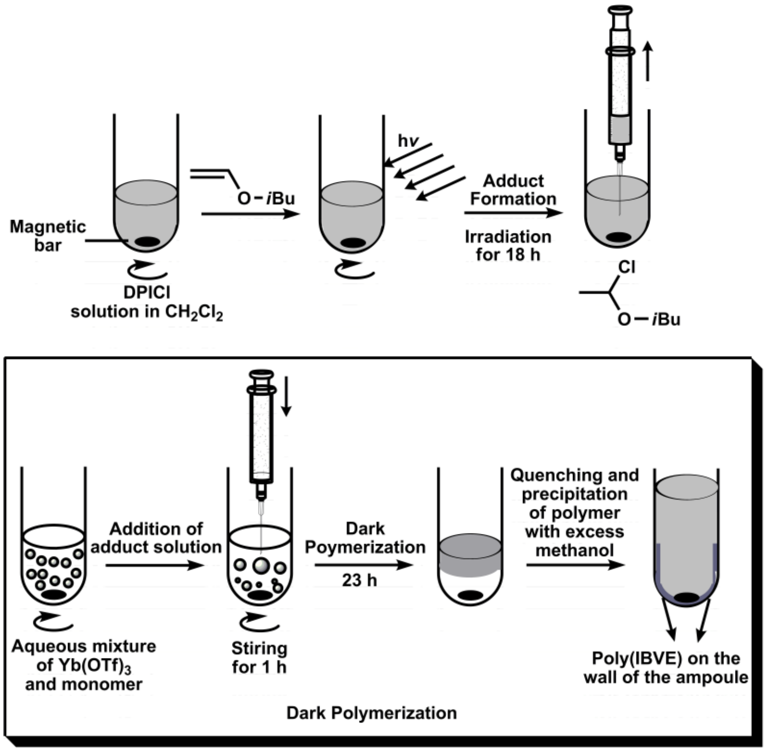


Figure 4.7 : Photochemically adduct formation from diphenyliodonium chloride (DPICl) and IBVE, and aqueous polymerization of IBVE with this adduct in the presence of $Yb(OTf)_3$.

Following the work of Satoh *et al.* [308] it was important to verify that the halide adduction of vinyl ether could be photochemically formed using a diphenyliodonium halide and that this adduct could then combine with an aqueous solution of the ytterbium salt to polymerize additional monomer in the absence of radiation. Using similar conditions to those employed in Satoh *et al*. [308], this was achieved with Ph_2I^+ Cl^- and IBVE. Thus, Ph_2I^+ Cl^- (6.63×10^{-3} mmol) was dissolved in a nitrogen-flushed Quartz ampoule of ca. 1 mL of CH_2Cl_2 (used as a polar solvent which is semi-miscible with water) followed by the addition of IBVE (1.92 mmol). The ampoule was then sealed under dry N_2 gas and was irradiated for 18 hours at room temperature with 300 nm radiation. No significant change in viscosity of this solution was observed, indicating that no polymer had formed, which is consistent with the conclusions of Crivello [325]. Using a microsyringe, a 0.1 mL sample of this solution containing the adduct (approximately 0.2 mmol) was then added into a mixture containing IBVE (1.54 mmol) and $Yb(OTf)_3$ (1.3×10^{-4} mmol) solution in water (Figure 4.7). The ampoule was placed in the dark for 23 hours to allow polymerization of the monovinyl ether. The resultant sticky polymer was precipitated in methanol yielding 8 % (0.12 mmol) conversion of the added monomer. These results indicate that the photoinduced process contributes only to the formation of the adduct and that propagation occurs in the dark in aqueous media with the aid of $Yb(OTf)_3$. In contrast to the divinyl ether, IBVE yielded an uncrosslinked which fully dissolved in the THF used for the GPC studies.

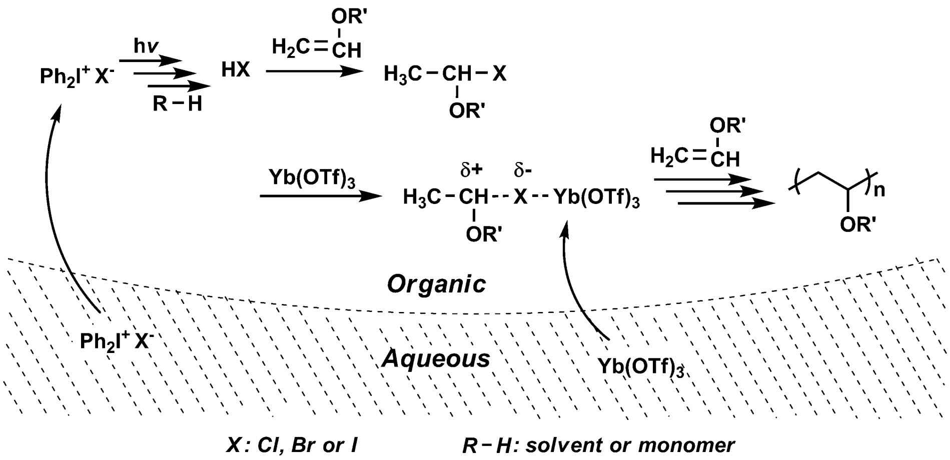


Figure 4.8 : Photoinitiated cationic polymerization of vinyl ethers by using diphenyliodonium iodide in the presence of ytterbium triflate in aqueous medium.

To further validate the mechanism proposed in Figure 4.8, irradiation experiments using the 350 nm source were performed with IBVE, the indirect photoinitiator system (Ph_2I^+ I^- and Irgacure 2959) and water, and in the presence or absence of the Lewis acid ($Yb(OTf)_3$) or the organic solvent (acetonitrile). In the presence of both $Yb(OTf)_3$ and acetonitrile, (Table 4.5, Entry 1-4), significant polymerization occurred. In the absence of $Yb(OTf)_3$ no polymerization was observed. This agrees with the fact [325] that the photolysis products of the iodonium iodide is incapable of initiating polymerization because the counter ion of acid generated (HI) is quite nucleophilic. Similarly, experiments in the absence of acetonitrile failed to produce any precipitable polymer. This indicates that acetonitrile enhances dispersion of the monomer in water leading to successful transfer of the reactants and intermediates between these phases [316]. In the light of the role of iodonium salts in photoacid generation and previous reports [23, 308, 392], a plausible reaction mechanism for the heterogeneous polymerization by the direct initiation is proposed in Scheme 2. According to this mechanism, photoinitiator is transferred from the aqueous to organic phase in the presence of acetonitrile. Upon irradiation, the diphenyliodonium compound is decomposed into HI and other compounds, and then the HI adds to the monomer leading to formation of the adduct. A small amount of the highly water-soluble $Yb(OTf)_3$ transferred from the water to the organic phase appears to be sufficient to activate the adduct and lead to a successful propagation.

Table 4.5 also lists the molecular weights and polydispersities of IBVE photopolymerized using the indirect method. The molecular weights are relatively low (varying from 1800 to 2600 $g \cdot mol^{-1}$) as are the polydispersities. The latter is consistent with a close to living polymerization process as suggested by Satoh *et al.* [308] Based on the ratio of monomer conversion to iodonium concentration, the predicted molecular weights were approximately 2000 g per mol which agrees with the experimental values.

Table 4.5 : Effect of temperature and stirring on photoinitiated polymerization of IBVE (1 mL) by using diphenyliodonium iodide (2.4×10^{-3} $mol \cdot L^{-1}$, 0.12 wt%) and Irgacure 2959 (5.58×10^{-3} $mol \cdot L^{-1}$, 0.15 wt%) in the presence of $Yb(OTf)_3$ (6.37×10^{-3} $mol \cdot L^{-1}$, 0.47 wt%) in aqueous media (V_{water} : $V_{acetonitrile}$: V_{IBVE} = 1:1:2, total volume 2.0 mL) at various temperatures and stirring conditions. Light inensity and duration of irradiation was 1.04 $mW \cdot cm^{-2}$ ($\lambda \sim 350$ nm) and 120 min repectively.

Entry	T (^oC)	Stirring Rate (rpm)	Conversion (%)^a	M_n ($g \cdot mol^{-1}$)	PDI
1	RT	1000^b	49.7	1830	1.11
2	10	1000^b	60.3	2090	1.26
3	10	1000^b	34.6	2070	1.23
4	0	1000^b	21.5	2640	1.32
5	0	500^c	32.5	2300	1.25
6	0	1000^c	0	-	-
7	0	1500^c	0	-	-

^{a}Conversion: determined from weight of the precipitated polymer in proportion to weight of the monomer.
^{b}The mixture was only stirred at 1000 rpm at the beginning of irradiation for 30 seconds.
^{c}Each mixture was stirred continuously at various stirring rates during the irradiation.

Environmental factors including temperature, stirring manner and rate significantly affect the polymerization (Table 4.5). Some polymerizations were repeated several times to evaluate the reproducibility of the system. Unfortunately, identical experimental conditions did not give reproducible results. For example, photopolymerization of IBVE when sensitized by Irgacure 2959 in the presence of diphenyliodonium iodide and $Yb(OTf)_3$ in aqueous media at 10 ^oC for 2 h gave conversions in the range of 34.6-60.3 %, (see Table 4.5, Entry 2 and 3). In some cases of linear polymerization, explosive and exothermic polymerizations occurred, as observed in the crosslinking. Similar inconsistency in experimental data has been observed [308] for the non-photochemical cationic polymerization of vinyl ethers in aqueous media and there it was attributed to heterogeneous nature of the medium.

Continuous stirring at high rates during irradiation would be expected to facilitate the transfers of reactants from one phase to other and enhance the polymerization process. However, surprisingly, results listed in Table 4.5 (Entry 6 and 7) show that experiments with continuous stirring at high rates did not result in any polymerization. This anomalous result may be due to the rapid transfer of the hydrogen iodide from the non-aqueous phase into the water thus preventing adduct formation during the photoirradiation stage. In contrast, when the mixture was stirred initially and then left quiescent during irradiation, significant polymerization occurred (Table 4.5, Entry 4).

Table 4.5 also lists the results from the investigations of the effect of temperature on the IBVE conversion, molecular weight and PDI. No systematic variation in these parameters is evident. The relatively low polydispersities observed in our case may be due to the less nucleophilic nature of the triflate ion which has a greater stabilizing influence on the propagating ytterbium-halide-alkyl ether species involved in the present polymerization system.

4.3 Photoinitiated Cationic Polymerization of Vinyl Ethers Using VHs

Many cationic photoinitiators are known, and their photochemistry has been studied in detail. Among them, the onium-type photoinitiators such as iodonium [216], sulfonium [393], and alkoxypyridinium [394] salts are important due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis. A common strategy employed for improving the performance of these photoinitiators, particularly at long wavelengths, is to combine them with radical sources or with photosensitizers or via the formation of charge transfer complexes with strong electron donors [268, 269, 272, 274, 394, 395]. Beside epoxides, vinyl ethers comprise another important class of monomers for UV-curable coatings. These monomers offer environmentally friendly formulations and cationically polymerize more rapidly than epoxides. Conventionally, UV-radiation curing or cross-linking of vinyl ether monomers and oligomers is achieved by the photochemical generation of Brønsted acids from onium salts with non-nucleophilic counter anions [216, 396]. Recently, Endo and co-workers reported phosphanates as non-ionic (Endo *et al.* uses the term "non-salt") type thermally latent initiators for vinyl ether polymerization.[397] Although these initiators eliminate the contamination of the polymer by the inorganic residues arising from the counter anion of the salt, the high temperatures required for the activation limits their practical application. Recently, a new photoinitiating system eliminating the use of toxic AsF_6^- and SbF_6^- anions for the controlled polymerization and cross-linking of vinyl ethers has been reported [25]. The system presented in Figure 4.5 is essentially based on the concept of living cationic polymerization of vinyl ethers [150] developed by Higashimura and Sawamoto [100], and utilizes diphenyliodonium halides as photoinitiator in the presence of zinc halide as a Lewis acid [23, 25]. Quite recently, it was also demonstrated that the polymerization can be performed even in aqueous medium when the Lewis acid is changed to water-tolerant ytterbium triflate ($Yb(OTf)_3$) in the initiating system [24].

Photolysis of aryl-substituted VHs leads to the formation of vinyl cations in a two-step process (Figure 2.50) [321-324]. It appears that the addition of onium salts with non-nucleophilic counterions to the formulations containing the vinyl halide provides an alternative mechanism of initiating cationic polymerization of various cyclic and vinylic monomers [326]. This study describes the activity of substituted vinyl halides in conjunction with zinc iodide as a photochemically initiating system for the cationic polymerization of vinyl ethers. This initiating system provides several advantages. Substituted VHs are highly soluble in organic medium, in particular bulk monomer, and have absorption at longer wavelengths (up to 380 nm). Moreover, the environmental drawback caused by toxic counter anions is overcome as the initiating system does not require onium salts of any kind.

Figure 4.9 shows the absorption spectra of the VHs used in this study and their chemical structures. VHs, AAAVB; PPAVB and PPPVB, absorb strongly above 300 nm presumably due to the conjugation of their three phenyl groups through the vinyl bond. In addition, vinyl halides substituted with phenyl rings containing electron donating group (such as $-OCH_3$), absorb light at longer wavelengths. For example, vinyl bromide substituted with three anisole moieties (AAAVB) has a broad spectral absorption which extends to near UV region (up to 380 nm) that makes AAAVB particularly useful for long-wavelength applications (see Figure 4.9).

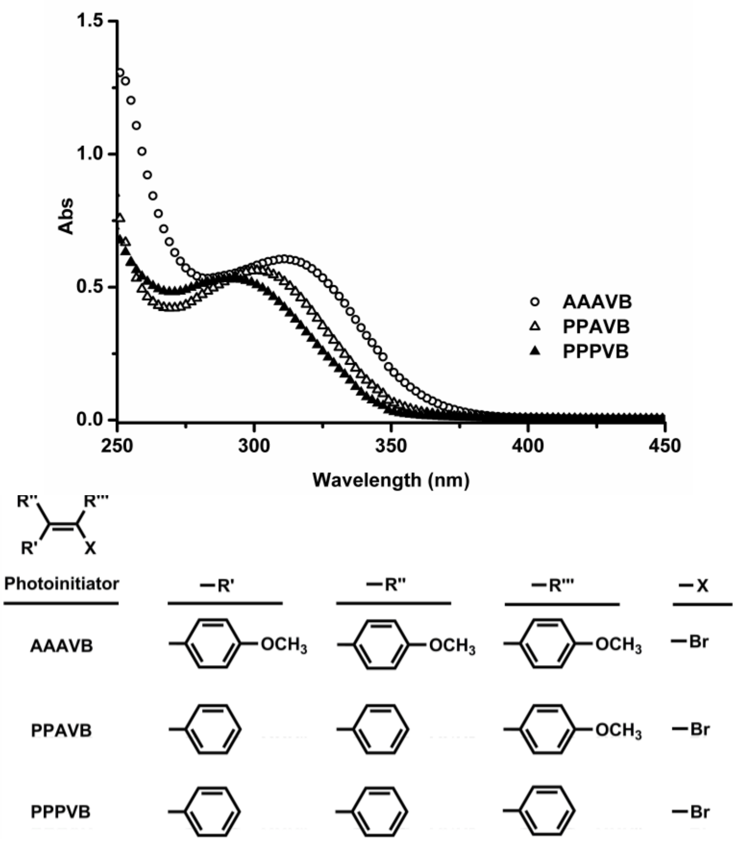


Figure 4.9 : UV-Vis spectra of 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (AAAVB); 1-bromo-1-(*p*-methoxyphenyl)-2,2-phenylethene (PPAVB); and 1-bromo-1,2,2-triphenylethene (PPPVB) in CH_2Cl_2 (C= 3.3×10^{-5} $mol\cdot L^{-1}$).

The photoinitiated polymerization of IBVE with each of the VHs was studied in the presence of zinc iodide. As can be seen from Table 4.6, IBVE was polymerized quite effectively with all of the vinyl halides. The extent of polymerization and thus the initiator efficiency increased in the order AAAVB > PPAVB > PPPVB, which correlates well with the absorbance of these initiators at around 350 nm. For comparison with the photoinitiation efficiency of the vinyl halides, the photopolymerization of IBVE with Ph_2I^+ I was also performed (see Table 4.6).

The observed low activity of Ph_2I^+ I may be due to its weak absorption at the wavelengths of the radiation source (350 nm), whereas all vinyl halides show fairly strong absorptions at wavelengths above 350 nm and therefore better initiator activity. The electron donating substitutents of the vinyl halides also favor the redox reaction leading to the formation of vinyl cations.

To further investigate the polymerization process, experiments were performed where either the vinyl halide or the zinc halide was omitted (350 nm). This omission of either of the two components failed to produce polymer, which is consistent with the proposed mechanism shown in Figure 4.10. In this mechanism, vinyl cations photochemically generated from the rupture of C-halide bond followed by electron transfer can directly react with the monomer. The direct evidence for the reaction of vinyl cations generated this way with vinyl ethers was previously obtained by laser flash photolysis and bimolecular rate constant was found to be in the range of $k = 10^5$ l mol^{-1} s [398]. The rapid reaction of bromide ions eventually leads to the formation of the monomer adduct with a structure resembling those used in conventional living cationic polymerization initiated by HI/ZnI_2 system [101]. Further activation by the coordinating effect of ZnI_2 affords the desired chain growth.

Table 4.6 : Photopolymerization of IBVE (1.0 mL, 7.7×10^{-3} mol) induced by irradiation of various photoinitiators (1.5×10^{-3} mol·L^{-1}) at 350 nm (I = 3.0 mW·cm^{-2}) at 0 °C in the presence of ZnI_2 (6.3×10^{-3} mol·L^{-1}) dissolved in CH_2Cl_2 (1.0 mL) by the aid of poly(ethylene glycol) (3.3×10^{-3} mol·L^{-1}). Time of irradiation was 240 minutes.

Entry	Photoiniator	Conversion (%)[a]	M_n[b]	PDI[c]
1	AAAVB[a]	53.7	28660	1.77
2	PPAVB[a]	29.9	22800	1.67
3	PPPVB[a]	23.8	30900	1.47
4	Ph_2I^+ I	5.2	9950	1.43

[a] Monomer conversions were determined gravimetrically.
[b] Number average molecular weights (M_n) and PDIs were determined using GPC.

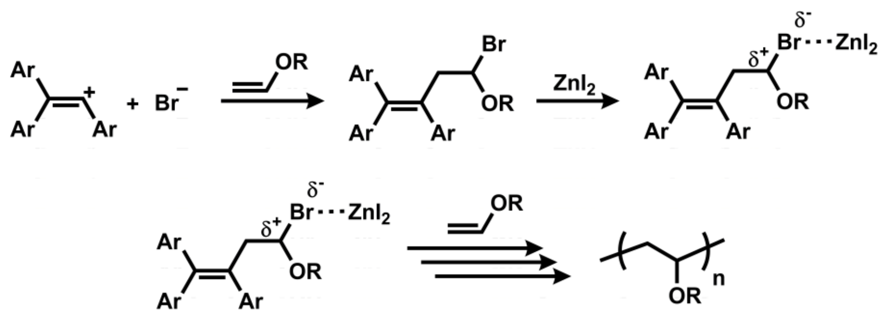


Figure 4.10 : Photoinitiated cationic polymerization vinyl ethers by vinyl cations in the presence of zinc iodide

In order to gain more insight to the initiation mechanism, the change in the optical absorption spectrum of the polymerization solution was recorded as a function of irradiation time. As can be seen from Figure 4.11, with increasing irradiation time, the absorption spectra maximum at 253 nm and the shoulder at 315 nm decrease while a concomitant new maximum at 266 nm grows as indicated by the isosbestic points at 260 and 291 nm. The new band at 266 nm is attributed to the formation of the adducts. Therefore, it is concluded that vinyl halides very effectively degrade and take part in the initiation process.

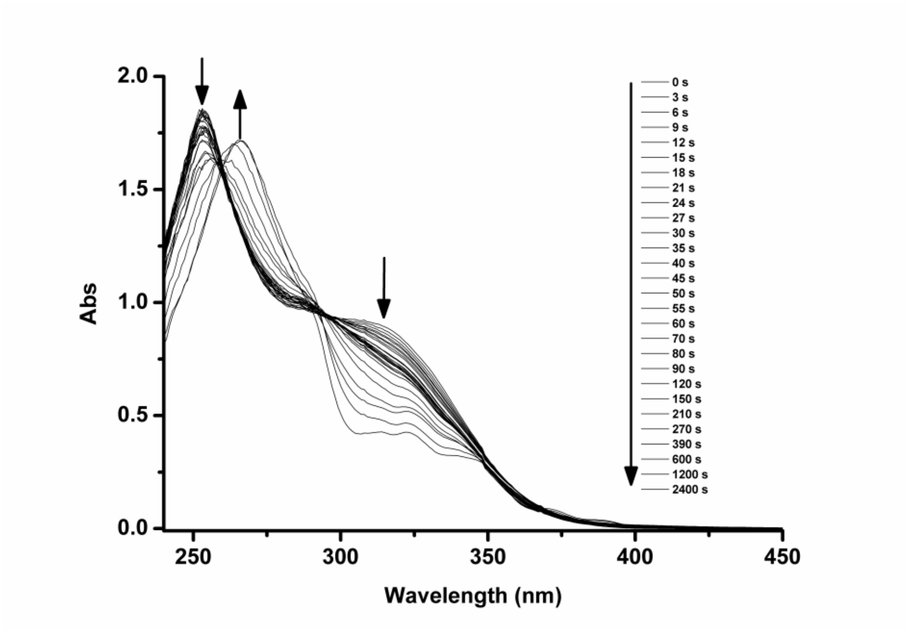


Figure 4.11 : Photobleaching behavior of the photoinitiating system in a formulation consisting of AAAVB (0.05 wt%)/ZnI_2 (0.05 wt%) in tri(ethylene glycol) divinyl ether during irradiation at 350 nm in a Quartz cell with 0.5 mm-thickness at room temperature (I = 11.5 mW·cm^{-2}).

Additional support for the crucial role of vinyl halides in the initiation process was obtained by ^{1}H-NMR analysis of the polymerization mixture in $CDCl_3$ in the absence of ZnI_2 where IBVE and AAAVB were used as monomer and photoinitiator, respectively. In this case, while the adduct is expected to form, the subsequent chain growth does not occur because the adduct can not be activated when no Lewis acid is present in the system. Figure 4.12 shows ^{1}H-NMR spectra of the solutions before and after photolysis. The spectrum of the solution before irradiation (Figure 4.12A) consists of only traces of IBVE and AAAVB. However, in the NMR spectrum of the irradiated sample (Figure 4.12B), in addition to protons of a series of side products occurring from different combination and coupling of active species, the new signals corresponding to the terminal CH-Br protons [111] at 5.58 ppm and CH_2 protons between 2.4 and 3.1 ppm were detected. These results substantiate the suggested photoinitiation mechanism according to which adduct formation is the initial step.

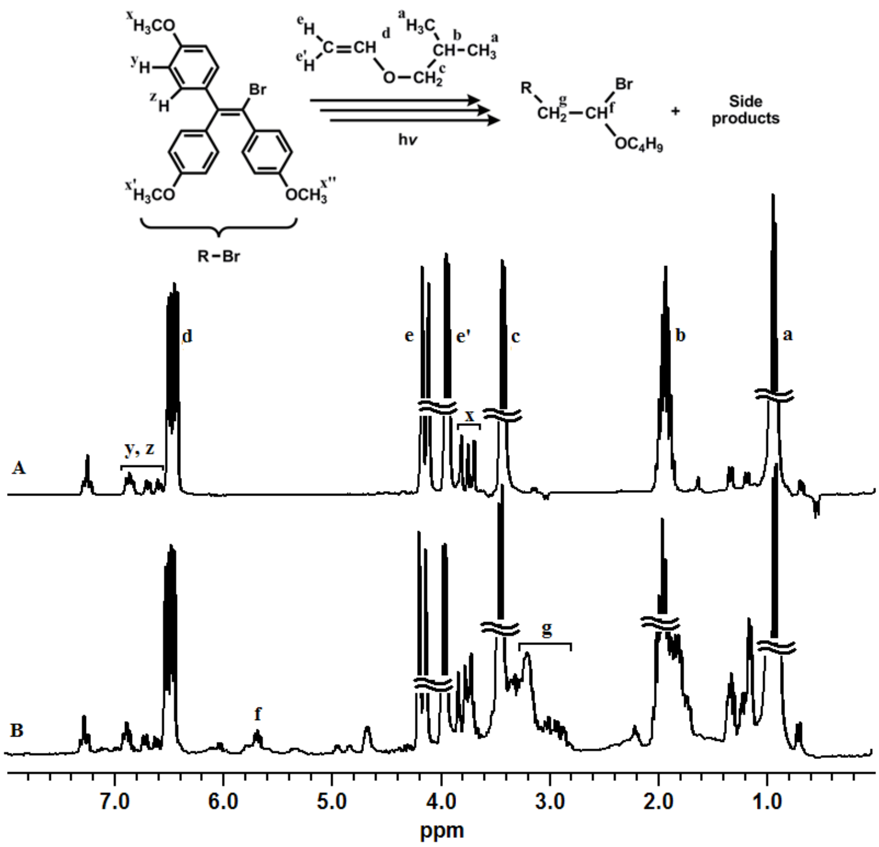


Figure 4.12 : ^{1}H-NMR traces of solution consisting of isobutyl vinyl ether and 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene in $CDCl_3$ but in the absence of ZnI_2 before (A) and after (B) irradiation for150 min.

In the initiation of this type of polymerization,[23] the reaction of the halide adduct with ZnI_2 leads to the formation of suitable nucleophilic counter-anion which stabilizes the growing carbocation and thus prevents chain termination and chain transfer processes. In order to examine the possible living nature of the described photoinitiated cationic polymerization of IBVE, studies of the time dependence of conversion, number average molecular weight (M_n) and PDI were carried out (see Figure 4.13 and 4.14). After a period of retarded polymerization which presumably corresponds to the consumption of the reactive species by the impurities, accumulation of the adduct and the initial stages of chain growth, the conversion of monomer increased almost linearly with polymerization time and then leveled off

(Figure 4.13). The final plateau value may correspond to the stage when all of the vinyl halide is consumed. This behavior may also be due to light absorption effects, where the light is absorbed completely within a small layer of the sample.

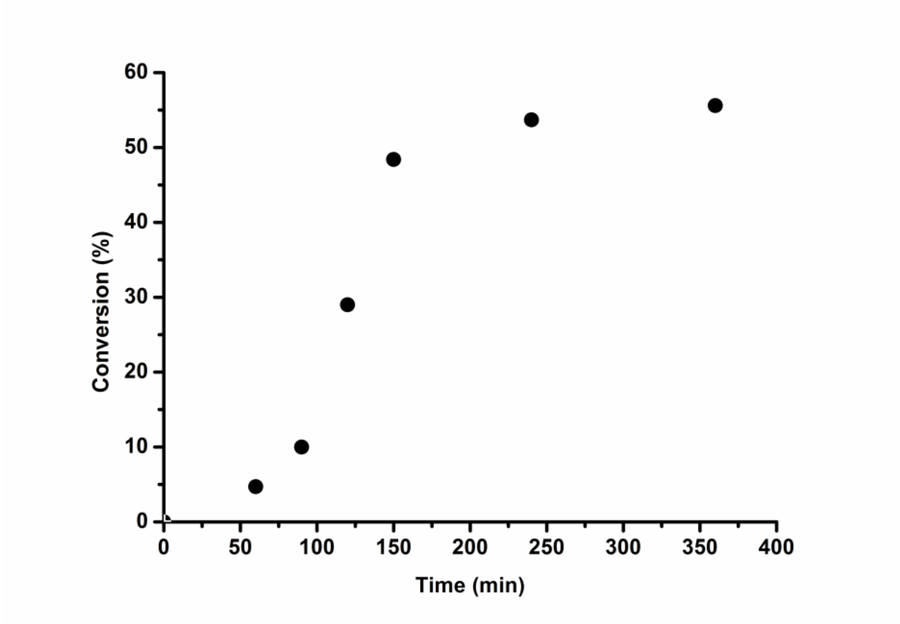


Figure 4.13 : Time-conversion profile in photopolymerization of IBVE (1.0 mL) induced by irradiation of AAAVB (1.6×10^{-3} mol·L^{-1}) at 350 nm (I = 3.0 mW·cm^{-2}) at 0 ^{o}C in the presence of ZnI_2 (6.3×10^{-3} mol·L^{-1}) dissolved in CH_2Cl_2 (1.0 mL) by the aid of poly(ethylene glycol) (3.3×10^{-3} mol·L^{-1}).

The plot of M_n versus conversion studies (Figure 4.14) exhibits two stages: initially the molecular weight rises rapidly and then increases almost linearly with conversion. Figure 5 also shows that the polydispersity is relatively constant and close to 1.5 which is consistent with a controlled polymerization process, if not true living polymerization. These results indicate that although true controlled/living polymerization was not completely achieved, a reasonable control over the molecular weight was attained. The fact that the polydispersity is significantly different from unity is expected since the initiating species, the adduct in this case, is generated continuously so that growing chains with large differences in chain lengths are present at the same time.

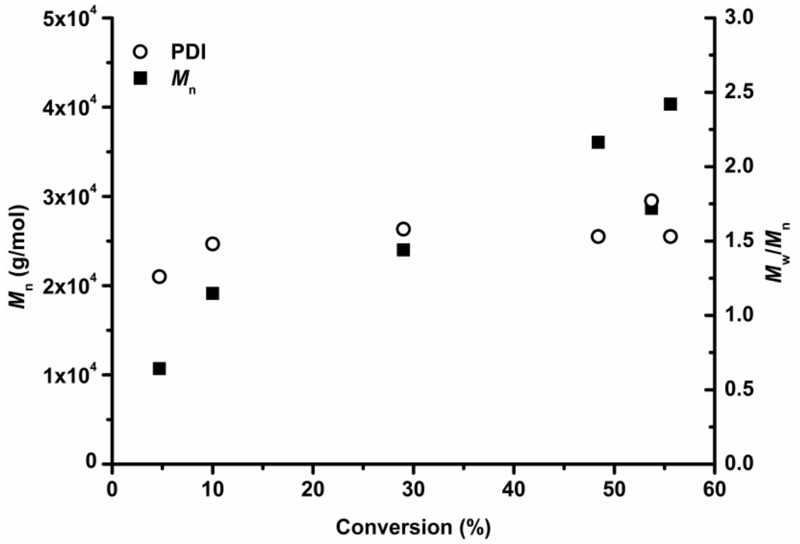


Figure 4.14 : Conversion-M_n and conversion-molecular weight distribution (M_w/M_n) profiles in photopolymerization of IBVE induced by irradiation of AAAVB (see caption of Figure 4.13 for details).

To evaluate the value of this photoinitiating system in practical applications, the efficiency of the AAAVB/ZnI_2 system, which absorbs light at wavelengths close to those of visible light, the photocuring of formulations containing difunctional monomers was studied by isothermal photo-DSC. Figure 4.15 shows the photo-DSC polymerization of the TEGDVE with 350 nm radiation.

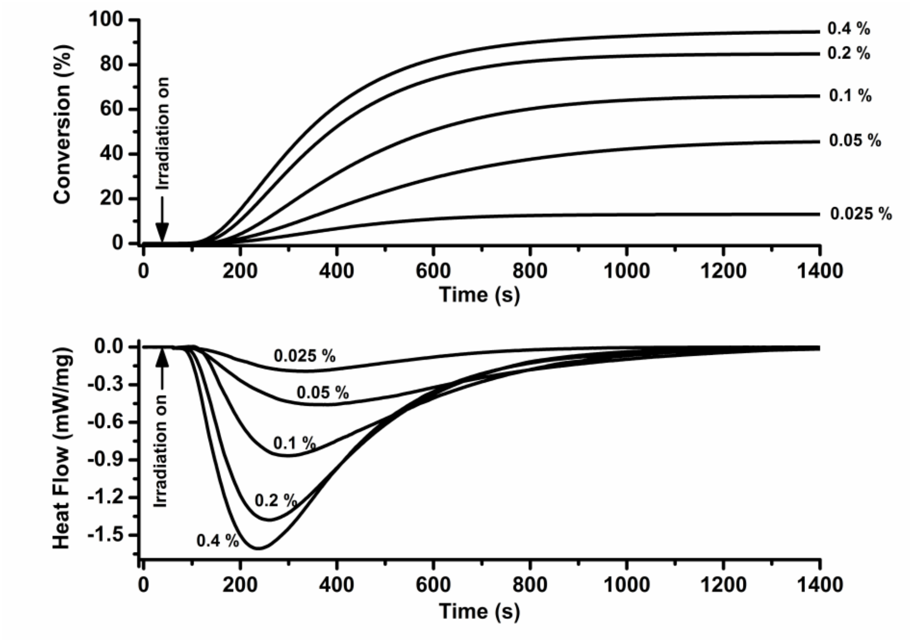


Figure 4.15 : Photopolymerization of TEGDVE initiated by irradiation of various amount of AAAVB in the presence of ZnI_2 (0.05 wt%) around 350 nm (I = 8.0 mW·cm^{-2}).

As is shown in the lower part of Figure 4.15, the heat flow (related to the polymerization rate) exhibited an induction period, followed by an exotherm peak which occurred at a shorter time and with a larger heat flux maximum as the concentration of AAAVB was raised. This behavior is consistent with the effect of raised AAAVB concentration on the rate of initiation and thus the rate of polymerization, as can be seen from the upper part of Figure 4.15. In addition, the final conversion of vinyl groups increased as the initiator concentration was raised. This suggests that there exists a slow termination process in this system or that the propagation step is an equilibrium reaction with some reversible characteristics.

Apart from TEGDVE, several other difunctional vinyl ether monomers were also examined. All monomers polymerized readily in solutions containing AAAVB and ZnI_2. Typical results are shown in Table 4.7. As can be seen by comparison of the data Entry 4 and 5 (in Table 4.7), DPII is an efficient initiator when irradiated at shorter wavelengths, i.e, at 300 nm where it absorbs strongly, however, when the polymerization is performed at 350 nm, no gelation is observed after prolonged irradiation times.

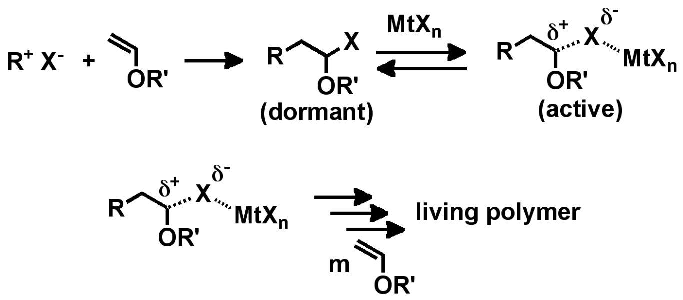
Table 4.7 : Photo-induced crosslinking of various divinyl ethers (0.5 mL) initiated by irradiation of AAAVB or $Ph_2I^+ I^-$ (2.0×10^{-3} mol·L^{-1}) at 350 nm (I = 3.0 mW·cm^{-2}) at room temperature in the presence of ZnI_2 (8.4×10^{-3} mol·L^{-1}) dissolved in CH_2Cl_2 (1.0 mL) by the aid of poly(ethylene glycol) (4.4×10^{-3} mol·L^{-1}).

Entry	Monomer	Initiator	Iradiation wavelength (nm)	t_{gel} (min.)[b]	Monomer Conversion (%)c	Gel Content (%)d
1	BDVE	AAAVB	350	9	60.7	100
2	HDVE	AAAVB	350	8	52.3	95.1
3	DEDVE	AAAVB	350	8	50.4	95.6
4	BDVE	$Ph_2I^+ I^-$	350	-	0	0
5	BDVE[a]	$Ph_2I^+ I^-$	300	2	50.2	95.8

[a] Irradiation intensity was 1.0 mW·cm^{-2}.
[b] Gelation was followed qualitatively by simply inverting the tube, and the system was considered to have gelled when there was no flow of solution on inverting the tube.
[c] Conversion of monomer to polymer was determined from weight of the precipitated cross-linked polymer in proportion to weight of the monomer. Note that for the divinyl ethers, this is not the same as the conversion of vinyl groups.
[d] Gel content was determined by measuring the weight loss after 24 hours extraction with methylene chloride at room temperature.

4.4 Photoinitiated Cationic Polymerization of Vinyl Ethers Using Instantly Formed Zinc Halide from Metallic Zinc

For decades, living cationic polymerization has been principally achieved by tuning nucleophilicity of counteranion generated in the presence of a metal halide, an externally added weak Lewis base, or an added salt [16, 20]. Among the living cationic polymerizations, the Lewis acid-catalyzed approach has been perfectly adapted to light-induced living cationic polymerization [21-25]. In this methodology, photochemically generated cationic species (either carbocation or Brønsted acid) from photoinitiators containing halogen react with monomer (i.e. vinyl ether) and form a halide-monomer adduct required in the first stage of the propagation. Addition of new monomers to the adduct is catalyzed by Lewis acid, namely metal halides, by coordination of metal ion with the halogen of the adduct (Figure 4.16).



R^+: H^+ or carbocation; X: Cl, Br or I

Figure 4.16 : Living cationic polymerization of vinyl ethers.

Although onium salts are the most widely employed photoinitiators in cationic photopolymerization, new photoinitiation modes [207, 399] such as vinyl halides [321-324] in conjunction with co-initiators have recently been proposed as alternative photoinitiators with improved solubility and spectral response. Principally, photolysis of VHs generates vinyl/halogen radicals and subsequently vinyl cations [321-324, 400] that initiate cationic polymerization in the presence of metal halides such as zinc halides as discussed in Section 4.3 [26].

Lewis acid or metal halide plays the central role in the activation of propagating chains in this type of living polymerization. The common metal halides including ZnX_2, TiX_4, SnX_4, WX_6 and MoX_5 employed in such polymerizations are extremely sensitive to water and can be deactivated or transformed to less active Lewis acids in the presence of even small amount of air moisture and become useless in the activation process.[20, 93, 308, 309, 314] Thus, such polymerizations must be carried out under strictly dry conditions. One possible way to overcome this drawback is to use of water-tolerant Lewis acids such as $Yb(OTf)_3$ as described in Section 4.2 [24]. Alternatively, the Lewis acid (e.g. zinc halide) can be produced in the polymerization medium. As reported previously, metallic zinc is readily converted to $Zn(OH)_2$ by peroxide radicals when it is treated with H_2O_2 aqueous solution and consequently oxidized to ZnO [401]. Essentially, zinc can be utilized as a reducing agent for free radicals leading to the formation of zinc salts. This redox process is also valid for halogen radicals; for instance, when vinyl halides are exposed to light at appropriate wavelengths [321-324], they produce both vinyl, which then can be transformed to vinyl cation by spontaneous electron transfer, and halogen radicals capable of oxidizing metallic zinc. Therefore, photolysis of VHs affords not only formation of vinyl cations required in the initiation step but also concomitant generation of zinc halides required in the propagation step (Figure 4.17).

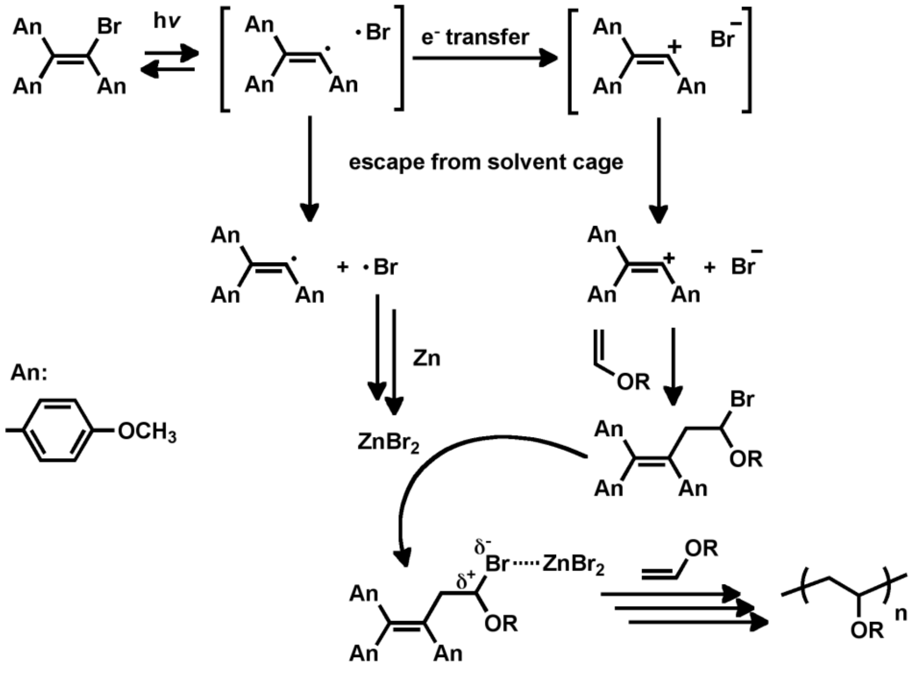


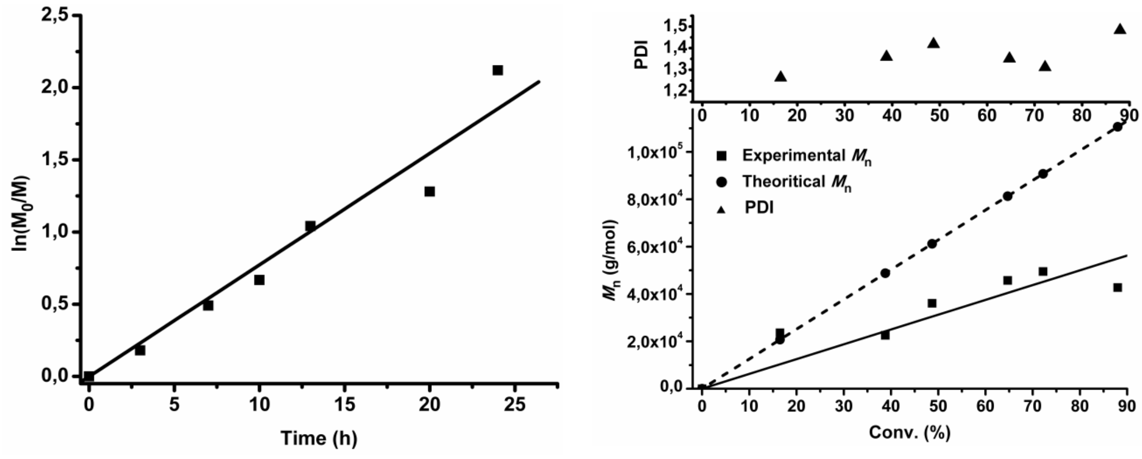
Figure 4.17 : Photo-induced cationic polymerization of vinyl ethers in the presence of metallic zinc.

The current study reports the cationic living polymerization of IBVE initiated by the photolysis of a substituted vinyl halide, AAAVB, in the presence of metallic zinc. The capability of this novel photoinitating system to induce crosslinking was also evaluated utilizing several difunctional monomers.

As proposed previously, photolysis of a VH in the presence of vinyl ether monomer yields an adduct through a reaction between the photochemically generated vinyl cation and the monomer [26]. In the subsequent step, a zinc halide coordinates with the halogen atom leading to insertions of the monomers to the adduct and, in turn, triggers chain propagation (Figure 4.10). In this approach as presented in Figure 4.17, Lewis acid (i.e. $ZnBr_2$) was produced *in situ* during the photoinduced decomposition of vinyl halide, AAAVB. In addition to their participation in zinc bromide formation, some portion of the photochemically generated vinyl radicals undergo spontaneous electron transfer reaction yielding vinyl cations that essentially form monomer adducts. Subsequently, chain propagation proceeds after the activation of the adduct thus formed by the coordination with zinc bromide. The polymerization then continues in the usual manner as described for conventional living cationic polymerization mechanism [20-23, 88, 101, 402]. Due to its limited solubility in organic medium, 10-fold excess of metallic Zn with respect to photoinitiator concentration was used throughout the polymerizations.

Possible living nature of the polymerization of IBVE initiated by photolysis of AAAVB in the presence of excess metallic zinc at 0 °C was examined by the investigation of reaction kinetics (Figure 4.18). As can be seen, the polymerization proceeded with first-order kinetic with respect to monomer concentration. Moreover, reasonably low PDI values were attained. However, the experimental molecular weights are lower than the calculated values. Although the propagation of the polymerization proceeds in a controlled manner, the new initiating species are produced photochemically at the any stage of the process and relatively low molecular weight polymers are also formed. Thus, the polymerization exhibits a quasi-living character.

Figure 4.19 indicates ^{1}H-NMR spectra of AAAVB and PIBVE resulted from the photopolymerzation. Aromatic peaks of the PIBVE observed around 6.5-7.3 ppm obviously resulted from the addition of vinyl cations to IBVE in the initiation step.



(a) **(b)**

Figure 4.18 : Kinetic plots of cationic living photopolymerization of IBVE (7.68 mol·L^{-1}) initiated by photolysis of AAAVB (6.12 × 10^{-3} mol·L^{-1}) in the presence of metallic zinc (6.12 × 10^{-2} mol·L^{-1}); and PDI values of resulting polymers. T = 0 °C; λ = 350 nm; I = 3.0 mW·cm^{-2}.

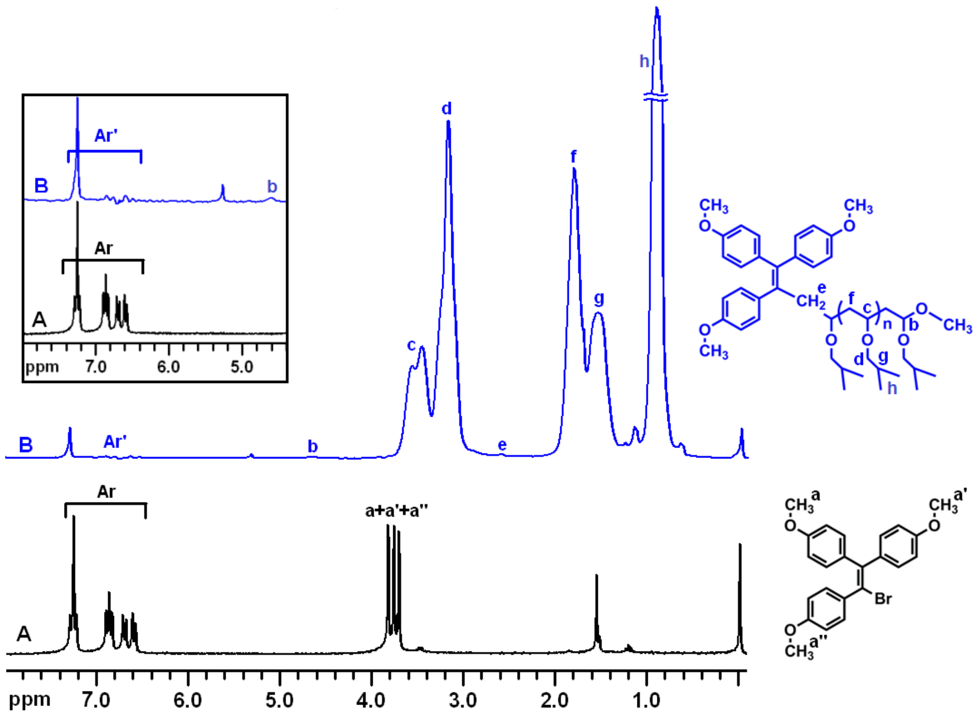


Figure 4.19 : ^{1}H-NMR spectra of AAAVB and PIBVE with aromatic end moiety.

Figure 4.20 and Table 4.8 summarize the effect of metallic zinc amount on the polymerization. As seen in Figure 2, the final conversion increases with increasing metallic zinc concentration up to 0.122 mol·L^{-1}, and levels off thereafter. The behavior is probably due to the limited light absorption. At sufficiently high Zn concentrations, the solution becomes almost opaque and the penetration of the light into solution is prevented. Furthermore, at this Zn concentration, the amount of vinyl halide may not be sufficient as it was utilized for the generation of both vinyl cation and $ZnBr_2$.

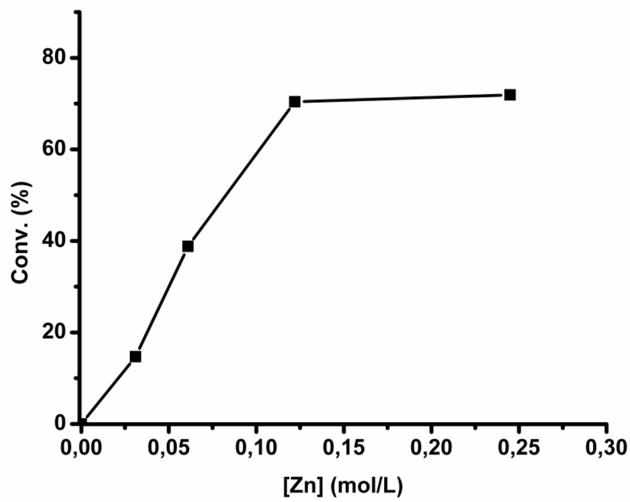


Figure 4.20 : Effect of metallic zinc concentration on cationic living photopolymerization of IBVE (7.68 mol·L^{-1}) initiated by AAAVB (6.12×10^{-3} mol·L^{-1}). T = 0 °C; t = 7 hours; λ = 350 nm; I = 3.0 mW·cm^{-2}.

Notably, polymerizations under identical experimental conditions utilizing ZnI_2 directly resulted in the formation of polymers with high conversions but lower molecular weight and higher polydispersity (Table 4.8, Entry 5). This clearly indicates that metallic zinc assisted polymerizations proceed in a more controlled manner.

Table 4.8 : Photoinitiated cationic polymerization of IBVE (7.68 mol·L^{-1}) initiated by AAAVB (6.12×10^{-3} mol·L^{-1}). T = 0 °C; t = 7 hours; λ = 350 nm; I = 3.0 mW·cm^{-2}.

Entry	**Catalyst (mol·L^{-1})**	**Conv. (%)**	**M_n (g·mol^{-1})**	**PDI**
1	Zn (0.031)	14.7	12,800	1.64
2	Zn (0.061)	38.8	22,500	1.36
3	Zn (0.122)	70.4	67,900	1.34
4	Zn (0.245)	71.9	59,100	1.35
5[a]	ZnI_2 (0.061)	85.2	48,500	2.03

[a] Irradiation was ceased after 6 hours since the solution became extremely viscous.

The described approach can also be employed in UV curing applications of alkylvinyl ethers. Thus, potential activity of the photoinitiating system was examined in crosslinking of several difunctional monomers, namely TEGDVE; BDVE; and

DEGDVE. The formulations containing AAAVB, metallic zinc and cross-linkable monomer were exposed to light. As presented in Table 4.9, all the monomers employed underwent crosslinking upon irradiation confirming possible value in practical applications involving UV curing of vinyl ether based formulations.

Table 4.9 : Photo-induced crosslinking of various difunctional vinyl ethers using AAAVB (1.22×10^{-2} mol·L^{-1}) and zinc (6.12×10^{-2} mol·L^{-1}). T = room temp.; λ = 350 nm; I = 3.0 mW·cm^{-2}.

Entry	Monomer (mol·L^{-1}) [a]	t_{gel} (min.) [b]	Conversion (%) [c]	Gel Content (%) [d]
1	TEGDVE (4.90)	45	46.9	86.1
2	BDVE (6.32)	30	76.6	95.4
3	DEGDVE (6.12)	90	29.3	72.4

[a] TEGDVE: tri(ethylene glycol) divinyl ether; BDVE: 1,4-butanediol divinyl ether; DEGDVE: di(ethylene glycol) divinyl ether.
[b] Gelation was followed qualitatively by simply observing motion of the magnetic bar in the tube, and the system was considered to have gelled when there was no flow of solution. Irradiation was ceased at this moment.
[c] Conversion of monomer to polymer was determined from weight of the precipitated polymer in proportion to weight of the monomer.
[d] Gel content was determined by measuring the weight loss after 24 hours extraction with methylene chloride at room temperature.

4.5 Synthesis of PIBVE-*g*-PEO Copolymer with Pendant Methacrylate Functionality and Its Photo-curing Behavior

The integration of functional groups on to the polymer surfaces or into polymeric chains can increase the value of polymers. For example, the direct functionalization of polymer surface or surface modification by graft copolymerization can improve the surface morphology, biocompatibility, adhesion, *etc.* [403-405]. Synthesis of functional graft copolymers can manage not only to tune the properties of the surface, but also the molecular architecture and chemical composition of the polymer for specific applications [406].

Poly(vinyl ether)s has excellent adhesive properties, especially PIBVE is frequently used in pressure sensitive adhesives industry [407]. PEO is the simplest structure of water-soluble polymers and well known for its biocompatibility [408]. At room temperature, the combination of hydrophilic (PEO) and hydrophobic (PIBVE) segments provides the copolymers with surfactant properties [409].

photoinitiated polymerization is a versatile surface modification technique and can be easily applied at room temperature [207, 271, 406, 410]. It has several advantages over conventional polymerization techniques. These include spatial and temporal control over polymerization, high reactivity (less than a second to a few minutes), solvent free formulation, and minimal heat production. For example, Liu *et al.* reported the synthesis of PVEC-*b*-PIBVE copolymer containing photo-crosslinkable cinnamate groups [411, 412]. After the block formation, PVEC block can readily be cross-linked by photochemical means by intermolecular dimerization of the cinnamate groups (Figure 4.21).

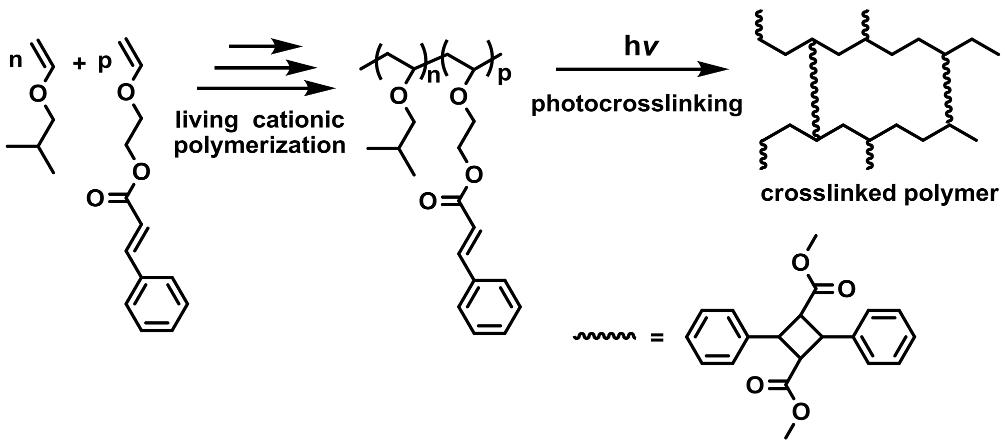


Figure 4.21 : Living cationic copolymerization of (β-(vinyl oxy)ethyl cinnamate and IBVE followed by photocrosslinking of its cinnamate group.

A new synthetic strategy for the preparation of heterofunctional macromonomers carrying methacryloyl group in one end, dimethyl amino, thiophene, styryl, and vinyl ether functional groups in the other end was recently described [413-419]. In this strategy, first anionic polymerization of EO was initiated with functional potassium alcoholates, and then living ends were reacted with methacryloyl chloride. These macromonomers were further utilized in various macromolecular architectures via concurrent or selective thermal free radical [419, 420], oxidative [415] and photoinitiated free radical [371, 413, 421] and cationic polymerization [371] methods. It was also shown that graft copolymers with completely and perfectly alternating hydrophilic side chains can be prepared by charge-transfer-polymerization of the styrene functional macromonomers with phenyl maleimide [420].

As part of the thesis in expanding utilization of PEO based macromonomers in synthetic polymer chemistry, the current study describes the preparation of PIBVE-*g*-PEO graft copolymer with pendant methacrylate groups by living cationic copolymerization of IBVE with VE-PEO-MA macromonomer. Copolymerization was initiated by photochemically using diphenyliodonium halides in the presence of a Lewis acid, ZnI_2.

α,ω-Hybrid PEO macromonomer containing vinyl ether and methacrylate end groups was synthesized by living anionic polymerization of EO, initiated by the corresponding potassium alkoxide followed by reaction with methacryloyl chloride. The backbone was designed as a random copolymer of IBVE and VE-PEO-MA, and prepared by the photoinitiated living cationic polymerization [21-23, 25, 88, 422]. The polymerization consists of two-steps; (*i*) photoinduced adduct formation and (*ii*) subsequent propagation with activated by the coordinating effect of ZnI_2. This activation leads to generation of suitable nucleophilic counter anion by stabilizing the growing carbocation, which leads to insertion of a weakly basic monomer or macromonomer (Figure 4.22).

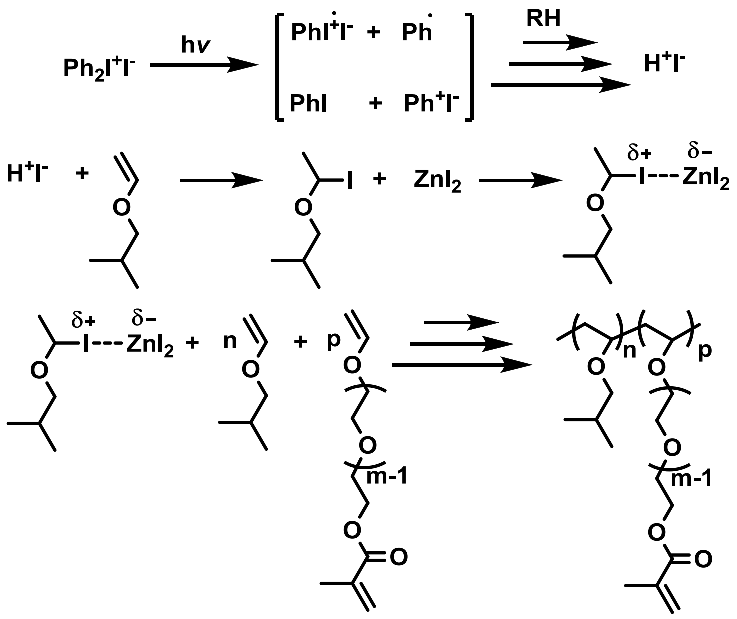


Figure 4.22 : Synthesis of PIBVE-*g*-PEO copolymer with pendant methacrylate functionality.

The results of photoinitiated cationic living copolymerization are shown in Table 4.10. As can be seen, the concentration of the macromonomer and irradiation time affects the molecular weight of the resulting graft copolymers. However, in all cases polymers with relatively low polydispersities were obtained.

Table 4.10 : Synthesis of PIBVE-*g*-PEO copolymer with pendant methacrylate functionality via photoinitiated living cationic polymerization[a,b] using $Ph_2I^+ I^-$ (6.60×10^{-3} mol·L^{-1}) / ZnI_2 (3.20×10^{-3} mol L^{-1}).

Entry	[VE-PEO-MA] (mol L^{-1})	Time (h)	*M*n[c]	*M*w/*M*n[c]
1	0.031	19	6000	1.28
2	0.031	23	7300	1.36
3	0.062	19	9400	1.32

[a]Photopolymerization was carried out at 300 nm with the light intensity of 3 mW cm^{-1}
[b][IBVE] = 0.38 mol·L^{-1}
[c]Determined by GPC.

Figure 4.23 shows GPC traces of macromonomer and graft copolymer. The peak with short retention volume was attributed to the corresponding graft copolymer. Notably, no traces corresponding to the precursor macromonomer was detected. The pronounced molecular weight shift, observed in the case of graft copolymerization, is due to the living nature of the cationic polymerization. It is known that conventional photoinitiated cationic polymerization of vinyl ethers using onium salts with nonnucleophilic counter anions leads to the formation of polymers with low molecular weights due to the dominant chain transfer reactions. However, such chain breaking reactions are minimized when the photo polymerization is performed in the presence of onium salt with nucleophilic counter anion and a Lewis acid such as ZnI_2 [23-25].

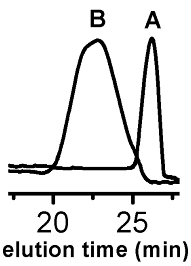


Figure 4.23 : GPC traces of the precursor VE-PEO-MA (A) and PIBVE-*g*-PEO copolymer containing methacrylate functionality (B).

The chemical structure of the graft copolymer obtained was confirmed by both ^{1}H-NMR and FT-IR spectroscopy. ^{1}H-NMR of the graft copolymer (Figure 4.24B) showed the strong characteristic peak for -O-CH_2- of PEO side chain at 3.7 ppm. Additionally, -OCH_2-, -CH- and -CH_3 protons of isobutyl vinyl ether units at 3.5, 1.7, and 0.9 ppm, respectively indicate successful chemical incorporation of IBVE and macromonomer into the graft copolymer. As far as the subsequent use of the graft copolymer in photocross-linking is concerned, the effect of cationic polymerization on the stability of methacrylate group was an important issue. Thus, $-CH_2$ protons of the olefinic structure appearing at 6.1 and 5.6 ppm, respectively, clearly indicates the retention of the methacrylate functionality during the cationic polymerization.

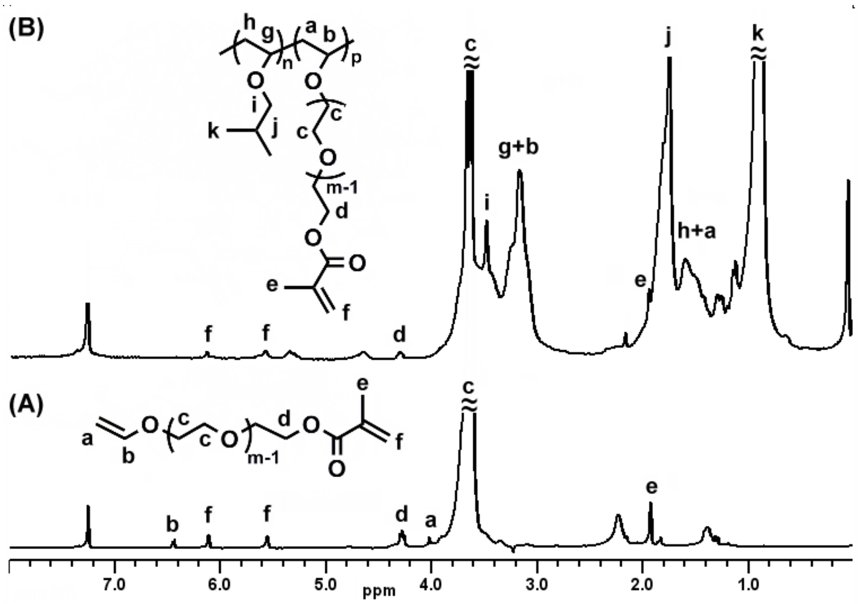


Figure 4.24 : [1]H-NMR spectra of the precursor VE-PEO-MA (A) and PIBVE-*g*-PEO (B) graft copolymer containing methacrylate functionality in $CDCl_3$.

The IR spectrum of the graft copolymer showed characteristic peaks of 930-1150 cm^{-1} due to the C-O-C symmetric and asymmetric stretching of ether bonds of both PEO side chain and PIBVE side chain [417, 423]. The remaining bands of methacrylate group such C=O and C=C at 1740 and 1630 cm^{-1} another spectral evidences detected from FT-IR (Figure 4.25B).

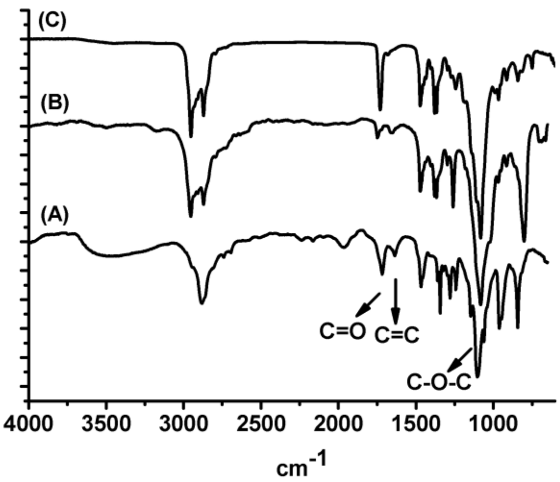


Figure 4.25 : FT-IR spectra of VE-PEO-MA (A), PIBVE-g-PEO copolymer (B) and cross-linked polymer (C).

Due to the presence pendant methacrylate groups, the resulting graft copolymer is expected to undergo cross-linking upon irradiation [424]. As an experimental demonstration, PIBVE-*g*-PEO copolymer in dichloromethane was irradiated in the presence of small amount of MMA by using DMPA at 350 nm (see section 3.3.6 for details). Complete gelation occurred after 3h irradiation according to the following reaction (Figure 4.26).

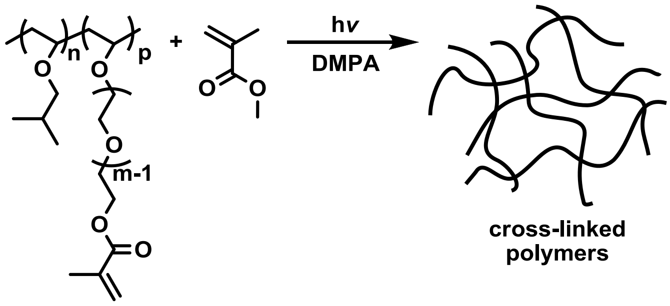


Figure 4.26 : Photo-curing of PIBVE-*g*-PEO copolymer and methyl methacrylate

The IR spectrum of the cross-linked polymer exhibited characteristic bands of the all components of the network structure, namely vinyl ether, methacrylate and ethylene oxide segments (Figure 4.25C). Notably, the signals appearing at 1630 cm^{-1} corresponding to C=C bond disappeared after successful cross-linking.

4.6 Synthesis of Block Copolymers by Combination of ATRP and Visible Light-Induced Free Radical Promoted Cationic Polymerization

The possibility of using $Mn_2(CO)_{10}$ combination with suitable co-initiators such as CH_2Cl_2 in the presence $Ph_2I^+PF_6^-$ as a novel initiating system for visible light induced cationic polymerization [425] prompted us to employ the same redox process for the mechanistic transformation. Accordingly, block copolymers were obtained via two discrete steps. In the first step, a series of halide end-functional PSt with different molecular weights was simply synthesized by ATRP (Table 3.1). In the second step, free radical promoted cationic photopolymerization of CHO or IBVE initiated by the photolysis of $Mn_2(CO)_{10}$ in the presence of the obtained macro-coinitiators resulted in formation of the corresponding block copolymers, PSt-*b*-PCHO or PSt-*b*-PIBVE, respectively (Table 4.11). Apparently the molecular weights increased after succesfull growth of the second segment (PCHO) (Figure 4.27).The overall process is presented on the example of CHO polymerization (Figure 4.28).

Table 4.11 : Properties of the block copolymers synthesized by visible light induced free radical promoted cationic photopolymerization[a] of CHO or IBVE (0.3 mL).

Polymer	Conv. (%)[b]	M_n ($g \cdot mol^{-1}$)[c]	PDI[c]	BC[d]	PSt (%)[e]
PSt(1)-*b*-PCHO	24.7	5200	1.07	30.3	85.7
PSt(2)-*b*-PCHO	34.7	6720	1.09	41.0	88.9
PSt(3)-*b*-PCHO	33.7	9990	1.13	40.2	83.3
PSt(2)-*b*-PIBVE	20.0	5420	1.13	-	-

[a] $[Mn_2(CO)_{10}]$ = 7.2×10^{-2} $mol \cdot L^{-1}$; $[Ph_2I^+PF_6^-]$ = 3.3×10^{-3} $mol \cdot L^{-1}$; [PSt] = 3.6×10^{-2} $mol \cdot L^{-1}$. [b] Conversion of each monomer was determined gravimetrically before extraction of the homo-PCHO with hexane. [c] Molecular weights and PDIs were determined with GPC. [d] Block copolymer content (BC, % w/w) was determined gravimetrically after the extraction. [e] PSt content (% mol) of the block copolymers was determined by ^{1}H-NMR analysis.

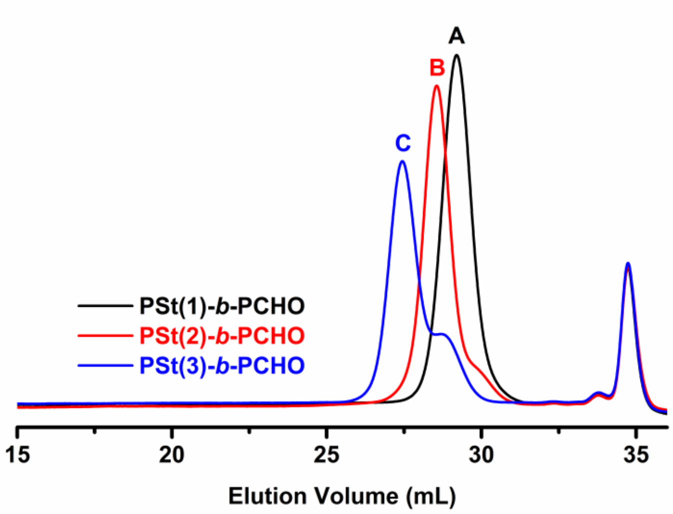


Figure 4.27 : GPC traces of PSt-*b*-PCHO block copolymers synthesized by visible light induced free radical promoted cationic photopolymerization of CHO (0.3 mL) using $Mn_2(CO)_{10}$ (7.2×10^{-2} $mol \cdot L^{-1}$) in the presence of Ph_2I^+ PF_6^- (3.3×10^{-3} $mol \cdot L^{-1}$) and PSt (3.6×10^{-2} $mol \cdot L^{-1}$) with various molecular weights (see Table 3.1) in toluene.

As can be seen from Table 4.11, the molecular weight of the block copolymers increases with increasing molecular weight of PSt, however, the contents of PSt segments in the block copolymers are not high accordingly. This is probably due to the steric hindrance, since when the PSt chain gets longer, transformation of bromo functionalities to radicals and consequently cations becomes difficult, and eventually addition of monomers to the chain end will be hard.

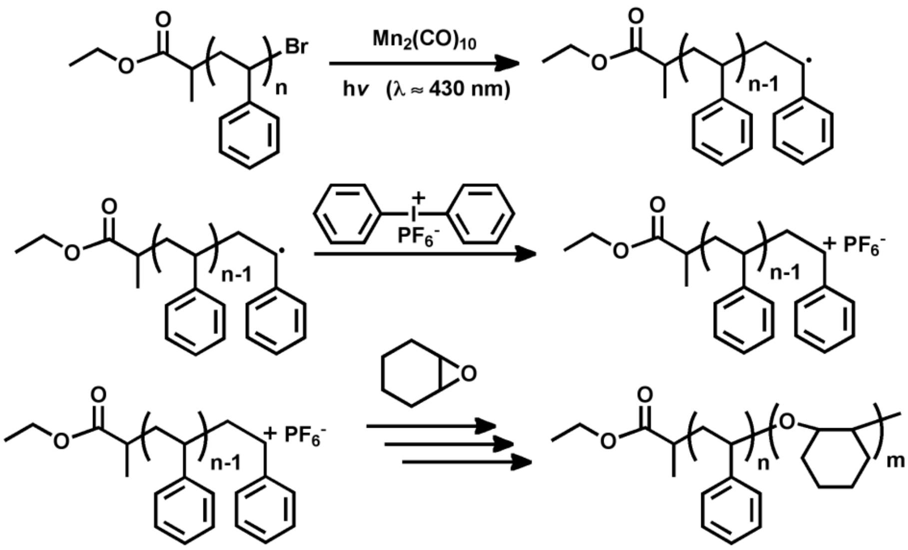


Figure 4.28 : Synthesis of PSt-*b*-PCHO by combination of ATRP and visible light-induced free radical promoted cationic polymerization.

The structure of the precursor polymer and the resulting block copolymers was confirmed by ^{1}H-NMR spectral analysis. The NMR spectrum of the block copolymer displays signals at 0.8-2.2 ppm CH_2, CH (PSt, PCHO), 3.43 ppm OCH (PCHO), and 6.5-7.2 ppm Ph (PSt) (Figure 4.29).

Unimodal GPC traces of precursor PSt(2), PSt(2)-*b*-PCHO, and unreacted PSt recovered from the control experiment completely correlate with the ^{1}H-NMR results. Expectedly, no polymerization took place in the control experiment in which $Mn_2(CO)_{10}$ was missing since Ph_2I^+ PF_6^- was transparent under the incident light. The identical GPC chromatograms of the precursor (Figure 4.30A) and the polymer from the control experiment (Figure 4.30B) approve that $Mn_2(CO)_{10}$ is necessary for the formation of polystyryl radical which is then oxidized to initiating end-chain polymeric cation by Ph_2I^+ PF_6^-. Apparently, when $Mn_2(CO)_{10}$ was added to the polymerization system, a shift to higher molar mass was observed indicating the central role of $Mn_2(CO)_{10}$ for free radical promoted cationic polymerization and consequently the formation of the block copolymer (Figure 4.30C). This result is in accordance with the proposed mechanism and with the report [425] in which control experiments omitting any components of the photoinitiating system failed to produce polymer.

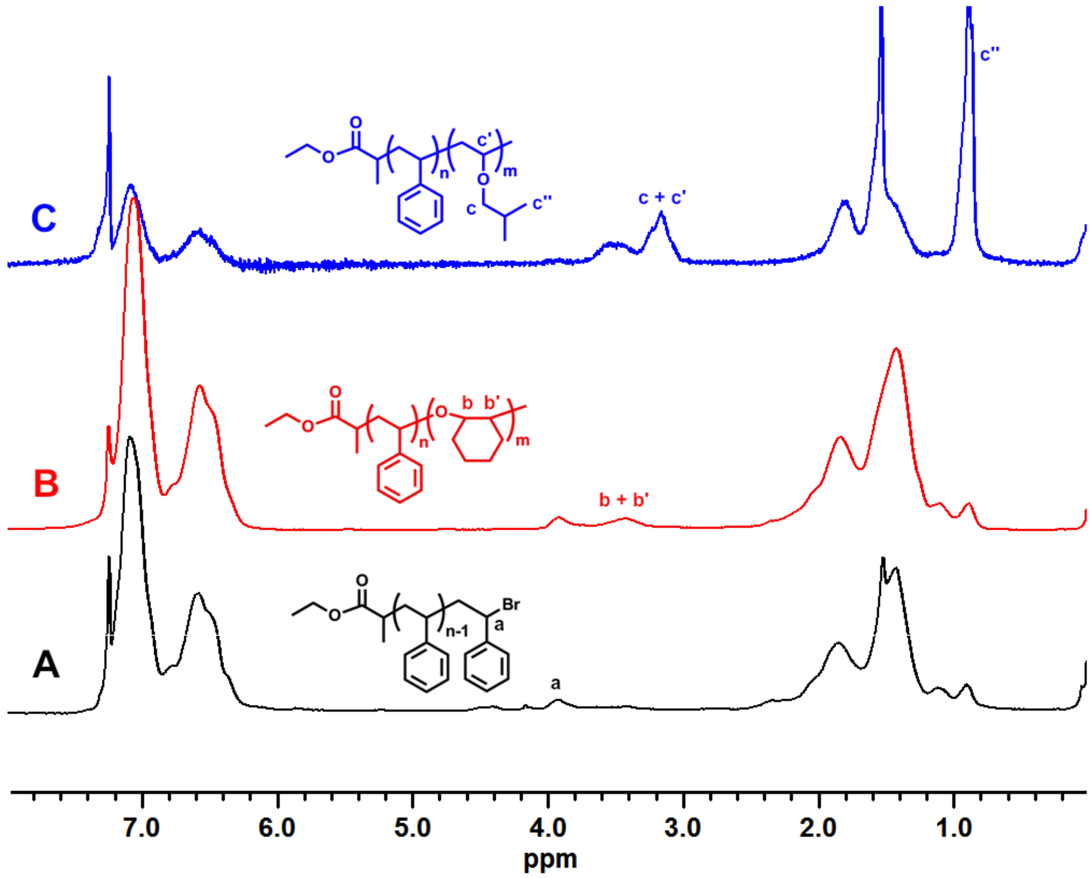


Figure 4.29 : [1]H-NMR spectra of bromo functional PSt (M_n: 2250 g·mol^{-1}) (A), PSt-*b*-PCHO (B) and PSt-*b*-PIBVE (C) obtained by combination of ATRP and visible light induced cationic photopolymerization.

It should be pointed out that the GPC traces of the crude block copolymers before extraction with hexane (solvent for PCHO) showed a shoulder at higher molecular weight elution volumes. Such homopolymer formation is unavoidable since phenyl radicals formed concomitantly from the decomposition of diphenyliodonium salt participate in further redox reactions to generate initiating cations (Figure 4.31) [395]. In this way, the initiation of growing (cationic) chains is multiplied. These additional chains do not consist of initial PSt segments. Notably, presence of the very small shoulder at higher elution volume is probably due to lose of bromo functionality of the fraction of PSt chains during the ATRP or photolysis processes.

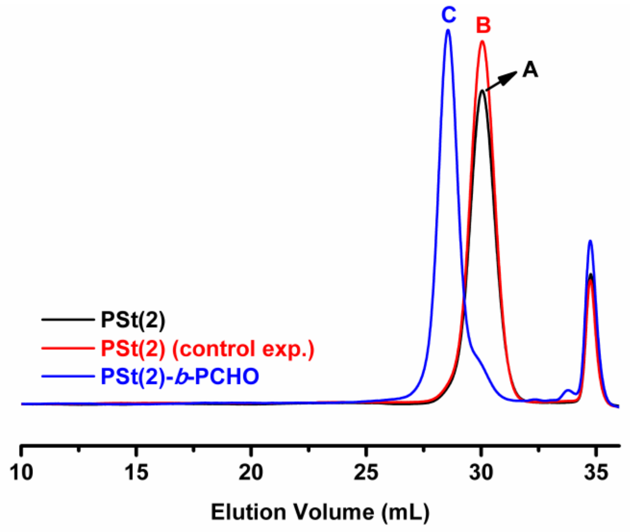


Figure 4.30 : Gel permeation chromatograms of bromo functional polystyrene (M_n: 3250 g·mol^{-1}) (A) and resulted polymers after irradiation of block copolymerization system with (C) or without (B) $Mn_2(CO)_{10}$.

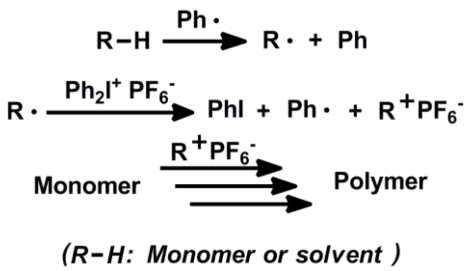


Figure 4.31 : Generation of additional cationic species.

Further thermal and spectroscopic analyses also confirmed the successful formation of block copolymers. Glass transition temperature (T_g) of the PSt-*b*-PCHO investigated by DSC was observed around 82 °C, between the T_g values of the precursor segments; homo-PCHO (65 °C) and homo-PSt (100 °C). This result obviously is not surprising for the block copolymer consisted of PCHO and PSt segments which are miscible. In FT-IR spectrum of the precursor PSt (Figure 4.32), characteristic bands such as aromatic C=C stretch bands around 1400-1600 cm^{-1} were observed; whereas, spectrum of the block copolymer contained additional band at 1077 cm^{-1} corresponding to typical etheric C-O-C stretch band.

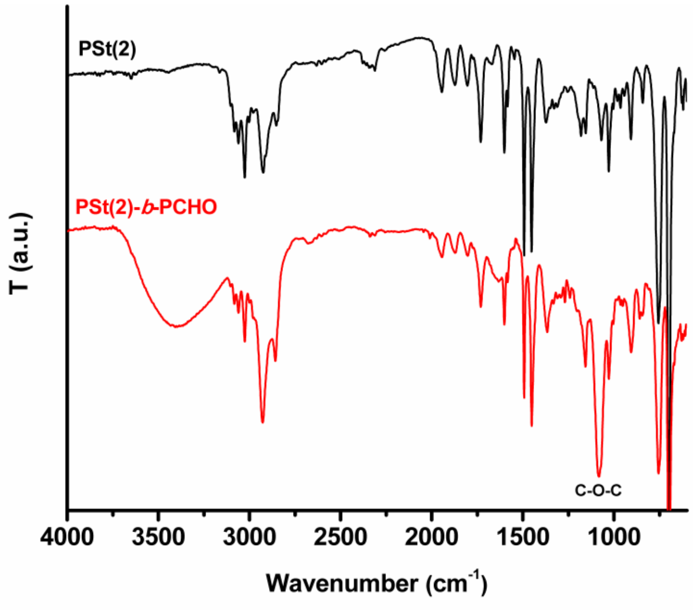


Figure 4.32 : FT-IR spectra of precursor PSt (M_n: 3250 g·mol^{-1}) and PSt(2)-*b*-PCHO block copolymer synthesized by visible light induced free radical promoted cationic photopolymerization of CHO (0.3 mL) using $Mn_2(CO)_{10}$ (7.2×10^{-2} mol·L^{-1}) in the presence of Ph_2I^+ PF_6^- (3.3×10^{-3} mol·L^{-1}) and PSt (3.6×10^{-2} mol·L^{-1}) in toluene.

To extend applicability of the approach, copolymerization of another cationically polymerizable monomer, IBVE, was also investigated. ^{1}H-NMR spectra of the resulting PSt-*b*-PIBVE revealed that the initiating system is also effective in the polymerization of vinyl type monomers. The expected molecular weight shifts were observed also in this case (Figure 4.33).

It must be pointed out that chain transfer is an important process as far as cationic polymerization of alkyl vinyl ethers is concerned. In our experiments, we have employed thiolane to prevent formation of initiating species resulting from chain transfer that are free of initial PSt segments [426, 427]. However, GPC traces indicate that polymer chains with different chain lengths are formed since propagating cations can be created not only by direct oxidation of the terminal polystyryl radical but also the radicals obtained by the addition of vinyl ether monomer (Figure 4.34).

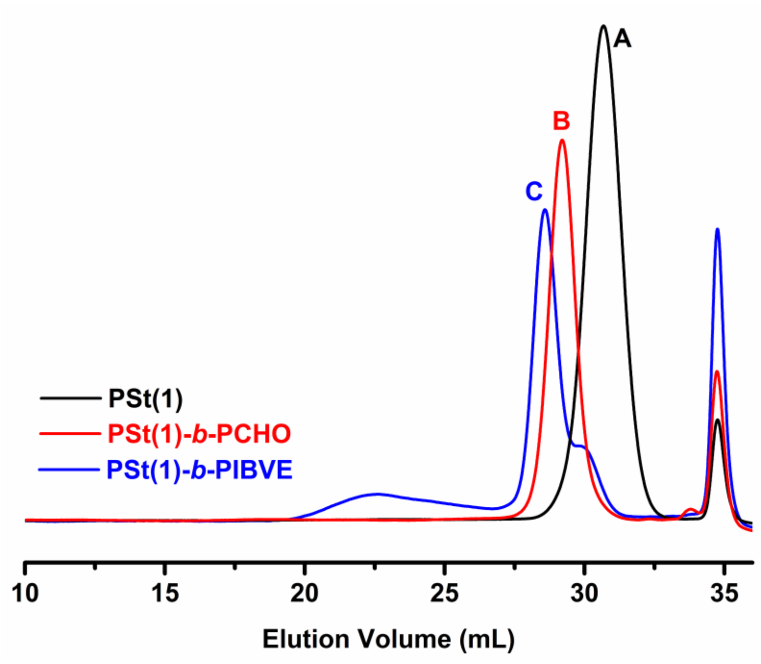


Figure 4.33 : Gel permeation chromatograms of bromo functional PSt (M_n: 2250 g·mol^{-1}) (A), PSt-*b*-PCHO (B) and PSt-*b*-PIBVE (C) obtained by combination of ATRP and visible light induced cationic photopolymerization.

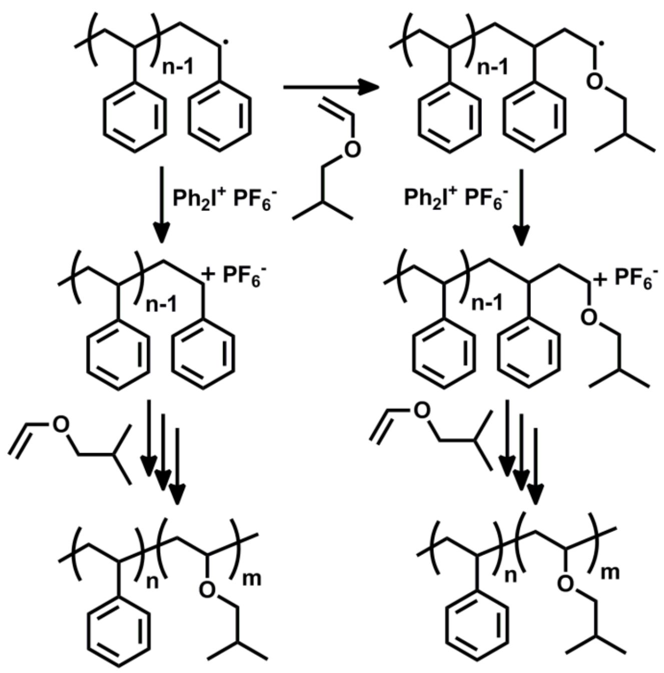


Figure 4.34 : Possible pathways for the production of cationic species during the block copolymer formation.

5. CONCLUSION

The recent demands for environmentally friendly and highly efficient polymerization processes encourage the development of mild, safe and more reactive systems. In this thesis, we described novel initiation systems for photo-induced cationic cross-linking of vinyl ethers to ensure these demands. These systems with such features would be expected to open new directions for industrial and practical applications.

In the first study, potential use of diphenyliodonium salt with highly nucleophilic counter anions in direct and indirect photoinitiated cationic crosslinking of divinyl ethers was evaluated. The direct system comprise only a diphenyliodonium salt with highly nucleophilic counter anion and a zinc halide, while indirect systems consist of a polynuclear aromatic photosensitizer such as anthrecene and perylene or an aromatic carbonyl compound such as DMPA, BP and TX, and a diphenyliodonium halide (Ph_2I^+ X^-) in combination with a zinc halide (ZnX_2) (Figure 5.1).

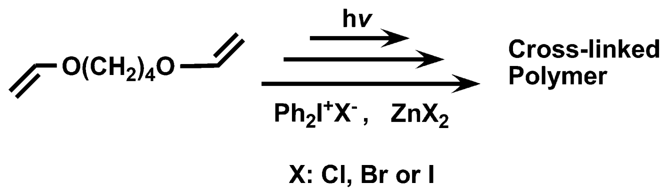


Figure 5.1 : Photoinitiated cationic crosslinking of divinyl ethers using diphenyliodonium in the presence of zinc halides

In the second study, photoinitiated cationic polymerization of vinyl ethers in aqueous medium in the presence of water-tolerant Lewis acid, ytterbium triflate was successfully achieved. In this process, hydrogen halide is photochemically generated from a diphenyliodonium salt and this reacts with the monomer to form an adduct which coordinates with the Lewis acid, leading to cationic chain propagation (Figure 5.2). In contrast to the normally observed deactivation of Lewis acids by even traces of water, successful cationic polymerization of vinyl ethers was performed in aqueous medium. Although the polymerization was found to be irreproducible and affected by experimental conditions due to the two phase nature of the process, this is the first example of photoinitiated cationic polymerization in aqueous medium. It is clear that the optimization of the conditions and achieving controlled and mild polymerization process would open new pathways for many applications employing water-borne systems with economical and environmental advantages.

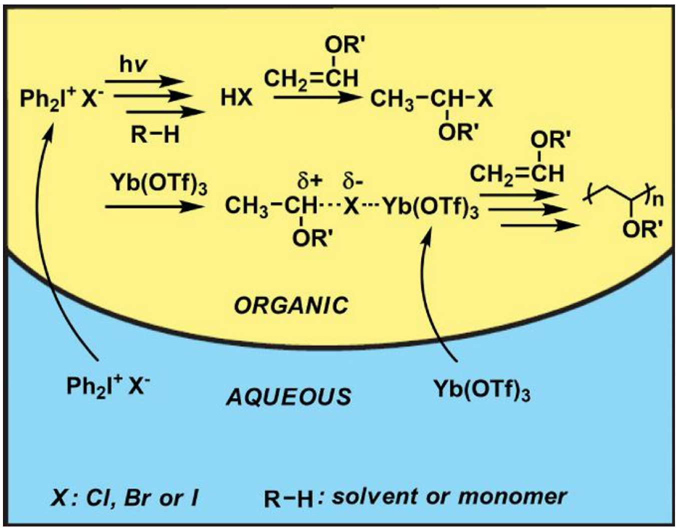


Figure 5.2 : Photoinitiated cationic polymerization of vinyl ethers in aqueous medium in the presence of water-tolerant Lewis acid, ytterbium triflate.

The third study is related to the combination of substituted vinyl halides with ZnI_2 leading to efficient photoinitiating activity for the cationic polymerization of vinyl ethers. The initiation mechanism involves photoinduced free radical generation by the homolysis of the carbon halide bond and subsequent electron transfer to yield reactive cations capable of forming an adduct with the monomer (Figure 5.3). The efficiency of the vinyl cation formation is controlled by the nature of the vinyl halide substituent. Apparently, an electron donating substituent provides more favorable thermodynamic conditions for the redox process and causes a shift of the absorption maximum to longer wavelengths, i.e. closer to the emission maximum of the radiation source. Once the adduct between vinyl halide and monomer is generated, complexation with ZnI_2 causes the formation of polymer of low polydispersity, which implies controlled polymerization.

The major advantage of these combined initiating systems is their applicability to pigmented systems which afford irradiation at relatively long wavelengths. Moreover, these systems do not require radical initiating sources, hazardous protonic acids or onium salts of any kind to form the intermediate adduct.

Development of a novel photoinitiation approach for Lewis acid-catalyzed cationic polymerization of vinyl ethers, based on *in situ* formation of zinc halide, is the another outcome of the thesis. In the process, zinc bromide, which plays central role in propagation step, was generated simultaneously by the reaction of metallic zinc with the photochemically produced bromine radicals (Figure 5.4). Polymerization formulation consists of a vinyl ether monomer, a vinyl halide type photoinitiator and a metallic precursor, zinc. The polymerization shows usual characteristics of living mode when polymerization kinetics and PDIs of the resulted polymers are evaluated. The photoinitiating system is also useful in photo-induced crosslinking of difunctional monomers.

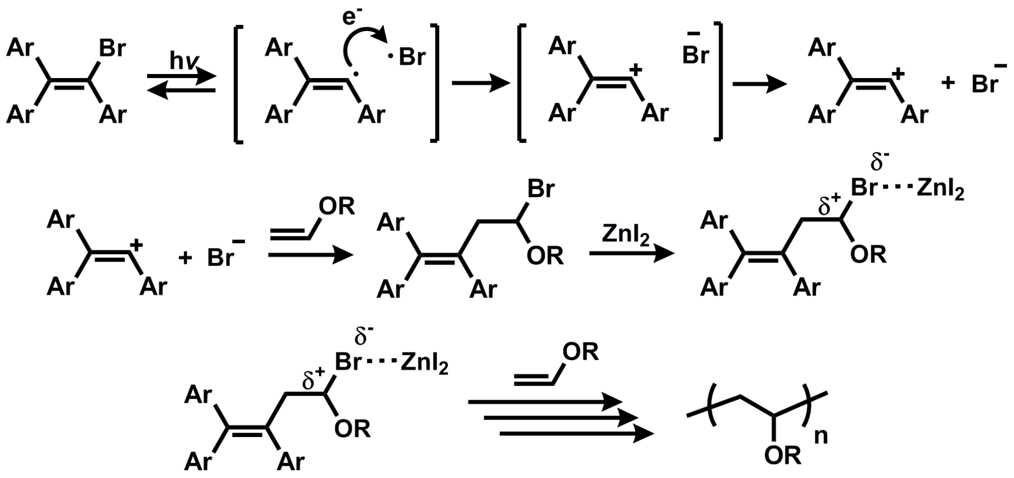


Figure 5.3 : Photoinitiating system based on photolysis of vinyl halides in the presence of zinc halide for cationic living polymerization of vinyl ethers.

A novel method for the preparation of graft copolymers with pendant methacrylate functional groups by combination of living anionic and photoinitiated cationic polymerization methods is another outcome of the thesis. It was also demonstrated that upon irradiation of the graft copolymers in the presence of photoinitiator and low molar mass monomer, the methacrylate groups can undergo cross-linking. Because of the fact that such formed network consists of both hydrophilic and hydrophobic domains and that backbone and the cross-linked sites are separated by long PEO chains, they offer potential use in biomedical application such as drug delivery. The thesis also offers a new synthetic route for the preparation block copolymers by mechanistic transformation from ATRP to visible light induced free radical promoted cationic polymerization is described. A halide end functional polystyrene synthesized by ATRP is utilized as macro-coinitiator in dimanganese decacarbonyl [$Mn_2(CO)_{10}$] mediated free radical promoted cationic photopolymerization.

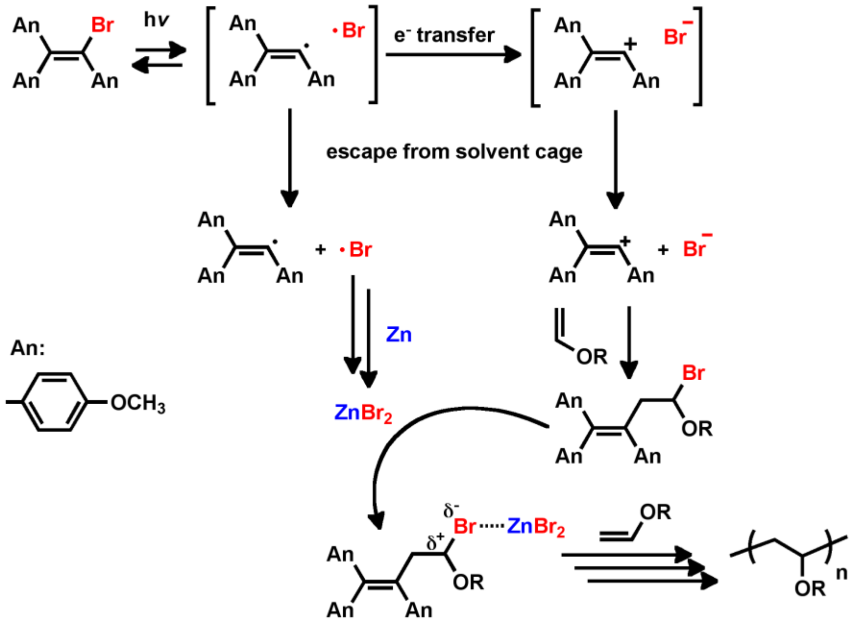


Figure 5.4 : Photoinitiating sytem based on *in situ* formation of zinc halide for Lewis acid-catalyzed cationic polymerization of vinyl ethers

Block copolymerization via radical (ATRP) and promoted cationic routes provides a versatile two-stage method applicable to vinyl and nucleophilic monomers. The method described here pertains to the direct use of polymers obtained by ATRP without any modification, in the subsequent visible light free radical promoted cationic polymerization process (Figure 5.5). Combination of macroradicals formed from the photolysis of $Mn_2(CO)_{10}$ and polymeric halide with diphenyl iodonium salt constitutes a redox couple that can be employed as a convenient and versatile initiator system for the cationic polymerization of epoxides and vinyl ethers.

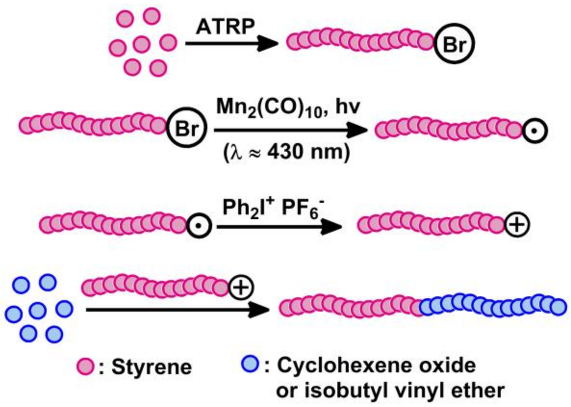


Figure 5.5 : Block copolymerization by mechanistic transformation from ATRP to visible light induced free radical promoted cationic polymerization.

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List of Publications and Patents:

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